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Applications of Ionic liquids in contaminants removal from Refinery Feedstocks: an industrial perspective

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Abstract

The purpose of this review is to provide appropriate details concerning the applications of ionic liquids for removing pollutants from refinery feedstocks, like remotion of sulfur-, nitrogen- and fluor-containing compounds, aromatics, naphthenic acids and asphaltenes. Furthermore, critical considerations, the problems and challenges for the applications of these technologies in petroleum industry are discussed.

Keywords: ionic liquids; desulfurization; denitrogenation; aromatics, pollutants

Abbreviations and nomenclature

BMIM: 1-butyl-3-methylimidazolium

$B(CN)_4$: tetracyanoborate

BSA: 4-butylsulfonic acid

CAR: carbazole

$[C_nBZI]AcO$: 1-alkyl-3H-benzoimidazolium acetate

$C(CN)_3$: tricyanomethanide (anion)

COSMO-RS: **CO**nductor like **S**creening **MO**del for **R**eal **S**olvents

DBP: dibuthylphosphate (anion)

DBT: dibenzothiophenes

4,6-DBT: 4,6-dialkyldibenzothiophenes

4,6-DMDBT: 4,6-dimethyldibenzothiophenes

DCLR: Direct Coal Liquefaction Residues

DEP: diethylphosphate (anion)

DFT : Density Functional Theory

[DMEE]CO_2Et: 2-[2-(dimethylammonium)ethoxy]ethanol propionate

[DMAPN]CO_2Et: 2-(dimethylammonium)propanenitrile propionate

DMP: dimethyl phosphate (anion)

EDS: extractive desulfurization

[$^1E^3M^5M^2PPy$]: 1-ethyl-3,5-dimethyl-2-propylpyridinium

[$^1B^3M^5M^2PPy$]: 1-btyl-3,5-dimethyl-2-propylpyridinium

[$^1H^3M^5MPy$]: 1-hexyl-3,5-dimethylpyridinium

$EtMe_2S$: ethyldimethylsulfonium (cation)

HDN: hydro-denitrogenation

HMIM: 1-hexyl-3-methylimidazolium

[HNMP][BF_4] : *N*-methyl-pyrrolidonium tetrafluoroborate

HDS: hydro-desulfurization

ILs: ionic liquids

K_N: partition coefficient

LLEMs: Liquid-liquid extraction using membranes

MSILs: Metal-based surfactant-type ILs

n-MeBuPy: 2, 3 or 4-methyl-*N*-butilpyridinium

[3-MeBuMPyrr]: 3-methyl-*N*-methyl-*N*-butylpyrrolidinium

[3MHPy]: 3-methyl-*N*-hexylpyridinium

$N(CN)_2$: dicyanamide (anion)

NCs: Nitrogen-Containing Compounds

N-ethyl-4-dimethylamino-pyridinium : $C_2{}^4$DMAPy

N-butyl-4-dimethylamino-pyridinium : $C_4{}^4$DMAPy

N-hexyl-4-dimethylamino-pyridinium : $C_6{}^4$DMAPy

NMP: *N*-methyl-2-pyrrolidone

[NTf_2] :(trifluoromethanesulfonyl)imide (anion)

[$OcSO_4$] : octylsulfate (anion)

ODS: Oxidative Desulfurization

[OMIM]: octylmethylimidazolium

ONCs: Organic Nitrogenenated Compounds

P: Permeability

PTC: Phase Transfer Catalyst

PTS: *p*-toluene sulfonate

PTSA: *p*-toluene sulfonic acid

PVDF: poly(vinylidene fluoride)
Py: pyridine
S: Selectivity
S2: tetrahydrothiophenium (cation)
3-(SA)proPy: 1-[3-(sulfonic acid)propyl]pyridine
SCN: thiocyanate
SCs: Sulfur-Containing Compounds
SILMs: Supported ILs Membranes
TA: trifluoroacetate
TPA: phosphotungstic acid
TS: thiophenes
VO(acac)$_2$: bis(acetylacetonate)oxovanadium (IV)
ρ: density
))): ultrasound

Introduction

A contaminant or pollutant is an external potentially undesirable substance (physical, chemical or biological) as part as a material or feed present at high enough levels to pose threats on human, animal or plant health. In petroleum refineries, the number of such contaminants is well varied comprising environmental pollutants (sulfurated-, nitrogenated-, fluorinated- and aromatic compounds) as feed contaminants including naphthenic acids, asphaltenes, salts as well as gases (e.g. H_2S, CO_2 and N_2).

Increasingly restrictive regulatory practices are more often imposed these days on oil refineries to reduce the content of toxic compounds levels of the fuels as well as to minimize their associated negative health and environmental effects. However, the exhaustive remotion of pollutants from refinery feedstocks (e.g. gasoline and diesel) is a highly challenging task which demands greener and more sustainable technologies able to provide equal efficiency to conventional methods. Refineries are also facing major challenges to meet the fuel pollutants specification to produce higher fuel qualities and higher value products. The developing of greener processes for engineers urges a move of petroleum technologies closer to sustainability.[1]

A significant emphasis has been placed on deep desulfurization and denitrogenation of oil products in the past decade. Hydrocarbon combustion releases SO_x and NO_x species and these compounds are responsible of environmental hazards including acid rain, air contamination and ozone consumption. Environmental regulations have been modified to call for lower levels of sulfur and nitrogenated compounds to be ejected toward the atmosphere. Recently, new non-hydrodesulfurization technologies for the production of clean oils have been studied in order to remove pollutants from the different cuts in the refinery industry including the use of ionic liquids (ILs) as extractive media. One alternative is the so called extractive desulfurization, which seems to be very attractive for this purpose because of its low energy costs, the elimination of hydrogen usage, the retaining of the chemical structures of fuels and the no-requirement of special equipment.[2]

ILs are versatile compounds (Figure 1) finding applications in a range of areas due to their interesting properties. The properties of ILs are variable and can be in theory adjusted for any application, i.e. they are also not all non-corrosive, but they can be designed to be non-corrosive, but in general, they are characterized by to have low vapor pressures, thermal and chemical stability, non-flammability,[3] which include microwave-assisted organic synthesis,[4] catalysis,[5a-5c] biocatalysis,[6] separation,[7] extraction,[8] electrochemistry,[9] nanomaterials synthesis,[10] polymerization reactions,[11] as well as corrosion inhibitors.[12] Interestingly, IL can also offer promising opportunities to reassess and optimize existing technologies and processes related to petroleum industry, as demonstrated by the large number of research studies on the evaluation of ILs in petroleum-derived applications.[13]

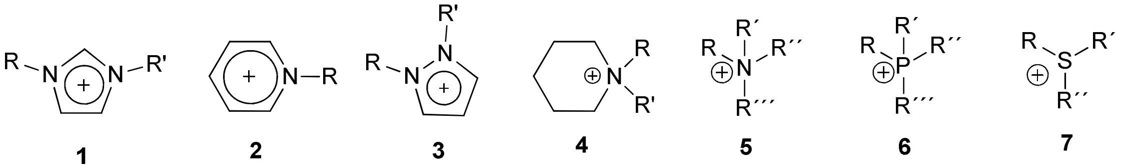


Fig. 1 Some common cations structures in ILs.

Nevertheless, to the best of our knowledge, there are no critical reviews aimed to compile methods and technologies on the assessment and utilization of ILs in pollutant-removal (including sulfur- and nitrogen- and flour-containing compounds, aromatics, naphthenic acids, asphaltenes) of refinery feeds. This is particularly the case as many of these ILs applications are still in their infancy in terms of industrial development for the petroleum industry, and currently restricted to some industrially important chemical processes.[14] In the light of these premises, this contribution is aimed to provide an account of chemical research to date on the use of ILs in the removal of various pollutants from oil products with a special emphasis on the industrial potential of such applications of these processes.

2. ILs for removing pollutants from refinery feeds

2.1 Desulfurization of light oil using ILs

The deep desulphurization of oil products has attracted a great deal of attention in recent years due to the emissions of SOx generated upon combustion of hydrocarbon fuels.

Industrially, the removal of organosulfur and organonitrogen compounds in fuel oils is conducted by means of a simultaneous hydro-desulfurization (HDS) and hydro-denitrogenation (HDN). The process entails C-S and C-N bond cleavage to produce H_2S and NH_3, respectively.[15-18]

HDS is the primary desulfurization technology used today. The HDS reaction in refineries is carried out in trickle-bed reactors. These reactors are commonly operated at temperatures in the range 300–450 °C, and at H_2 pressures of 3.0–5.0 MPa, usually with $CoMo/Al_2O_3$ or $NiMo/A1_2O_3$ catalysts. In the HDS reactor, sulfur is reduced liberating H_2S which is then removed from the flue gas by amine scrubbing. Most HDS operations also remove nitrogen compounds and some metal impurities.[19]

Deep desulfurization of diesel fuels is particularly challenging due to difficulties associated to aromatic SCs reduction using conventional HDS processes (particularly 4,6-dialkyldibenzothiophenes). HDS process is generally only effective to remove aliphatic and alicyclic-type organosulfur compounds. The conversion of aromatic sulfur molecules including thiophenes (TS), dibenzothiophenes (DBT) and their alkylated derivatives into H_2S through HDS catalysts is highly challenging and deep HDS requires more efficient catalysts and larger consumption of energy and hydrogen.

Refiners today decrease the sulfur content to about 30 ppm but as the sulfur limits are decreased, there will be a need to increase the number of HDS units, which will tremendously increase the demand for hydrogen. Higher temperatures and pressures will also be needed to remove the recalcitrant sulfur compounds which raise operating costs. H_2S generated is removed by the CLAUSS process by recovering elemental sulfur from gaseous H_2S. A novel SUPERCLAUS process has also been implemented in some refineries to recover elemental sulfur from H_2S containing gases originating from gas treating plants such as alkanolamine units or physical solvent plants. SUPERCLAUS plants are also able to process H_2S/NH_3 containing gases originating from Sour Water Strippers with the objective to yield up to 99% overall sulfur recovery without any further tail gas clean-up.[20]

New processes and non-hydrodesulfurization technologies to produce ultra-low sulfur clean oils have been studied to remove sulfur from the different cuts in the refinery industry.[21-26] A promising alternative denoted as extractive desulfurization (EDS) could be particularly suitable to this aim owing to its low energy cost, avoidance of molecular hydrogen, no requirements of special equipment as well as the possibility to retain chemical structures of fuels.

Liquid-liquid extraction is an extensively employed industrial methodology to separate mixtures. The advantages of this method are simplistic operation option, mild process conditions, and low energy consumption. However, the extraction efficiency is largely dependent on the careful selection of solvents for specific separation processes. Conventional solvents for extraction purposes are highly volatile, flammable, and often hazardous, being ILs a potentially useful alternative in this process (Figure 2).

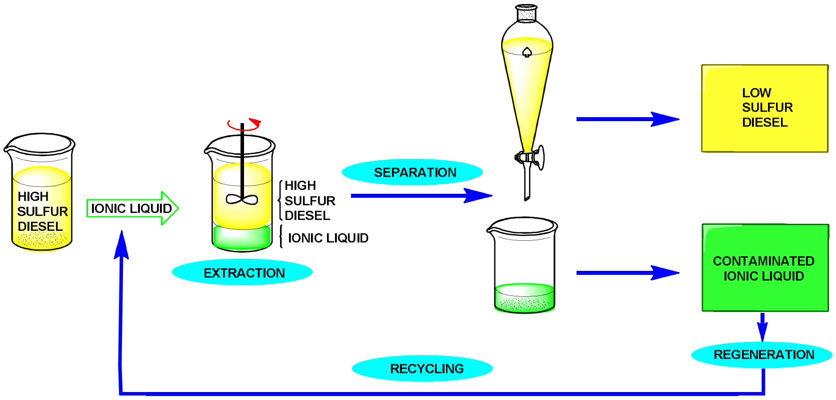


Fig. 2 Schematic representation of Diesel desulfurization by liquid-liquid extraction employing ILs.

The pioneering work highlighting the extractive properties of ILs on sulfur-containing compounds in refinery feeds was published by Bosmann and coworkers in 2001. In their research, a series of ILs were described to possess properties to remove SCs from a model feedstock (500 ppm of DBT in *n*-dodecane). Nevertheless, a deep desulfurization (higher than 90% of sulfur removed) was exclusively achieved when Lewis acid ILs containing tetracloroaluminates were utilized ([BMIM]Cl/$AlCl_3$ (0.35:0.65, mol/mol) and [EMIM]Cl/$AlCl_3$ (0.35:0.65, mol/mol)). The efficiency of optimum IL-prototypes was subsequently investigated in a multistage desulfurization experiment using a real pre-desulfurized diesel oil sample (without additives, sulfur content: 375 ppm) at 60 °C with a mass ratio oil/IL = 5/1 and 15 minutes of contact time. Lewis acid ILs showed the best performance after four extraction steps.[27]

Desulfurization studies via extraction with similar Lewis acids and halogen-free ILs followed this preliminary work. The influence of *S*-species and *S*-concentration on the extraction with halogen-free ILs, cross solubility of oil in the IL and vice versa was conducted. Furthermore, important results on the extraction of *N*-containing compounds (NCs), continuous extraction in a mixer-settler system, possibilities of regeneration of S-loaded ILs and possible scenarios for the integration of this technology in existing refinery networks were also reported. Results confirmed the potential of ILs in terms of selective extraction properties, especially with respect to challenging *S*-compounds difficult to remove by HDS (e.g. DBT derivatives present in middle distillates including diesel oil). The application of mild process conditions (ambient pressure and temperature) and the absence of any molecular hydrogen to be fed in the systems can be considered as additional advantages compared to conventional HDS. Highly promising ILs include [BMIM][$OcSO_4$] and [EMIM][$EtSO_4$], as halogen-free compounds available from relatively cheap starting materials.[28]

Thereafter, a significant number of related studies have been reported on the design of ILs for the treatment of refinery feedstocks. Desulfurizations with ILs have been focused on gasoline and diesel coming from FCC units, which contained sulfured aromatic compounds as principal SCs.

Bowing and Jess investigated kinetic and continuous reactor design aspects for scaled-up synthesis of ethylmethylimidazole ethylsulfate ([EMIM][$EtSO_4$]), one of the most promising halogen-free ILs for sulfur extraction. Compared to batch reactors, reaction times are reduced by a factor of 1000, which is particularly advantageous when employing toxic reactants (e.g.

diethyl sulfate). Beyond the synthesis of [EMIM][EtSO$_4$], these results may pave the way to the utilization of related ILs as well as other exothermic processes with a temperature limit.[29]

Many other papers have been published about the desulfurization of oils by liquid-liquid extraction using ILs, some of them are presented in the Table 1.

Table 1 Papers describing desulfurization of oils by liquid-liquid extraction using ILs.

IL(s) studied	**T (°C)**	**IL:feed ratio (w:w)**	**Removal efficiency (%) or K_N (mg S kg^{-1} IL)/(mg S kg^{-1} oil)**	**Observations**	**Ref.**
[EMIM][BF$_4$] [BMIM] [BF$_4$] [EMIM][PF$_6$]	25	1:2	[EMIM]BF$_4$: 17% sulfur removal for low sulfur model gasoline (240 ppm) and 11% for high sulfur gasoline (820 ppm) as compared to 29% and 13% for [BMIM]PF$_6$.	ILs showed high selectivity for the absorption of aromatic SCs from gasoline, but their extraction capacity was very low. ILs saturated with SCs were readily regenerated by either direct distillation or by successive dissolution in water followed by water vaporization.	30
[DMEE]CO$_2$Et [DMAPN]CO$_2$Et	25	1:1	First extraction cycle: 59 and 98 after five cycles.	The recycling of ILs was performed under vacuum distillation. The properties and extraction efficiency of ILs did not significantly change upon recycling.	31
[BMIM][CuCl] (1:2)	25	1:5	23% for model oil and 16-37% for gasolines (196-950 ppm).	Cu(I) anionic species such as $CuCl_2^-$, $Cu_2Cl_3^-$, and $Cu_3Cl_4^-$ were found in the IL. Improved extraction values at decreasing S-content. The extraction with CuCl-based IL has the advantage of no polymerization reaction of the olefins in the gasoline.	32
[MMIM][DMP] [EMIM][DEP] [BMIM][DBP]	25	ND[a]	K_N was between 0.94-1.81. K_N for DBT: [MMIM][DMP]: 0.4 [EMIM][DEP]: 1.27 [BMIM][DBP]: 1.59	K_N for each phosphoric IL and S-component (namely, 3-MT, BT, and DBT) is virtually a constant irrespective of the S-content in gasoline.	33
[OMIM][BF$_4$]	25	ND	TS: 79% and DBT: 87% after three stage experiment	TS distribution ratio (β), and solvent selectivity (S) were determined to calculate solvent extraction capacity for ternary systems involved in desulfurization. The IL showed low extraction efficiency.	34
[EMIM][DEP] [BMIM][DBP]	25	1:1	K_N for DBT: MIM + 20% [BMIM]DBP: 2.63. MIM + 20% [EMIM]DEP: 2.28	K_N values were measured between straight-run fuel oil and *N*-ethylimidazole, *N*-methylimidazole and its mixture with a dialkylphosphate ILs, viz. [EMIM][DEP] or [BMIM][DBP].	35
[MMIM]MeSO$_4$ [EMIM]EtSO$_4$ [EMM]MeSO$_4$ [EEIM]EtSO$_4$ [BMIM]MeSO$_4$ [BEIM]EtSO$_4$	25	1:1	[EMIM]MeSO$_4$: 4 [MMIM]MeSO$_4$: 70	DBT was successfully extracted after one round of extraction at a IL/model fuel mass ratio 1.0.	36
[BMIM]AlCl$_4$	25	1:6	90-95	High levels of S and N removal were achieved after drying the fuel with	37

				molecular sieves. In all cases, the dark green IL turned black immediately when it contacted the fuels, indicating IL decomposition of the Lewis acid ILs even in the absence of water.	
[BPy]BF_4 [HPy]BF_4 [OPy]BF_4	25	1:1	[OPy]BF_4: 46.7, [HPy]BF_4: 36.7 after three cycles.	The extractive performance using pyridinium-based ILs followed the order [BPy][BF_4] < [HPy][BF_4] < [OPy][BF_4], and selectivity to sulfur compounds followed the order TS < BT < DBT.	38
[BMIM]][Cl/$FeCl_3$] (1:2) [BDMIM][Cl/$FeCl_3$] (1:2) [HDMIM][Cl/$FeCl_3$] (1:2) [HMIm][Cl/$FeCl_3$] (1:2) [HHIm][Cl/$FeCl_3$] (1:2)	25	1:5	Up to 99 in ratios higher than 2. Ratios of $FeCl_3$/[BMIM]Cl: 0.5, 0.7, 1.0, 1.5, 2.0, 2.5, 3.0 and 5.0 were evaluated.	Lewis acidic ILs [BMIm][Cl/$FeCl_3$] and [BDMIm][Cl/$FeCl_3$] in ratios higher than 2.0 exhibited quantitative extraction of SCs in model and real oils.	39
[EMIM][DMP] [EEIM][DEP] [BEIM][DBP]	25	ND	K_N for DBT: [EMIM][DMP]: 1.17 [EEIM][DEP]: 1.61 [BEIM][DBP]: 1.72	K_N between IL and gasoline followed the order of [BEIM][DBP] > [EEIM][DEP] > [EMIM][DMP], and for a specific IL, the sulfur partition coefficient always followed the order of DBT > BT > 3-MT. The extractive ability of the alkylphosphate ILs was dominated by the structure of the cation.	40
[BMIM][BF_4] [BMIM][PF_6] [BSAMIM][HSO_4] [BSAPy][HSO_4] [$BSAEt_3$][HSO_4] [BSAMIM][PTS] [BSAMIM][PTS]	80	!:4	[BSAMIM][PTS]: 89% after 5 extraction stages with real diesel (438 ppm)	[BSAMIM][HSO_4] and [BSAMIM] [PTS] were the optimum extracting agents. [BSAMIM]PTS could be recycled five times (after washing with hexane) without considerable loss in its extractive performance.	41
3-MePy-based ILs: [C_8MPy][BF_4] [C_6MPy][BF_4] [C_4MPy][BF_4]	25	1:1	[C_8MPy][BF_4]: 60% after 3 steps with real diesel (97 ppm).	The extractive performance followed the order of [C_8MPy][BF_4] > [C_6MPy][BF_4] > [C_4MPy][BF_4].	42
[BMIM] [BF_4] [BMIM]PF_6 [BMIM][$FeCl_4$] (1:1)	25	1:1	[BMIM][$FeCl_4$]: 49% after 3 steps of extraction for model diesel.	[BMIM][$FeCl_4$] was generally optimum as extractant. This IL could be recycled five times (after washing with hexane) without considerable loss in their extractive performance. [BMIM]$FeCl_4$ was prepared as a neutral (not Lewis acidic) ILs (ratio [BMIM]Cl/$FeCl_3$, 1:1).	43
Several imidazolium phosphate ILs were tested (twenty two ILs with Me_2PO_4, Et_2PO_4 and Bu_2PO_4 as anion and SILP materials.	25	1:1	ILs: 40 for the first step and up to 99 after seven steps. SILP: 80 for the first step and 90 after multistage.	Regeneration of the IL was achieved by distillation or re-extraction procedures. SILP exhibited a significantly higher extraction performance reducing SCs 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.	44
[BMIM][$N(CN)_2$] [EMIM] [$N(CN)_2$] [S2][$N(CN)_2$] [$EtMe_2S$][$N(CN)_2$]	20-55	1:1	[BMIM][$N(CN)_2$]: 48.5 (gasoline) and 68.5 (diesel) and up to 99 after 5 stages for gasoline and 4 stages for diesel. TS extraction 46.7% (20°C) and 40.6% (55°C).	S-extraction ability follows the order [BMIM][$N(CN)_2$] > [EMIM][$N(CN)_2$] > [S2][$N(CN)_2$] > [$EtMe_2S$][$N(CN)_2$], with DBT being more efficiently extracted than TS. The mutual solubility is not pronounced and the extraction efficiency does not significantly change after six	45

				regeneration cycles.	
[BMIM][OcSO$_4$]	60	1:1	ND	The influence of mass ratio (IL/fuel), extraction time and temperature was studied under optimized conditions for BT removal. Analysis conducted using Central Composite Face-Centered Experimental Design provided satisfactory optimum mild conditions for a mass ratio (IL/fuel) of 1:1, extraction time 9 min at 60^{o}C.	46
[EMIM][SCN] [MMIM][MP] [(EtOH)$_3$NMe][MeSO$_4$]	25	1:1	[EMIM]SCN: 94% TS in model gasoline and 88% in model diesel. DBT is completely extracted from diesel in the third process stage with [EMIM]SCN.	LLE measurements of ternary mixtures for five systems were measured ar rtp and desulfurization of model gasoline and model diesel by the use of selected ILs. [EMIM]SCN] has a good capacity for fuels desulfurization.	47
[BMIM][OTf]	25	1:1	[EMIM][SCN]: 94% TS in model gasoline and 88% in model diesel. DBT is completely extracted from diesel in the third process stage. Model gasoline: TS: 96 after three stages. Model diesel: DBT: 97.5 and TS: 93.	Liquid-liquid equilibrium (LLE) data for new three ternary systems {TS + *n*-heptane + [BMIM]OTf}, {pyridine + *n*-heptane + [BMIM]OTf}, {benzene + *n*-heptane + [BMIM]OTf}, at T = 298.15 K were determined. The NRTL model was used to correlate LLE experimental results.	48
ILs derived from 1,2,3,5-tetralkyl-pyridinium and bis(trifluoromethane-sulfonyl)imide: [^{1}E^{3}M^{5}M^{2}PPy][NTf$_2$] [^{1}B^{3}M^{5}M^{2}PPy][NTf$_2$]	25	1:1	Solute distribution ratio (β) and selectivity (S) for the ternary systems (heptane + TS + [^{1}E^{3}M^{5}M^{2}PPy][NTf$_2$]) at *rtp* were used to evaluate extractive desulfurization performance.	An increase of the cation alkyl chain length leads to lower selectivity values, achieving a higher selectivity when using [^{1}E^{3}M^{5}M^{2}PPy][NTf$_2$]. β and S obtained for these ILs are higher than those of [^{1}H^{3}M^{5}MPy][NTf$_2$], implying a greater extractive ability when having substituents in position 2 of the cationic ring.	49
[3-MeBuPy][N(CN)$_2$] [4-MeBuPy][N(CN)$_2$] [4-MeBuPy][SCN] [BMIM][C(CN)$_3$] [BMIM][N(CN)$_2$] [BMIM][SCN]	25	1:1	Model oil: [3-MeBuPy][N(CN)$_2$]: 86 and 78%, [4-MeBuPy][N(CN)$_2$]: 85 and 76, [4-MeBuPy]SCN: 86 and 77 for DBT and TS. Light Catalytically Cracked Spirit: TS: 25 and pyrrole: 45.	N-containing aromatic components are significantly better extracted as compared to SCs. Experiments with real refinery streams confirmed that SCs and NCs can be removed from these streams, albeit with a lower efficiency with respect to model feeds.	50
[EtMIM]Cl	25	1:1	Model oil: 90 for Py, 76 for indole and 99 for DBT.	IL was evaluated by using model oil (dodecane) with indole as a neutral nitrogen compound and pyridine as a basic nitrogen compound. (DBT). Regeneration of the IL was carried out with toluene back-extraction. A 1:1 toluene-to-IL mass ratio at RT was utilized.	51
[C$_2$^{4}DMAPy[]][N(CN)$_2$] [C$_4$^{4}DMAPy][N(CN)$_2$] [C$_6$^{4}DMAPy][N(CN)$_2$]	25	1:1	K_N for TS in model gasoline: [C$_2$^{4}DMAPy][N(CN)$_2$]: 0.885 [C$_4$^{4}DMAPy][N(CN)$_2$]: 1.028 [C$_6$^{4}DMAPy][N(CN)$_2$]: 1.218	The sulfur partition coefficient (K_N) and extractive selectivity (S) were used to evaluate extractive desulfurization performance. K_N for different N(CN)$_2$ ILs in model gasoline or model diesel followed the order: [C$_2$^{4}DMAPy] < [C$_4$^{4}DMAPy] < [C$_6$^{4}DMAPy]. K_N for different aromatic compounds	52

				comparably complied with the following sequence: TS < 4,6-DMDBT < BT < DBT.	

[a]Not defined

As can see in this table, the distribution ratio (the ratio of the total sulfur between IL and hydrocarbon phase), selectivity (specific extraction of an specific S-containing compound respect to the overall compounds extracted by the IL from the hydrocarbons mixture) and capacity of extraction (how much S-containing compounds can be extracted from the hydrocarbon to the IL) of the ILs depend on their chemical structure.

Holbrey and coworkers studied the influence of structural aspects of ILs in their performance as SCs extractants. The study was carried out with different cations (imidazolium, pyridinium, and pyrrolidinium) and a range of anion types using liquid-liquid partition studies and QSPR (quantitative structure-activity relationship) analysis. The partition ratio DBT/ILs showed a clear variation with cation class (dimethylpyridinium > methylpyridinium > pyridinium approximate to imidazolium approximate to pyrrolidinium), with much less significant variation with type of anion. Polyaromatic quinolinium-based ILs showed even greater extraction potential, but were compromised by higher melting points, for example, 1-butyl-6-methylquinolinium bis{(trifluoromethyl)sulfonyl} amide (mp 47°C) extracted 90% of the available dibenzothiophene from dodecane at 60°C.[53]

A screening of ILs for the extraction of SCs was recently reported employing, for the first time, a real sample of natural gasoline. The gasoline sample was a highly volatile liquid recovered from natural gas, with a vapor pressure between that of condensates and liquefied natural gas. In this study, the effect of the molecular structure of seventy five ILs on the desulfurization efficiency of gasolines with high sulfur content (210 ppm) was evaluated. Results indicated that the anions played a more important role with respect to that of cations in the desulphurization process. Interestingly, ILs based on halogen-ferrates and halogen-aluminates displayed the highest efficiency in sulfur removal (up to 94% for IL:gasoline ratio of 1:10 at 25°C). These results were remarkably improved under an excess of metallic salt (Lewis acid ILs).[54] Additionally, an ingenious method of recovery, regeneration and reuse of the water sensitive tetrachloroferrate ILs was patented.[55]

In contrast to results obtained by Holbrey and coworkers,[53] these studies also showed that, under actual experimental conditions (real gasoline containing many hydrocarbons and more that 15 SCs, ratio IL/gasoline 1:10, 10 minute extraction time and RT), the extracting properties of ILs containing a NTf_2^- anion were poor, yet any ILs containing an organic anion displayed good performance (efficiency lower than 28% and in many cases lower than 10%) as sulfur removal compounds. Only for Lewis acidic ILs (containing an anion with Fe, Al or Mo) extractions superior to 90% of SCs were obtained. In these cases, the anion played the most important role on the IL efficiency.

A Density Functional Theory (DFT) study of the interaction between ethanothiol (most abundant SCs on gasolines), and Fe-containing ILs provided insights into the excelling performance of [BMIM][$FeCl_4$] under $FeCl_3$ excess to remove SCs from gasolines. The high desulfurization performance was suggested to be due to a donation-backdonation Dewar-Chatt-Duncanson-like model mechanism. This was a consequence of sulfur interaction (from ethanethiol molecules) and the metallic centers of $Fe_2Cl_7^-$ anions present in the solution. Such interaction was most probably promoted because of the symmetry relationship among molecular orbital of ethanethiol HOMO and the atomic d_{xy} -type orbital on Fe sites in $Fe_2Cl_7^-$ LUMO.

According with this theoretical study, he main mechanism is that sulfur transfers an amount of electron density to Cl_2 and Cl_3 through Fe_1 when ethanethiol approaches $Fe_2Cl_7^-$ to form the complex Fe_2Cl_7-R; thus Fe_1 responses to backside electron density flow to C_1 and moreover some electrons move further to Cl_1 and Cl_4. The net effect is that the total charge of -1e from $Fe_2Cl_7^-$ is distributed within complex Fe_2Cl_7-R in such a manner that later subdivides in two regions having similar negative charges: $FeCl_4$ and $FeCl_3$-R with -0.538 and -0.461 e, respectively, and then by both electrostatics repulsion complex and antisymmetry of the now- occupied old $Fe_2Cl_7^-$ LUMO, breaking occurs. This interchange of electronic density is the known donation-backdonation mechanism for desulfurization; *i.e.*, ethanethiol donates electrons through sulfur to a Fe of anion $Fe_2Cl_7^-$, which himself retrodonates electrons to the ethanethiol carbon bonding sulfur, leading to weakening or activation of the S-C_1 bond (Figure 3).[56]

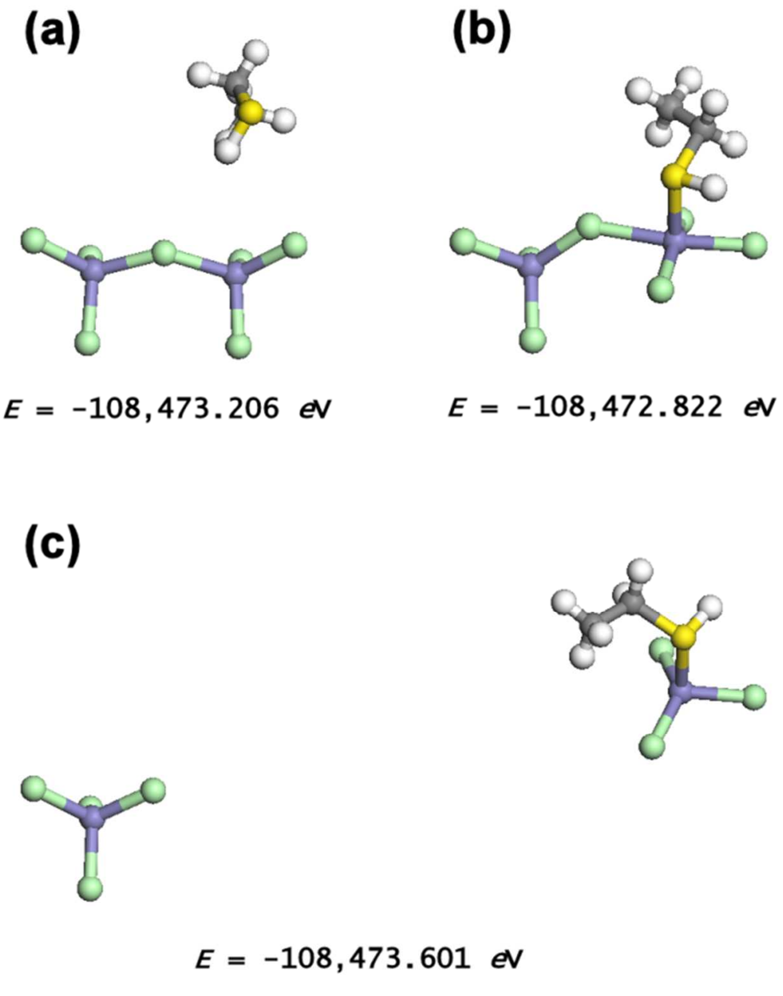


Fig. 1 Possible steps of reaction between ethanethiol and $Fe_2Cl_7^-$. (*a*) Initial approximation; (*b*) chemisorption; and (*c*) breaking of the complex. Each snapshot is resulting from energy minimization of the geometrical structure.

Other theoretical studies of desulfurization employing ILs have also been carried out. Zhou, Mao and Zhang employed *ab-initio* calculations using tiophene as SC model and two ILs, [BMIM][PF_6] and [BMIM][BF_4].[57-59] Results showed that tiophene interactions with both anions and cations of ILs were mainly dependent on electrostatic attractions as well as on structure and property of the anion and the compactness between cation and anion. As example, [BMIM][PF_6] exhibits a strong electron donation of phosphorous to fluorine atoms. Consequently, fluorine atoms in [PF_6] anion possess a relatively high negative charge and PF_6^- can also provide more native charged fluorine atoms to TS molecules as compared to [BF_4]. The degree of compactness for [BMIM][PF_6] is lower to that of [BMIM][BF_4], which allows a facile restructuration of the IL in the process of tiophene dissolution.[60]

Theoretical studies have also been employed to develop predictive models for the estimation of thermodynamic properties of ILs. Such methods constitute a highly useful tool for the design of novel ILs with specific properties, providing at the same time a simple and efficient property screening in the rapidly growing field of (potentially) available ILs. Several predictions of these properties can be conducted using a range of methods from molecular dynamics (MD) via atomistic force fields,[61] quantitative structure-property relationship (QSPR) models,[62] to classical thermodynamic models such a UNIQUAC,[63] or UNIFAC,[64] and COSMO-RS (**CO**nductor like **S**creening **MO**del for **R**eal **S**olvents) model.[65-72]

Phase equilibrium data for the systems between ILs and sulfur-containing compounds (SCs) have also been widely studied as well as a series of theoretical model studies.[73-79]

Recently, a property study was carried out to measure the experimental liquid–liquid phase equilibria for the ternary systems containing {1-ethyl-3-methylimidazolium tricyanomethanide, [EMIM][TCM] + thiophene + *n*-heptane} at different temperature and {[EMIM][TCM] + benzothiophene + *n*-heptane} at 308.15 K at ambient pressure was carried out. The values of selectivity S and solute distribution ratio β were calculated directly from the experimental data. These parameters for the studied systems are higher than for analogous systems with the same [EMIM] cation and more popular [NTf_2] and [$EtSO_4$] anions. This results indicates that [EMIM][TCM] is a perspective solvent for the extraction of studied aromatic sulfur compounds from *n*-heptane. Another important factor in favor of this result is the low impact of the temperature upon the phase diagram, which suggests that the separation processes can be carried out at room temperature, reducing the energy requirements. The density (**ρ**) as a function of temperature at P = 0.1 MPa for [EMIM][TCM] obtained in this work,[80] were very similar to those reported in a recently study and those very similar to the water density.[81]

2.2 Oxidative desulfurization of fuels using ILs

The oxidative desulfurization (ODS) is a promising alternative for fuel desulfurization by liquid-liquid extraction. Such methodology comprises a direct *in-situ* oxidation of SCs to sulfoxides and sulfones upon addition of the extractant, aiming to increase their polarity to make a subsequent liquid-liquid IL-assisted extraction more efficient for SCs removal (Fig. 4). The extraction of oxidized sulfur compounds can be conducted using conventional volatile organic solvents as well as a combination of catalytic oxidation and extraction with ILs, so far reported as a greener desulfurization system.

ODS combined extraction is considered to be one of the most promising alternative processes to HDS for fuel desulfurization, featuring short contact times at ambient conditions, high efficiency, and selectivity. The oxidation process can also be carried out in the absence of catalyst as often the ILs plays both the role of solvent/extractant and catalyst (e.g. decomposing hydrogen peroxide into hydroxyl radicals).

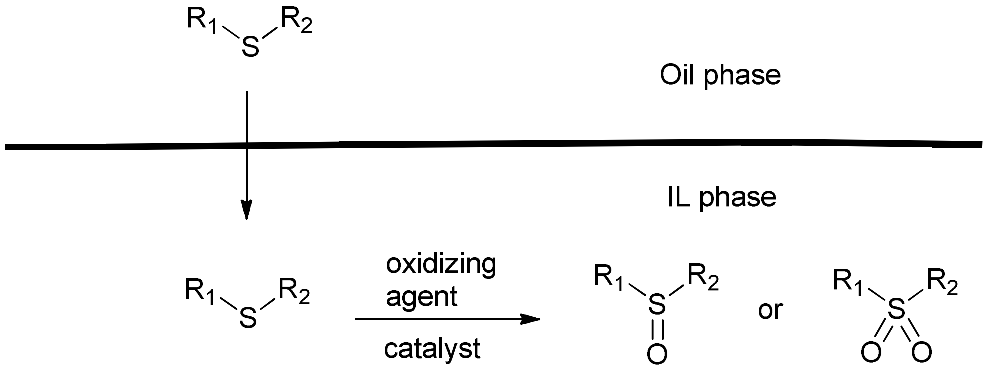


Fig. 4 General scheme for ODS process using ILs as extractant.

Different ODS processes have utilized oxidants including molecular oxygen,[82] H_2O_2 in combination with polyoxometalates,[83, 84] acetic acid,[85] ozone,[86] and *tert*-butylhydroperoxide.[87]

Lo and coworkers reported the first procedure of ODS using ILs as extractants in 2003. Tetradecane doped dibenzothiophene (DBT) was selected as model feedstock and [BMIM][PF_6] and [BMIM][BF_4], immiscible with light oils, as solvents for the liquid-liquid extraction systems. DBT was extracted from the model feedstock and oxidized in the IL phase. The ODS system (H_2O_2-acetic acid/[BMIM]PF_6) resulted in a high oxidation rate of DBT and the desulfurization process was comparably more efficient to that using the same ILs as sulfur extractant without previous oxidation. In a one-pot operation, SCs in the light oils were extracted and then S-oxidized (H_2O_2-AcOH) to form the corresponding sulfones at 70 °C. The sulfur content of unoxidized light oil was 7370 and 7480 ppm in the presence of [BMIM]PF_6 and [BMIM][BF_4], respectively, after 10 h of oxidation and extraction and ratio IL:hydrocarbon of 1:1. The sulfur content was reduced to 1300 and 3640 ppm, respectively. The use of [BMIM][BF_4] and [BMIM][PF_6] increased the desulfurization yields from 7 to 55% and 8 to 84%, respectively for a combination of oxidation and extraction with ILs.[88]

In another example, SCs could be deeply removed from a model oil (due to formation of hydroxyl radicals) using Brønsted acidic ILs 1-hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF_4],[89] and *N*-methyl-pyrrolidonium tetrafluoroborate [HNMP][BF_4],[90] in combination with H_2O_2. DBT removal reached 93% for [HMIM][BF_4] under the investigated conditions (a mixture of 3.2 mL model oil, 5.0 mL IL under stirring at 90 °C for 6 h). In the case of [HNMP][BF_4] , the efficiency of sulfur extraction was 99.4% for diesel fuel (total sulfur: 3240 ppm) using a 1:1 feedstock:IL ratio and 2 h of contact time at 60°C. Importantly, the IL was recycled 7 times without a significant decrease in desulfurization efficiency.

There are several different reports describing ODS procedures that employ ILs, some of them have been summarized in Table 2.

Table 2 Papers describing ODS of oils using ILs.

IL(s) evaluated	**Oxidizing agent**	**Catalyst**	**Time (min)**	**T (°C)**	**Removal efficiency (%) or K_N (mg S kg^{-1} IL)/ (mg S kg^{-1} oil)**	**Conditions of desulfurization**	**Observations**	**Ref.**
Octadecyl- (STAB), cetyl- (CTAB), tetradecyl- (TTAB), and dodecyl- (DTAB) trimethyl-ammonium bromides	H_2O_2	TPA	Several times (kinetic study)	25	ND	Model oil: DBT in *n*-octane (3000 ppm) A certain amount of STAB and 0.06 g of TPA were added under vigorous stirring. 1 mL of 30% H_2O_2. The apparent activation energy (E_a) of 28.70 kJ/mol was obtained under experimental conditions	A conceptual model was established in the DBT oxidation process based on the interaction between TPA and STAB. Mass transfer of DBT suggested taking place from the organic media towards the interface.	91
[BMIM][BF_4] [OMIM][BF_4] [BMIM][PF_6] [OMIM][PF_6]	H_2O_2	$WO(O_2)_2.Phen.H_2O$ $[MoO(O_2)_2.Phen]$	180	70	98.6%	Model oil: DBT in *n*-octane S-content 1000 ppm. Reaction conditions: oil/IL: 5:2 (V/V), [*n*(DBT)/*n*(catalyst) = 25], *n*(H_2O_2)/*n*(DBT) = 10.	ODS of model oil using H_2O_2 in IL, was 30-63%. Simultaneous introduction of H_2O_2 and catalyst remarkably improved sulfur removal. ODS for $WO(O_2)_2$. $Phen.H_2O/H_2O_2$ only reached 50.3% sulfur removal in the absence of IL.	92
[BMIM][PF_6]	K_2O-H_2O_2-CH_3COOH	$(Oct)_4N^+F^-$ As Phase Transfer Catalyst (PTC)	K_2O: 360 H_2O_2: 180	70	Model diesel BT, DBT > 98 Real diesel: 75	Model diesel: BT or DBT in mineral oil (S content: 1000 ppm).Higher desulfurization conditions: sulfur/oxidant ratio: 1:23 (with K_2O) and 1:140 (with H_2O_2), ratio oil/IL (2:1). Real diesel (26000 ppm S-content). Oil and acid/IL phases were separated by a centrifuge. The oil phase was mixed with alumina powder for sulfone adsorption.	In comparison to hydrogen peroxide, the use of potassium superoxide as an oxidant can achieve very similar desulfurization efficiencies in both model compounds and real diesel samples, with a significantly lower sulfur/oxidant ratio. K_2O is safe and stable even in high purity, with less mass and volume required for the process.	93
[BMIM][$MeSO_4$]	H_2O_2	CF_3COOH	10 ( )))) + 170 (stirring)	50	100	Model oil (500 ppm S) in mineral oil or *n*-dodecane is mixed (5 g) with 5 g of 30% H_2O_2 and 1.5 g of 20% trifluoroacetic acetic acid and 0.3 g of tetraoctylammonium fluoride is introduced. Ratio hydrocarbon/IL: 1:1.	In this work ultrasound-assisted oxidative desulfurization (UAOD) was employed to accelerate the oxidation process. The newly UAOD process was also used for desulfurization of Navy diesel (F-76) with a sulfur concentration of 4220 ppm. The overall sulfur renoval was reported as 100%.	94
[BMIM][BF_4]	H_2O_2	$Q_3\{PO_4[MoO(O_2)_2]\}$ Q: $[(C_4H_9)_4N]^+$, $[C_{14}H_{29}N(CH_3)_3]^+$, $[C_{16}H_{33}NC_5H_5]^+$.	H_2O_2	70	92	Model oil (1000 ppm), DBT in *n*-octane) were carried out with 0.00156 mmol of catalyst [*n*(DBT)/*n*(catalyst)) 100], 0.032 mL of 30 wt % H_2O_2 [*n*(H_2O_2)/*n*(DBT) = 2]. IL/oil: 1:5.	The catalyst with the short alkyl chain exhibited higher catalytic activity than that with the long alkyl chain. The system containing H_2O_2, [BMIM][BF_4], $[(C_4H_9)_4N]_3$ $\{PO_4[MoO(O_2)_2]_4\}$ can be recycled four times without significant loss of activity.	95
$[(CH_3)_3NC_{16}H_{33}]_4[W_{10}O_{32}]$ $[(CH_3)_3NC_{14}H_{29}]_4[W_{10}O_{32}]$ $[(CH_3)_3NC_{12}H_{25}]_4[W_{10}O_{32}]$ $[(CH_3)_3NC_{10}H_{21}]_4[W_{10}O_{32}]$	H_2O_2	--	30	60	Model diesel:99.6 Real diesel: 93.5 after five times extraction.	Model oil :(BT, 1000 ppm; 4,6-DMDBT, 500 ppm in *n*-octane). The most suitable condition: *n*(DBT):*n*(catalyst):*n*(30% H_2O_2) = 1:0.01:3.	The length of carbon chains of quaternary ammonium cations played a vital role in the catalytic activity of surfactant-type decatungstates. $[(CH_3)_3NC_{16}H_{33}]_4W_{10}O_{32}$ exhibited	96

							the best catalytic performance and can be recycled for six times without significant decrease in catalytic activity.	
[BMIM][BF_4]	H_2O_2	V_2O_5	240	30	98.7	Experimental conditions: model oil/IL = 1:5, n(DBT)/n(V_2O_5) = 20, n(H_2O_2)/n(DBT) = 6.	[BMIM][BF_4] can be recycled seven times without a significant decrease in activity.	97
[BMIM][BF_4] [BMIM][PF_6] [OMIM][BF_4] [OMIM][PF_6]	H_2O_2	$H_3PW_{12}O_{40}\cdot 14H_2O$	60	30	100	Model oil: DBT dissolved in *n*-octane (S-Content = 1000 ppm). Conditions: [BMIM]BF_4 = 1 mL, model oil = 5 mL, *n*(DBT)/*n*(HPW) = 100:1.	The commercially available $H_3PW_{12}O_{40}\cdot 14H_2O$ combined with H_2O_2 and [BMIM][BF_4] was effective for removing DBT, 4,6-DBT, and BT.	98
$Me_3NCH_2C_6H_5Cl\cdot 2ZnCl_2$	H_2O_2	CH_3COOH	30	25	94	Ratio H_2O_2/DBT = 6 and *V* (IL):*V* (*n*-octane) = 1:5,	Extraction with IL (28.9%) without oxidation. The $Me_3NCH_2C_6H_5Cl\cdot 2ZnCl_2$ IL could be recycled 6 times without a significant decrease in activity. Kinetics of ODS procedure of DBT by H_2O_2 and acetic acid was first-order with an a rate constant of 0.0842 min^{-1} and half-time of 8.23 min.	99
[EMIM][DEP]	H_2O_2	--	15	23	K_N: Model diesel: 5.2 Con-DO: 0.2 Preox-DO (100ppm): 2.1 Preox-DO (27ppm): 3.2	Pre-desulfurized diesel oil (Con-DO):130 ppm of S-content and pre-desulfurized diesel oil with completely oxidized SCs (Preox-DO): 100 ppm and 27 ppm of S-content. Model diesel (4,6DBTsulfoxide): 100 ppm, mass ratio oil:IL = 1:1.	The evaporation of water from the IL is the crucial step with regards to the energy consumption of the process. The energy demand is comparable to classical HDS, if a multi-stage evaporation is used.	100
[BMIM][BF_4] [OMIM][BF_4] [BMIM][PF_6] [OMIM][PF_6] [BMIM][TA] [OMIM][TA]	H_2O_2	$Na_2MoO_4\cdot 2H_2O$	180	70	[BMIM][BF_4]: 99.0 [OMIM][BF_4]: 67.6 [BMIM]PF_6: 69.8 [BMIM][PF_6]: 77.8 [BMIM][TA]: 49.0 [OMIM][TA]: 37.4	Model oil DBT in *n*-octane (S-content: 1000 ppm). Reaction conditions:, model oil = 5 mL, IL = 1 mL, [*n*(DBT)/*n*(Catalyst) = 20], [*n*(H_2O_2)/*n*(DBT)] = 4.	The catalysts hardly dissolved in oil. The catalytic oxidation system containing $Na_2MoO_4\cdot 2H_2O$, H_2O_2 and [BMIM][BF_4] could be recycled five times without a significant decrease in activity.	101
[BMIM][BF_4] [OMIM][BF_4] [BMIM][PF_6] [OMIM][PF_6]	H_2O_2	[(3-SA)proPy]$_3$ [$PW_{12}O_{40}$].$2H_2O$ (A)	60	30	Model gasoline: [BMIM][BF_4]: 81.5 [OMIM][BF_4]: 77.1 [BMIM][PF_6]: 96.2 [OMIM][PF_6]: 99.5 Real FCC gasoline: 80.5	Model gasoline: DBT dissolved in *n*-octane (S-content = 500 ppm). Reaction conditions: IL = 1 mL, model oil = 5 mL, *n*(H_2O_2)/*n*(DBT)/*n*([PSPy]$_3$PW) = 480:120:1.	The oxidation activity showed the order: DBT > 4,6-DBT > BT. The reaction rates increased with T, amount of the **A**, and the molar ratio of H_2O_2/SCs. **A** was very active for the catalytic oxidation of real FCC gasoline. The system could be recycled nine times without a significant decrease in activity.	102
[BPy][HSO_4] [BPy][H_2PO_4] [BPy][SCN] [BPy][BF_4]	H_2O_2-HCOOH	--	60	20 40 60 80	Model gasoline: 90.6 92.0 93.3 90.2 Real gasoline (60°C): 87.7	H_2O_2/sulfur molar ratio (O/S) is 4, S = 1000 µg/mL, **V** model oil/**V** IL = 1:1.	[BPy][HSO_4]act as PTC and it can be recycled five times without a significant decrease in activity. All these results indicated that ILs have a potential application in desulfurization technology.	103
[$(CH_2)_4SO_3HMIM$][Tos]	H_2O_2	$Na_2WO_4.2H_2O$	180	50	99.4	Reaction conditions: 3 ml model diesel (S 500 µg/g), 0.021 g $Na_2WO_4\cdot 2H_2O$, 2.5 mmol IL, 323 K, 0.7 mL H_2O_2 (30%).	The model diesel after oxidation could be easily separated by simple decantation. This system can be recycled five times without	104

							significant change on desulfurization. The mechanism of the catalytic oxidation process was also proposed based in a new kind of peroxytungstate ILs.	
[BMIM][BF$_4$] [OMIM][BF$_4$] [BMIM][PF$_6$] [OMIM][PF$_6$]		MoO(O$_2$)$_2$·C$_2$H$_5$NO$_2$ MoO(O$_2$)$_2$C$_3$H$_7$NO$_2$MoO(O$_2$)$_2$·C$_5$H$_9$NO$_4$	180	70	99 of total sulfur DBT, BT and 4,6-DBT reached 99.2%, 93.2% and 99.6%, respectively	*V*(model diesel) = 5 mL, *V*(IL) = 1 mL, (*n*(DBT)/*n*(Catalyst) = 10), (*n*(H$_2$O$_2$)/*n*(DBT) = 4.	Kinetic parameters of the oxidation of sulfur compounds were studied. The apparent rate constants of DBT, BT and 4,6-DBT were 0.0375 min^{-1}, 0.0157 min^{-1}, 0.0318 min^{-1} and the half-lives were 18.48 min, 44.14 min and 21.79 min, respectively.	105
Lewis acids: [BMIM][Cl/2ZnCl$_2$] (1:2), (**I**) [BMIM][Cl/ZnCl$_2$] (1:1), (**II**) Brønsted acids: [CH$_2$COOHMIM][HSO$_4$] [SO$_3$HBMIM][HSO$_4$] [HMIM][HSO$_4$] [BMIM][HSO$_4$]	H$_2$O$_2$	--	(**I**): 60 (**II**): 360	(**I**): 90 (**II**): 60	Model diesel: [BMIM][Cl/2ZnCl$_2$]/oil: 1/5: 92.2 1/1: 100 [SO$_3$HBMIM][HSO$_4$]/oil: 1:5: 93.9 1:1: 98.1 [BMIM][Cl/2ZnCl$_2$] Real diesel: 87.7 Coke diesel: 29.9	Model diesel (DBT in *n*-octane, 503 ppm) Real diesel: 64 ppm Coke diesel: 5380 ppm Desulfurization conditions for Real diesel: IL/oil: 2:1, 3 g IL and 0.136 g H$_2$O$_2$.	ILs acted as both extractants and catalysts. For [BMIM][Cl/2ZnCl$_2$] and [SO$_3$HBMIM]HSO$_4$, the desulfurization ability is not sensitive to mass ratio of IL/oil. The ILs can be recycled six times with negligible activity loss. [BMIM][Cl/2ZnCl$_2$] is effective for the desulfurization of real diesel with low S-content but not for high sulfur coke.	106
SiO$_2$-supported [BMIM]$_3$ [PMo$_{12}$O$_{40}$]	H$_2$O$_2$	--	120 180 180 180 180	60 50 60 70 80	100 (model diesel) Real diesel (530 ppm S) 84.1 91.3 95.1 97.9	O/S molar ratio of 3.0, atmospheric pressure. Real diesel: Reaction time: 180 min; sulfur content in the feed: 530 ppm; the obtained sulfones were removed by extraction using DMF with an oil/DMF volume ratio of 1.0.	The oxidation reactivity decreased in the order: DBT > 4,6-DBT > BT. [BMIM]$_3$ [PMo$_{12}$O$_{40}$]/SiO$_2$ and water phase were easily separated together from the oil phase by centrifugation, and no deactivation was observed after seven runs.	107
[EIMC$_4$SO$_3$H][NTf$_2$] [EIMC$_4$SO$_3$H][HSO$_4$] [C$_4$Py][NTf$_2$] [BMIM][NTf$_2$] [BMIM][PF$_6$]	H$_2$O$_2$ NaClO	--	180	30	Model diesel: 0.88 with NaClO and 81.2 with H$_2$O$_2$. Real diesel: 48 (30 °C) and 61 (60 °C).	Model oil (1600 ppm S): DBT (0.23 g) in *n*-octane (25 mL),1600 ppm. The reaction mixtures contained 5 g IL, 5 g model oil and 2 g oxidant (H$_2$O$_2$ or NaClO).	The order of extraction capability of ILs was [EIMC$_4$SO$_3$H]NTf$_2$ > [EIMC$_4$SO$_3$H]HSO$_4$ > [C$_4$Py]NTf$_2$ > [BMIM]NTf$_2$ > [BMIM]PF$_6$. [EIMC$_4$SO$_3$H]NTf$_2$ could be recycled 5 times without significant decrease in the activity.	108
	H$_2$O$_2$	[(C$_4$H$_9$)$_3$NCH$_3$]$_2$[W$_6$O$_{19}$] [(C$_8$H$_{17}$)$_3$NCH$_3$]$_2$[W$_6$O$_{19}$] [(C$_{12}$H$_{25}$)$_3$NCH$_3$]$_2$[W$_6$O$_{19}$]	60	60	[BMIM][BF$_4$]: 37.6 [OMIM][BF$_4$]: 53.1 [BMIM][PF$_6$]: 74.1 [OMIM][PF$_6$]: 97.7	Model oil: DBT, BT and 4,6-DMDBT in *n*-octane with *S*-content of 500, 250 and 250 ppm, respectively. 5 mL model oil, *V*(H$_2$O$_2$) = 24 μL, *m*([(C$_8$H$_{17}$)$_3$NCH$_3$]$_2$W$_6$O$_{19}$) = 3.5 mg, *V*(IL) = 1 mL.	The new catalytic system has several advantages: (1) formation of emulsion droplets gave a benign microenvironment for ODS with good S-removal efficiency for model oil and real gasoline; (2) accumulation of products do not influence the activity of the system and the system showed very good recyclability; (3) precipitated sulfones and clean oil could be readily separated; (4) the reaction process and the separation process generated no pollutants.	109
[BMIM][BF$_4$] [OMIM][BF$_4$] [BMIM][PF$_6$] [OMIM][PF$_6$]	H$_2$O$_2$	A series of Keggin-type polioximethalates (POM)-based ILs [MIMPS]$_3$PW$_{12}$O$_{40}$·2H$_2$O (1-(3-SA)-Pro-3-MIM-phosphortungstate	60	30	100 for [MIMPS]$_3$[PW$_{12}$O$_{40}$]·2H$_2$O for model diesel and 82% for real diesel (1113 ppm of total sulfur).	Model oil: DBT dissolved in *n*-octane (S-content = 500 ppm). IL:model oil = 1:5, Molar ratio:*n*(H$_2$O$_2$)/*n*(DBT)/*n*(Catal.) = 480:120:1.	The main factors affecting the process including T, catalyst dosage, and O/S (H$_2$O$_2$/DBT) molar ratio. Under the optimal conditions, DBT and 4,6-DBT could achieve high desulfurization efficiency. The reaction system could recycle 8-times with a slight decrease in activity.	110
1-(C$_n$H$_{2n+1}$)-3H-benzoimidazolium acetate ([C$_n$BZI][AcO]), n = 5 (A), 6 (B), 7 (C), 8 (D)	H$_2$O$_2$	--	180	70	A: 68.3 B: 77.7 C: 83.2 D: 87.5	Model oil (1500 ppm of TS) = 10 ml, V_{ILs}/V_{H2O2} = 1/1.1, V_{ILs}/V_{H2O2} = 20 ml.	The used ILs were recovered through re-extraction in dichloromethane, and could be recycled five times without any obvious decrease in activity.	111
[OMIM][BF$_4$]	H$_2$O$_2$	HPW-CeO$_2$	30	30	99.4	Model oil (DBT, BT, and 4,6-	Oxidative reactivity of different	112

						DMDBT in *n*-octane, with S-content of 500, 250, and 250 ppm, respectively. Typical run: 20 mg of catalyst, 48 μL of H_2O_2, and 1 mL of IL were added to the reactor (30 mL).	sulfur compounds decreased according to the following order: DBT > 4,6-DMDBT > BT. Besides, the oxidation system could be recycled for 10 times without a significant decrease in activity.	
$[3MHPy][Cl/nFeCl_3]$ (molar fraction n = 0.5, 1, 2, 3) and $[HMIM][Cl/FeCl_3]$ (molar fraction n = 0.5, 1, 2, 3)	H_2O_2	--	20	25	Lewis acidity of ILs reached 100% by $[3MHPy][Cl/FeCl_3]$ for model gasoline and 99.7% after seven ODS runs in the $[C_63MPy][Cl/FeCl_3]$-H_2O_2 system for real gasoline.	IL/oil mass ratio of 1/3, O/S molar ratio of 4/1	ILs acted as both extracting agent and catalyst	113
$[BMIM][PF_6]$	H_2O_2	Anderson-type $Q_4NiMo_6W\mathbf{x}O_{24}H_6$ (**x** = 0, 2, 4, 6)	180 240	30 60	Model diesel: 98 Real diesel: 96	Model diesel: 500 ppm (BT, DBT, 4-MDBT or 4,6-DMDBT) in ***n***-octane. IL/oil mass ratio: 1/10, 0.09 mL of 30 wt% H_2O_2 and cata-lyst [**n**(S)/**n**(Ni) = 100] Commercial diesel: 700 ppm, 0.2 mL H_2O_2, 4 mL $[BMIM]PF_6$ and catalyst **n**(S)/**n**(Ni) = 20	*S*-removal selectivity for SCs followed the order: DBT > 4-MDBT > 4,6-DMDBT > BT > 5-MBT. The reactivity of these SCs is sensitive to the electron density on S-atoms and the steric hindrance of the substituted groups of SCs. The ODS system for commercial diesel can be recycled ten times.	114
Surfactant-type polyoxometalate-based ILs: $[(C_8H_{17})_3NCH_3]_3\{PO_4[MoO(O_2)_2]_4\}$ (**A**) $[(C_{12}H_{25})_3NCH_3]_3\{PO_4[MoO(O_2)_2]_4\}$ (**B**) $[(C_8H_{17})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$ (**C**) $[(C_{12}H_{25})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$ (**D**)	H_2O_2	$H_3PMo_{12}O_{40}\cdot 26H_2O$ $H_3PW_{12}O_{40}\cdot 14H_2O$	120	60	$H_3PMo_{12}O_{40}\cdot 26H_2O$: 25.4 $H_3PW_{12}O_{40}\cdot 14H_2O$: 23.2 **A**: 73.2 **B**: 70.5 **C**: 49.7 **D**: 43.3 **A** + H_2O_2 : 100 **B** + H_2O_2 : 100 **C** + H_2O_2 : 100 **D** + H_2O_2 : 100	$n(H_2O_2)/n(DBT) = 6$, $m(\text{model oil})/m(SPIL) = 50$, $V(\text{model oil}) = 5$ mL, stirring rate: 500 rpm	Supposed mechanism and kinetics studies on the catalytic activity of SPIL with A revealed that the ODS could present a pseudo first-order kinetic. The catalytic activity for other SCs increased in the order BT < 4,6-DMDBT < DBT. There is little change for the oxidative desulfurization efficiency of SPIL after 8 recycles.	115
$[C_4{}^3MPy][FeCl_4]$ (1:1) $[C_4{}^3MPy][FeCl_4]$ (1:1) $[C_8{}^3MPy][FeCl_4]$ (1:1)	H_2O_2	--	10	25	Model gasoline: 100 Real gasoline: 44 at 1:3 (IL:gasoline)	m(IL/oil) = 1/5, **n**(H_2O_2)/**n**(DBT) = 6/1, initial *S*-content 1000 ppm.	The dialkylpyridinium-$FeCl_4$ ILs with H_2O_2 formed Fenton-like reagents and were effective in DBT removal from model oil.	116
$[(C_6H_{13})_3PC_{14}H_{29}]_2[W_6O_{19}]$	H_2O_2	IL act as catalyst	80	40 50 60	92 98 98	Model oil (DBT, BT, and 4,6-DMDBT in *n*-octane, with S-content of 500, 250, and 250 ppm, respectively. $[(C_6H_{13})_3PC_{14}H_{29}]_2[W_6O_{19}]$ IL, 30% H_2O_2 and model oil were added into the two-neck kettle in turn. 5 mL model oil, $V(H_2O_2)$ = 48 μL, m(IL) = 0.37 g.	The tungsten-containing task-specific IL not only acted as extraction media for the SCs and served as a catalyst for the H_2O_2 but also provided an oxidation micro-environment for the conversion from SCs to sulfones by forming IL emulsions. The self-emulsifiable IL showed very good recycling ability (ten cycles with the same *S*-removal).	117

Ge et al. described in 2013 an ODC employing $Na_2WO_4.2H_2O$ as catalyst, H_2O_2 as oxidant and several acidic ILs. They showed that when phase transfer catalyst (PTC) is used, under optimal conditions, the desulfurization efficiency is virtually 100%. Moreover, this acidic IL can be recycled five times without obviously decrease in activity (Table 3).[118]

Tabla 3 Sulfur removal of different desulfurization systems in model oil.

Entry	Type of IL	IL	IL + H_2O_2	IL + H_2O_2 + PCT + $Na_2WO_4.2H_2O$
1	$[(CH_2)_3SO_3HMIM][BF_4]$	16.4	33.8	99.9
2	$[(CH_2)_3SO_3HMIM][HSO_4]$	14.6	28.9	100
3	$[(CH_2)_3SO_3HMIM][H_2PO_4]$	15.7	29.4	94.5
4	$[(CH_2)_3SO_3TEA][BF_4]$	15.6	48.1	97.8
5	$[(CH_2)_3SO_3TEA][HSO_4]$	16.3	40.5	92.7
6	$[(CH_2)_3SO_3TEA][H_2PO_4]$	16.6	39.6	90.3

Reaction conditions: *n* (DBT)/*n* (catalyst) = 10, *n* (H_2O_2)/*n* (DBT)/n (PCT) = 60:20:1.
$V_{\text{model oil}}$ = 5 mL, V_{IL} = 1 mL, PTC = dodecyltributylammonium bromide, T = 60°C, t = 3 h.

The extractive and oxidative deep desulfurization of model fuel oils (model gasoline and diesel with ~500 ppm of sulfur content) using low-viscosity 1-ethyl-3-methylimidazolium dicyanamide ($[EMIM][N(CN)_2]$) has also been reported. The authors discussed mutual solubility between IL and model oils, EDS performance, along with factors affecting sulfur extraction including temperature, mass ratio of IL:oil, selectivity and reusability. After a single extraction, a rather low S-removal efficiency of 41.7% was obtained and TS could only be completely removed after five extraction cycles. ($[EMIM][N(CN)_2]$ showed a good selectivity for TS, since 41.7% of TS was removed from model gasoline (544 ppm of total sulfur in *n*-hexane) after one extraction at 25°C, 1:1 (IL:oil) and TS is almost completely removed after five extractions cycles. ($[EMIM][N(CN)_2]$ also showed a good reusability since after 5 cycles of regeneration and reused, the same SCs extraction performance was reported. However, considering the employed IL/oil ratio of 1:1 w/w, these results are essentially unpractical for industrial applications, as many of the studies showed in Tables 1 and 3. The oxidative removal of DBT in such a dicyanamide IL is comparatively ineffective, probably due to the strong intermolecular interaction between CH_3COOH or CH_3COOOH and ($[EMIM][N(CN)_2]$ phase as indicated by *ab initio* calculation results.[119]

ILs have also been used as immobilized catalysts for combined ODS heterogeneously catalyzed processes. Shi and Wei utilized two types of catalysts of peroxotungstates immobilized on IL-modified silica (**1** and **2**). Materials were synthesized by grafting the IL onto the modified mesoporous inorganic material via ion exchange, and subsequent anchoring of the catalytically active center (peroxotungstate) onto the immobilized IL (Figure 5). The catalytic systems were evaluated for the selective oxidation of sulfides to their corresponding sulfoxides and sulfones using 30% aqueous hydrogen peroxide as green oxidant. The oxidation proceeded rapidly and smoothly within a short period of time. The catalysts could be easily separated from the reaction system and reused.[120]

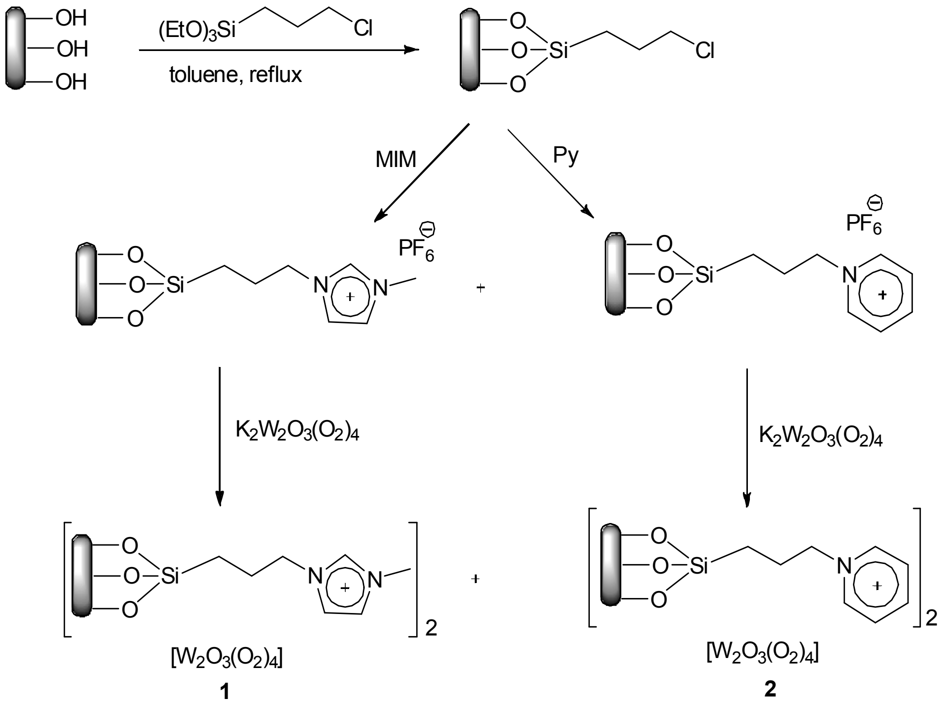


Fig. 5 Inmobilized IL as heterogeneous catalyst for ODS.

Metal-based surfactant-type ILs (MSILs) have been very recently proposed as alternatives in ODS. Methyltri-*n*-octylammonium peroxomolybdate $[(CH_3)N(n\text{-}C_8H_{17})_3]_2[Mo_2O_{11}]$ and peroxotungstate $[(CH_3)N(n\text{-}C_8H_{17})_3]_2[W_2O_{11}]$ were synthesized and characterized and evaluated in SCs removal using H_2O_2 as oxidant. The effects of H_2O_2/DBT (molar ratio), oil/MSIL (mass ratio) and the agitation rate were studied to estimate the optimal conditions for the desulfurization system. The quaternary ammonium cation could transfer the catalytic active species to the aromatic sulfur compounds under the investigated reaction conditions, leading to higher oxidative reaction rates.

Kinetic experiments revealed that the oxidative ODS reaction was in accordance with pseudo-first-order kinetics. Reaction rate constants and half-life were calculated and a mechanism for desulfurization was proposed. The optimal reaction conditions were oil/MSIL = 40:1, O/S = 8, reaction temperature: 30°C and agitation at 500 rpm. The MSIL $[(CH_3)N(n\text{-}C_8H_{17})_3]_2[Mo_2O_{11}]$ showed that the highest desulfurization activity (96.2%). This liquid catalyst possess contain the lipophilic cation and hydrophilic anion is amphiphilic favoring the oxidation of DBT by reaction-induced self-separation catalysis which made it play an essential role in the formation of the emulsion. Under these reaction conditions the catalyst forms micelles that create the right environment for the efficient oxidation of DBT (Figure 6). Moreover, the recovery of the heterogeneous catalyst was convenient for the ODS system.[121]

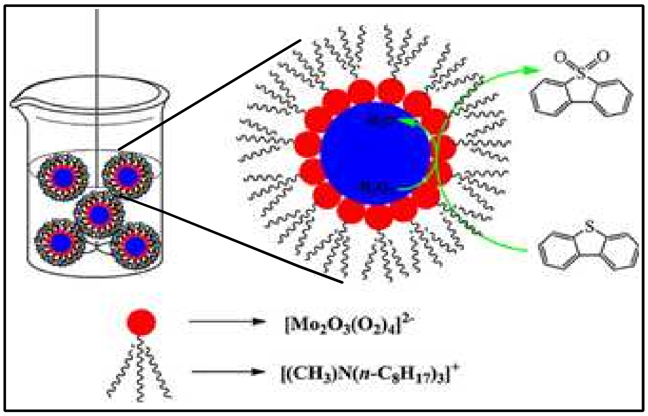


Fig. 6 Supposed catalytic oxidation desulfurization using MSIL $[(CH_3)N(n\text{-}C_8H_{17})_3]_2[Mo_2O_{11}]$ and oxidant H_2O_2 in emulsion droplets.

Related contributions on ODS using ILs as solvents,[122-127] or catalysts[128-138] have also been reported in the literature. Other deep desulfurization processes using ILs in the absence[139-142] or presence of oxidizing agents have also been patented.[143, 144]

2.3. Denitrogenation of gasolines and diesel

Denitrogenation is another important extractive process to remove pollutants from fuels. Selective removal of nitrogen compounds from feeds prior to HDS strongly enhances a further deep desulfurization and increase the catalyst lifetime.[145] Nitrogen compounds (NCs) and NH_3 produced during hydrocarbon reforming process are well known poisons to HDS catalysts. The development of novel and innovative approaches to reduce nitrogen content in fuels is a very important topic in petroleum chemistry.

The applications of ILs as extractants of NCs have also been the focus of recent studies. Eβer et al. and Zhang et al., were the first to described the ability of some ILs to remove nitrogenated compounds from hydrocarbons back in 2004.[28, 58]

Eβer et al. determined a high partition coefficient of 34 mg(N) $kg(IL)^{-1}$/mg(N) $kg(oil)^{-1}$ for an experiment using a model oil containing 1000 ppm of N (as indole in *n*-dodecane) using $[BMIM][OcSO_4]$. Comparably, partition coefficients were rather low (0.7 and 2.9) for piperidine and pyridine, respectively.[28]

The ability of $[BMIM][BF_4]$ to removed N-containing saturated and non-saturated heterocyclic compounds were comparably evaluated by Zhang et al. Organonitrogen and organosulfur compounds were proved to be extracted both for a model fuel consisting on n-C_{12} and another single compound (either DBT, pyridine, or piperidine). The efficiency of IL was reflected in a removal of 12% S (DBT), 45% N (pyridine), and 9% N (piperidine) all in n-C_{12} using $[BMIM][BF_4]$ (ratio IL/MF: 1/5). The most effectively extracted compound was the pyridine, fully miscible in the IL.[58]

In contrast with SCs, NCs can be very efficiently removed using stables and cheap chloride base-ILs (First generation) obtained in one-step synthesis protocols. These included four types of ILs with different carbon chain length and saturation of N-substituent groups, namely [BMIM]Cl, 1-allyl-3-methylimidazolium chloride ([AlMIM]Cl), 1-benzyl-3-methylimidazolium chloride ([BzMIM]Cl) and 1-octyl-3-methylimidazolium chloride ([OcMIM]Cl).[146]

The distribution coefficient of carbazole (CAR) and DBT between the ILs and the model fuel phase as well as the extraction selectivity of ILs for CAR and DBT were determined using a DBT and carbazole solution in toluene and *n*-dodecane as a model fuel. Results showed that CAR possessed a higher distribution coefficient as compared to DBT in these ILs phases. The CAR distribution coefficients in BMImCl and AlMImCl were found to be 46 and 14, and the selectivity of CAR/DBT 125 and 38, respectively.[147, 148]

Zn-containing imidazolium-based ILs bearing an alkylsulfate anion have also been reported for the extraction of nitrogen compounds present in hydrocarbon mixtures at RT. The denitrogenation process was studied using model oil containing 5000 ppm of quinoline and 20000 ppm of *n*-octane as an internal standard in *n*-heptane. The performance of dialkylimidazolium alkyl sulfate ILs for the extraction of basic NCs (e.g. quinoline and acridine) was significantly improved up to over 2 times by the co-presence of Lewis acidic $ZnCl_2$. The regeneration and reuse of the ILs was also investigated. Diethyl ether was found to be an efficient back-extractant for the regeneration of $[EMIM]EtSO_4$-$ZnCl_2$, as well as to recover trapped quinoline in the IL. Computational studies on the interactions of $ZnCl_2(EtSO_4)^-$ and $EtSO_4^-$ with quinoline and indole show that active Zn-containing anionic species including $[EMIM]ZnCl_2(EtSO_4)$ and $[EMIM]ZnCl(EtSO_4)_2$ could be generated from the interaction of $ZnCl_2$ with $[EMIM]EtSO_4$. Consequently, the extraction of quinoline could be facilitated through the coordination of quinoline to the Zn center (Figure 7). The bonding mode of ethylsulfate ligand in $ZnCl_2(EtSO_4)^-$ is changed from bidentate to monodentate for the coordination of quinoline, thereby retaining a tetrahedral environment around Zn.[149]

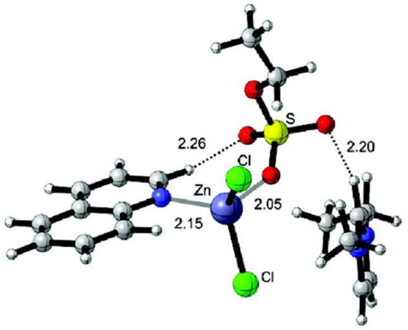


Fig. 7 Optimized structures showing the interactions of $[EMIm]ZnCl_2(EtSO_4)$ with quinolone to form: $[EtMIM]ZnCl_2(EtSO_4)$ + quinoline → $[EtMIM]Zn(quinoline)Cl_2(EtSO_4)$.

A screening of ILs was also recently reported to evaluate optimum conditions for nitrogen removal from a straight-run diesel sample (prior to HDS submission). In this work, 56 ILs were synthesized in parallel under microwave irradiation and evaluated as extracting agents. The experiments were conducted at 50°C using an IL/diesel ratio 1:10. According to previous data in the field, Lewis acid ILs should have been the optimum extract agents. However, "first generation" ILs containing a halogen as anion allowed an efficient removal of nitrogenated compounds, being excellent alternatives in the process.[150]

In terms of theoretical predictions on ILs performance (selectivity and capacity) for HDS and HDN, these studies have also been carried out using the quantum chemical based COSMO-RS methodology. Upon screening of 168 possible ILs, non-aromatic based cations combined with anions having steric shielding effect were proved to be the most favourable IL for desulphurization of TS, BT and DBT. COSMO-RS model achieved root mean square deviations of 4.36% and 7.87% (satisfactory considering that the method is *a priori*) for [EMIM][EtSO$_4$] and [EMIM][AcO]-based systems for performance prediction of single as well as mixed ILs in BT extraction.[151]

An inverse relation was comparatively observed between the activity coefficient at infinite dilution predicted via COSMO-RS model and actual interaction energies in IL-TS-pyridine complexes, in which CH-π interaction was evident.[152] For further information on IL screening using COSMO-RS methods, readers are kindly referred to recent reports in the field.[153, 154]

2.4 Desulfurization and denitrogenation employing supported IL membranes

An alternative strategy for the separation of SCs and NCs involves the use of supported IL membranes (SILMs). SILMs are IL-containing porous solids which can be used in pervaporation technologies. In pervaporation, a membrane based process for separating liquid mixtures and also employed in gas separation processes, the difference in chemical potential is mainly achieved by keeping the permeate pressure much lower than the feed pressure. (Figure 8).[155]

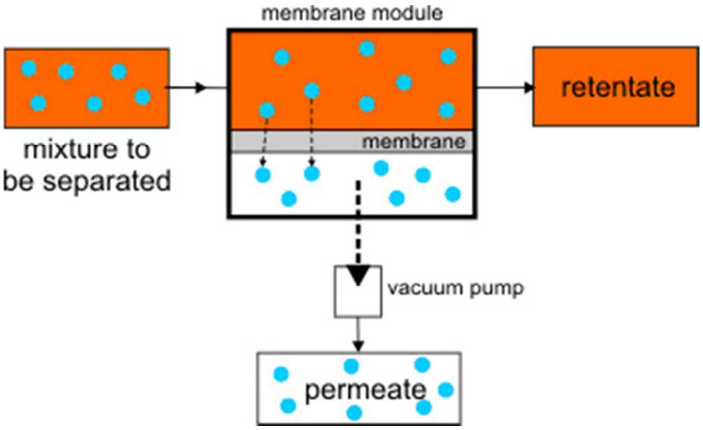
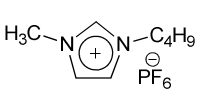
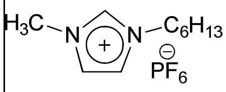
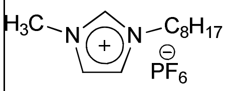
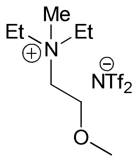
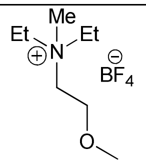


Fig. 8 Schematic representation of the pervaporation process (source: http://www.fz-juelich.de/ibt/index.php?index=635, 2009)

The supported IL phase technology can offer a very efficient utilization of ILs and circumvents mass transport limitations due to the small film thickness and large surface area, allowing a simple packed-bed column extraction to be applicable.

Matsumoto and coworkers originally explored the application of SILMs for the selective permeation of organosulfur and nitrogenated compounds including the selective separation of nitrogenated-heterocyclic compounds (e.g. quinoline, isoquinoline, and pyridine) from *n*-heptane using 1-alkyl-3-methylimidazolium and quaternary ammonium salts.[156] The authors examined the effect of organic nitrogen compounds (ONCs) on permeability and they observed that the permeation rate increased in the order of heptane << isoquinoline < quinolone ≤ pyridine for all SILMs investigated and water. This order corresponds to the hydrofilicity of the ONCs, isoquinoline (log $P_{O/W}$ = 2.08, where $P_{O/W}$ is the partition coefficient of the ONCs in 1-octanol and water and is a measure of the hydrofilicity), quinolone (2.00) and Pyridine (0.65) although the permeation rate through the SILM was mainly controlled by the polarity. On the other hand, SILMs containing more hydrophilic ILs yielded higher selectivity (Table 4).

Table 4 Effect of ILs on Permeability *P* and Selectivity *S* using PVDF membrane as a support when contents of ONCs were 50 vol%.

ILs	$\frac{10^3 P_{quinoline}\ [m/h]}{10^3 P_{heptane}\ [m/h]}$	*s*	$\frac{10^3 P_{isoquinoline}\ [m/h]}{10^3 P_{heptane}\ [m/h]}$	*s*	$\frac{10^3 P_{pyridine}\ [m/h]}{10^3 P_{heptane}\ [m/h]}$	*s*	Log $P_{O/W}$
	6.93 0.808	8.6	4.88 0.657	7.3	7.4 0.859	9.0	0.142
	7.05 0.966	7.3	5.41 0.788	6.9	9.42 1.23	7.6	0.324
	7.54 1.75	4.3	5.65 1.76	3.2	9.99 2.04	4.9	0.417
	6.9 0.814	8.5	4.28 0.604	7.1	7.69 0.898	8.6	- 1.53
	7.89	3.1	5.62	2.7	8.52	3.8	0.149

	2.25		2.06		2.27		
H_2O	9.72 6.75	1.4	7.51 6.36	1.2	10.2 7.12	1.4	--

A year later, the same group proved the separation of organic nitrogen and sulfur compounds from model fuels using SILMs based on 1-alkyl-3-methylimidazorium and quaternary ammonium salts. The ILs were retained in membrane pores after ten times repeated experiments.[157]

The first comparison between biphasic system (IL/hydrocarbons mixture) and supported IL phase was more recently reported. Dispersing small amounts of [BMIM][Cl/MCl$_x$] (1:1 to 1:1.7 and M = Sn, Zn) ILs on highly porous materials resulted in highly efficiently supported IL phases for desulfurization. Compared to the corresponding bulk ionic extraction, extraction times with the same chlorometallate ILs could be reduced by factors up to 50.

Several supports were evaluated in the process, finding that alumina-based Pural TH 60 and 100 were particularly suitable inert materials, also exhibiting a high surface area (205.7 and 131.3 m^2/g) and pore volume (0.691 and 0.848 $ML^{-1}.g^{-1}$) . Supported IL materials were tested in slurry phase extraction at 25□°C and exhibited a remarkably faster sulfur removal rate due to the significantly larger IL surface in these systems as compared to conventional biphasic processes.[158]

Very recently, the application of supported ILs membranes (SILMs) and liquid-liquid extraction using membranes (LLEMs) for removal of sulfur compounds and other pollutants from gases and liquids form feedstocks have been reviewed.[159, 160] In general, membrane separation technology involves selective transport of a material through the membrane, producing permeate, and leaving behind a retentate on the feed side of the membrane. Permeated components of the mixture are removed by various driving forces. SILMs-based technology has prompted great interest due to the combined characteristics of this system. On the one hand, supported membranes, using conventional solvents, are more stable and feature long-term performance; on the other hand, ILs are environmental friendly solvents that can be designed for every specific application. Particularly, the application SILM using *n*-butyl-3-methyl pyridinium methylsulfate to remove sulfurous species from hydrocarbons exhibits very low mass transfer coefficients (i.e., value of 8.75×10^{-7} to 2.1×10^{-4} $kg/m^2.s$ was obtained for different membrane materials, pore sizes and under different experimental conditions). This is attributed to diffusion of big molecules of sulfurous species, such as dibenzothiophene (DBT), as indicated from the low value of the estimated diffusion coefficient of DBT in IL (in the order of 10^{-11} m^2/s) obtained. The use of light naphtha is promising to act as an extractive liquid as it transfers under the osmotic pressure difference to the whole crude oil side, which prevents fouling and thus promotes faster diffusion of sulfurous species (Figure 9).

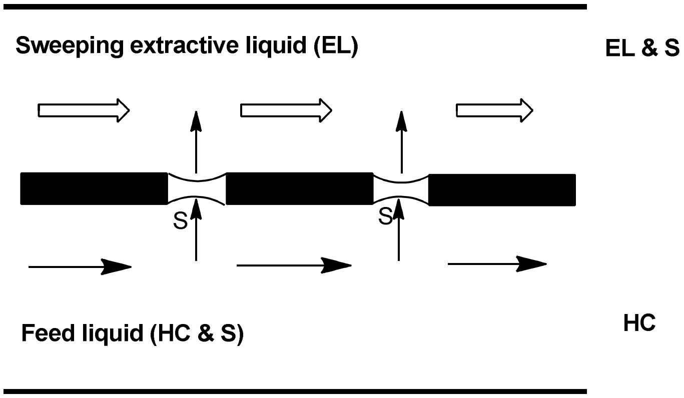


Fig. 9 Schematic of SILM and LLEM (adapted from ref. 159)

Throughout the present century, many studies have been performed to explore the prospects of ILs for gas separation applications and for finding the best prototypes for CO_2 capture.[161-166] Not only SILMs but also ordinary ILs, task-specific ILs and polymerized ILs-based solutions have shown promising results in capturing CO_2 from fuel gases. In term of the breadth of this topic, the readers are also referred to some recent and comprehensives reviews.[167-168]

Capute of SO_2 especially at lower SO_2 partial pressures is another hot topic. Chinese researchers have developed and efficient and reversible method for trapping SO_2 using ILs (1-(2-diethylaminoethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-(2-di-ethylaminoethyl)-3-methylimidazolium tetrazolate, ([Et_2NEMIM][Tetz]). Both ILs were very efficient for SO_2 absorption, but especially [Et_2NEMIM][Tetz] could absorb 0.47 g(SO_2) per g IL at 0.0101 MPa SO_2 partial pressure, which is the highest capacity reported to date under the same conditions. The main reason for the large capacity was explained for the ability of both the cation and the anion to capture SO_2 chemically. In addition, the IL could easily be regenerated, and the very high absorption capacity and rapid absorption/desorption rates were not changed over five repeated cycles.[169] Additionally three new hydroxylammonium dicarboxylate ILs have been synthesized and mixed with free dimethylethylamine and water to form novel hybrid solvents for SO_2 absorption. The mixed absorbents exhibited low viscosity in the range of 6-13 mPa s at 313.2 K, favoring the transfer performance of SO_2 absorption. Significantly, they reached SO_2 absorption equilibrium in less than 50 s, and their absorption capacities were as high as 0.1-0.6 mol SO_2 per mol IL at 313.2 K and 0.004 bar SO_2 partial pressure.[170]

Another ILs showing high efficiency for SO_2 capture are triethylbutylammonium dicarboxilics,[171] 1-butyl-3-methylimidazolium lactate,[172] and imidazolium ILs with less electronegative carbon and sulfur site in the anion (tiocyanate (SCN) and tricyanomethanide). [EMIM][SCN] shows the highest available capacity (up to 1.13 g per g IL for SO_2 absortion) on the basis of weight reported to date. In this last work, calculations (Gaussian 03 at the B3LYP/6-31++G(d,p) level) were performed to elucidate why [EMIM][SCN] exhibits a higher SO_2 absorption capacity than [EMIM][$C(CN)_3$] and also why the desorption of SO_2 by these nitrile-containing anion-functionalized ILs is so facile.optimized structures that reflect the interactions between the anions [SCN] and [$C(CN)_3$] with SO_2 indicated a stronger interaction for SCN (Figure 10). The calculated absorption enthalpies of SO_2 for [SCN] and [$C(CN)_3$] are −73.0 and −32.3 kJ mol^{-1}, which are in good relative agreement with the experimental values of −56.0 and −29.1 kJ mol^{-1}, respectively, resulting in the difference in SO_2 absorption capacity.[173]

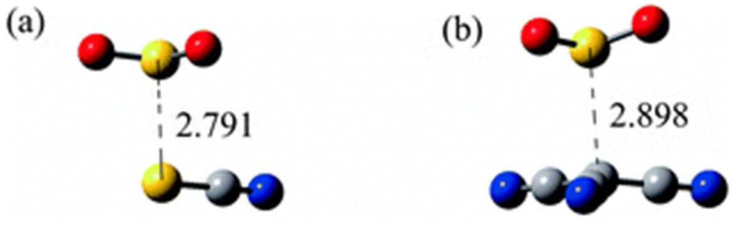


Fig. 10 Optimized structures showing the interactions between the anions [SCN] and [$C(CN)_3$] and SO_2: (a) [SCN]–SO_2, ΔH= −73.0 kJ mol^{-1}; (b) [$C(CN)_3$]–SO_2, ΔH = −32.3 kJ mol^{-1}.

Selection of ILs for acidic gases capture is essentially based in empirical criteria. Ren, et al. found a way to distinguish if the ILs are functional or not before use, which greatly influences the design of functional ILs. In this work, a series of ILs were synthesized and used to determine functional or normal ILs for the capture of acidic gases. It has been found that the pK_a of organic acids forming the anion of ILs can be used to differentiate functional ILs from normal ILs for the capture of acidic gases from flue gas. If the pK_a of an organic acid is larger than that of sulfurous acid (or carbonic acid), the ILs formed by the organic acid can be called functional ILs for SO_2 (or CO_2) capture, and it can have a high absorption capacity of SO_2 (or CO_2) with low SO_2 (or CO_2) concentrations. If not, the IL is just a normal IL. The pK_a of organic acids can also be used to explain the absorption mechanism and guide the synthesis of functional ILs.[174]

ILs are starting to leave academic labs and find their way into a wide variety of high-scale applications. Industrial implentation of Ils in petroleum refineries have been described for Difasol and Ionikylation. The former is a process to dimerize short chain alkenes into branches alkenes of higher molecular way and Ionikylation is an IL-based process for the alkylation of four-carbon olefins with isobutane which produce more than 65000 tonne/year using ILs.[13, 175]

2.5. Cross-contamination IL/feedstock

The cross-solubility is an important factor in evaluating the applicability of an extractant, because the variation of diesel composition and quality can be affected by the cross-solubility of the ILs and the hydrocarbons mixture (diesel or gasoline). Negligible cross-solubility implies that there will be no cross-contamination and the IL will be a non-pollutant in fuel after extraction. Further, the amount of hydrocarbon in the IL-rich phase is very small.

In other words, if the ILs have negligible solubility in the feedstock, this feed was never contaminated with ILs. In the case of ILs have noticeable solubility in the hydrocarbons mixture, they may on one hand contaminate the fuel and further lead to a NO_x pollution (for *N*-containing ILs), as well as increase the cost of recycling ILs.

Lamentably many of research paper published about ILs as extractant of contaminants from hydrocarbons do not attend that important problematic that could limit the applicability of certain ILs. In general, given the ionic nature of ILs and hence their relatively high polarity, with hopefully a little cross between them and the oil solubility, although sometimes the LIs have a greater solubility would be expected as it has been shown Gao et al. for a family of 3-methylpyridinium-based ILs. In this study by analyzing the IL-saturated diesel sample using HPLC, no IL peak was found. Therefore, the 3-methylpyridinium-based ILs studied have negligible solubility in the diesel. The solubility of diesel in ILs was measured using a gravimetric method by weighing the mass difference of a given amount of ILs and the ILs saturated with diesel. The results showed that the diesel has a certain solubility in 3-methylpyridinium-based ILs and its solubility in 3-methylpyridinium-based ILs varies to a large extent for different IL species and follows the order [$C_8{}^3$MPy][BF_4] > [$C_6{}^3$MPy][BF_4] > [$C_4{}^3$MPy][BF_4], with the solubility being 9.5, 7.6 and 6.1 wt% respectively. This diesel solubility order was attributed to the hydrophobic increase from [$C_4{}^3$MPy][BF_4] to [$C_8{}^3$MPy][BF_4] as the alkyl substituents in the ILs increase from butyl to octyl. The reason may be that hydrophobicity of these three 3-methylpyridiniu-based ILs is stronger than those mentioned in our previous reports because of the alkyl substituent in the ring of pyridine.[42]

Eβer, Wasserscheid and Jess made a serious study of the effect in cross-solubility for [BMIM][$OcSO_4$] and [EMIM][$EtSO_4$], which showed a good performance as halogen-free extractants of SCCs. They determined the cross-solubility of pure hydrocarbons in these ILs at rt showing the drawback of [BMIM][$OcSO_4$] is the "cross-solubility" of hydrocarbons, *i.e.* in addition to the extraction target (S-compound) a small amount of the oil matrix was coextracted.

By means a triangular diagram of the system "*n*-dodecane, methylnaphthaline and [BMIM][$OcSO_4$]" they showed that within the biphasic area, which is an absolute must for extraction, an IL-rich phase and an IL-free oil phase are established. The IL-rich phase contains both the paraffinic and the aromatic hydrocarbon to a relatively small extent, whereby the extraction selectivity for the latter is higher. However, the cross-solubility of real oil in the IL is practically independent of the oil to IL ratio used for the extraction. So in case of a high ratio of oil to IL, the portion of the oil transferred into the IL would be small, in this case about 2.5%.

They remarked that the cross-solubility of hydrocarbons in the IL is an unwanted effect, as the coextracted hydrocarbons will have to be separated from the IL together with the S-compounds during IL-regeneration by distillation or reextraction. So a high cross-solubility will lead to a loss of oil or at least to an increase of process costs. For a technical application of extractive desulfurization no or only a small cross-solubility of oil in IL is desirable. A promising IL with a significantly lower cross-solubility than [BMIM][$OcSO_4$] is [EMIM][$EtSO_4$], which is also available from relative cheap starting materials. The distribution coefficient for S-compounds is by a factor of about two lower than that for [BMIM][$OcSO_4$], but the cross-solubility is – depending on the hydrocarbon – by a factor of 4 to 16 lower. So this extracting agent is therefore probably better for a technical extraction process. It is important to state that the oil phase was never contaminated with IL, as proven by elemental N-analysis during all experiments: The N-content (respectively the IL-content) in the oil phase is at least less than 1 ppm. This important finding is supported by numerous experiments (about 1000).[42]

As finding this topic should be noted that any serious proposal for a potential technological use of ILs as extracting agents of contaminants from hydrocarbons at industrial level requires a thorough study of cross-contamination.

2.6. ILs reextraction/regeneration and recycling

For the technical application of an IL extraction, the regeneration and subsequently recycling of IL is of vital importance. As have been showed in this section (see Table 1 and 3), in most of studies in desulfurization and denitrogenation the authors devote a section to the study of regeneration and recycling of the ILs, showing in most of the cases, the ILs can be reused more than five (sometime until ten) cycles of extraction without “significant loss” in their performance, however, very few research has focused on quantifying the mass loss of LI and hydrocarbon in such process, which is especially important in the ODS process in which due to the increase in polarity by oxidation increases the affinity of these contaminants with the IL. Removal of sulfur compounds from an IL can be done by a few methods, such as, heating the IL to remove the sulfur compounds,[58] or for removing the water and the oxidant (generally H_2O_2) in the case of ODS, or precipitating the sulfur compounds by a water dilution process,[33, 35] and reextraction sulfur compounds with low-boiling hydrocarbons pentane or hexane in the case of extractive desulfurization,[42] or CCl_4 in the case of ODS.[116]

In the early cycles of extraction by ODS after the decantation of the hydrocarbon phase, the IL only is subjected to vacuum to remove volatile impurities and reused in other cycles (commonly 3-6 cycles, depends fundamentally of the ILs type and the ratio IL/feed) until the IL is virtually saturated by oxidative products and then the sulfones are separated by washing with a solvent or centrifugation and in some case after cooling the oxidation products precipitate and can be separated by filtration. Some authors suggest that if the IL phase is extracted with CCl_4 after each run, no loss in activity could be found after nine cycles.[122, 130]

To this respect, Yu et al.[106] published in 2011 a deep ODS of diesel by acidic ILs (Lewis acid: [BMIM][Cl//2ZnCl$_2$] and [BMIM][Cl//ZnCl$_2$] and four Bronsted acidic species imidazolium derivatives with different acidic groups such as -H, -COOH, and –SO$_3$H are appended to the cations and HSO$_4$ as anion using H_2O_2 as oxidant. They reported that the ILs [BMIM][Cl//2ZnCl$_2$] and [SO$_3$H-BMIM][HSO$_4$] can be recycled six times with merely a “negligible loss in activity”, the S-removal is dropped from 98.4% to 90.7% with [BMIM][Cl//2ZnCl$_2$] and from 95.7% to 90.4% with[SO$_3$H-BMIM][HSO$_4$]. The slight drop of S-removal after several cycles may be ascribed to the accumulation of the oxidative product in the recycled ILs phase, the S-saturation of the ILs, and the resultant decrease of desulfurization activity.[99, 101, 122] After several cycles, the oxidative product (mainly DBTO$_2$) can be reclaimed from the IL by using tetrachloromethane-reextraction.

Seeberger and Jess also discussed about de regeneration and reuse of IL in a work about a competitive process design of ODS of diesel by selective oxidation and extraction of oxidized S-especies using H_2O_2/[EMIM]DEP. According to their results work combines the extraction of oxidized S-compounds from diesel oil by ILs and the subsequent IL regeneration, i.e. the removal of the oxidized S-species from the S-loaded IL by means of water addition which leads to a displacement of the S-compounds from the IL. Thus, water separation by evaporation is needed before the IL can be re-used for extraction.[100]

In general authors report that the mutual solubility in these processed is not pronounced and the extraction efficiency is not conspicuously changed after several cycles of extraction for both direct desulfurization and ODS.

2.7. Industrial perspective for desulfurization and denitrogenation od hydrocarbons using ILs

According to the results showed by ILs for both desulfurization and denitrogenation, a conceptual industrial integration for production of ultra-low-sulfur diesel can be proposed including both, pre-HDS ILs denitrogenation and partial desulfurization of the feedstock to increases the efficiency of the conventional HDS process and to prolong the useful life of the HDS-catalyst, and a post-HDS ILs treatment to remove the rest of SCs presents in desulfurized diesel (Figure 11).

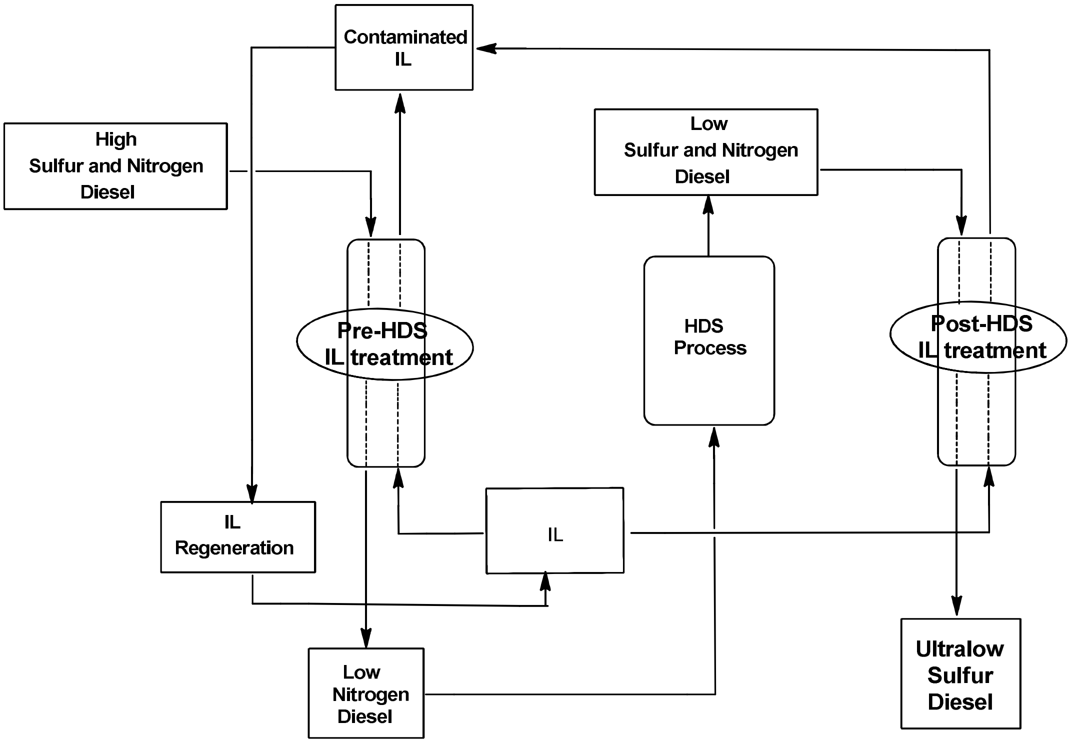


Fig. 11 Conceptual integration of pre- and post-IL treatments to conventional HDS process.

From our perspective, the industrial implementation of these liquid-liquid extractions of SCs and NCs employing ILs from the practical viewpoint presents a series of limitations including:

- Many ILs show extractive properties of pollutants from hydrocarbons (e.g. sulfur and nitrogen-containing compounds) but many of these required several extraction cycles for quantitative removal. Even when in some cases, a 1:1 ratio (IL/hydrocarbons) is required, which is very poor for large scale applications.

- The Nernst partition coefficient (K_N) favors the extraction of most aromatic components of the fuel oil; this being a potential limitation of the extractive method.
- Reported studies have mostly been conducted to date with model feeds under laboratory scale. Results obtained in these cases are far from results obtained under actual conditions and these can only be validated at larger scale and with real samples. The extraction of actual feeds is indeed much more complicated due to its complex composition, the presence of different types of SCs, NCs, oxygen-containing compounds, aromatic hydrocarbons and other impurities.
- Lewis acid ILs (containing anions as [Cl/$AlCl_3$] and [Cl/$FeCl_3$] on ratio 1/1.2 or higher) are by far, the most efficient extractanting agent for desulfurization; however, these ILs are water sensitive and can be exclusively employed in one extraction cycle prior to decomposition. Furthermore, these chlorine-containing ILs can originate important environmental issues related to global warming and acid rain.
- Considerable volumetric loss of hydrocarbons can take place under these liquid-liquid extraction practices due to difficulties to achieve a sufficient separation between phases and most importantly partial hydrocarbon dissolution in the ILs (co-miscibility or cross-contamination of the ILs and feed, selectivity and specificity of the extracting phase) upon extraction from hydrocarbons feedstocks.
- Proposed processes for ILs recycling (e.g. solvents washing) are high energy consuming and would be difficult to integrate in a continuous process at industrial scale. Handling and post-treatment of SCs and NCs and other impurities separated in this process is not trivial and requires special attention.
- ILs reuse is limited to a certain number of cycles when the contaminant concentration makes them unusable for a particular purpose and turns them into waste.
- Some ILs show negative effects on fuel quality.

In the case of ODS procedures, the efficiency of process is relatively increased, however the synthetic process for catalysts preparation is generally complicated and difficult to be commercialized. In addition, the oxidation process is hazardous and dangerous, therefore rather complex for industrial implementation. Last, but not least, the most efficient and promising catalysts (i.e. molybdic compounds) are hardly dissolved in oil.

Seeberger and Hess made in 2010 an important contribution to the study of the feasibility of implementing ODS technology using ILs by means the estimation of their energy demand as a function of the energy consumption of the extractive desulfurization process based on the experimental results of ODS for a model and real diesel employing [EMIM][DEP] without using catalyst.[100]

IL regeneration was carried out by water addition which leads to a displacement of the S-compounds from the IL. Thus, water separation by evaporation is needed before the IL can be re-used for extraction. The evaporation of water from the IL is the crucial step with regards to the energy consumption of the process. A water content of 50 mass-% in the IL/water mixture leads to an almost complete displacement of the sulfur species. Thereby, a S-free IL/water–mixture and a S-rich oil phase is formed which consists of all sulfur species and of hydrocarbons which are also solved to a small extent during the extraction.

The basic design data of a four-stage evaporation process with integrated heat transfer was proposed. For the design of such a process, the normal boiling points of different water/IL-mixtures were measured and a correlation between the water content and the activity coefficient of water was determined.

The extraction process is realized in a counter current operated column. Based on the experimental results of the cross flow extraction using [EMIM][DEP], the classical McCabe-Thiele approach leads to a ratio of IL to oil of 1.4, if the number of theoretical separation (extraction steps) is limited to five stages which is a reasonable order of magnitude. After several assumptions the total energy consumption was determined, taking in account energy is needed for heating the water to the boiling temperature of stage 1 and to evaporate the respective amount of water (12 mass-% of the feed) and the specific energy demand for the vapor compression between stage 3 and 4.

The total energy requirements for the desulfurization of 1.0 kg of diesel oil, 1.4 kg of IL are regenerated by the addition of 1.4 kg of water was 1401 kJ/kg oil. This value is about 3.3% of the heating value of diesel oil (42500 kJ kg^{-1}) if we neglect other energy expenses (pumps, pre-oxidation step to produce oxidized S-species). This value is close to the classical HDS process where the energy consumption is in between 1.5% (without H_2-production) and 4% (incl. H_2-production) of the heating value of the processed diesel oil.

The other highlighted alternative (Supported ILs phases, SILPs) is a novel concept with promising perspectives particularly for sulfur removal as it allows the application of simple packed-bed column extraction more amenable to industrial practices. However, ILs leaching from the support, the speed of transport process as well as lifetime and regeneration of SILPs will be the main limitations and need to be optimized for industrial implementation. Covalent anchoring of IL as well as clever engineering of the SILP material with respect to capillary forces and wettability are envisaged to enhance the stability of ILs on the solid support but these need to be tested in actual conditions.

2.8. Separation of Aliphatic/Aromatic Hydrocarbons using ILs

Aromatic compounds are another type of important contaminants in refinery feedstocks. The feed stream of naphtha crackers may contain up to 25% aromatic hydrocarbons, which need to be removed. In general, these compounds are highly toxic by inhalation and their evaporation into the atmosphere produce detrimental effects both on the environment and human health. The presence of excessive aromatic content in the feed also has a negative influence on thermal efficiency. The separation of these environmental pollutants (e.g. BTX: benzene, toluene, ethyl benzene and xylenes) from aliphatic hydrocarbon mixtures is highly challenging as these hydrocarbons have boiling points in a close range and several combinations form azeotropes mixtures (conventional distillation is not suitable).

The conventional process to separate aromatic and aliphatic hydrocarbon mixtures is liquid extraction (for aromatic content in the 20-65 wt% range). Extractive distillation can be utilized to removing aromatic contents between 65-90 wt% while azeotropic distillation works for contents over 90 wt% of aromatics. Typical solvents employed for the extraction are polar compounds such as sulfolane,[176] *N*-methyl pyrrolidone (NMP),[177] dimethyl sulfoxide,[178] and propylene carbonate.[179] A distillation step to separate the extraction solvent is subsequently required.

In principle, ILs can be an interesting alternative for the extraction of aromatic compounds due to their negligible vapor pressure and low toxicity which in principle does not required a final distillation step. Azko Novel patented a procedure for the extraction of aromatic compounds from an aliphatic phase using an IL.[180] In subsequent years, a significant degree of attention has been devoted to studies of liquid-liquid equilibrium in mixtures of aliphatic and aromatic hydrocarbons.[181, 182] More recently, several investigations have also focused in physicochemical aspects of two ternary systems comprising aliphatic/aromatic/ILs compounds.[183-196]

Meindersma et al. reported that several ILs were suitable for toluene extraction from toluene/heptane mixtures. Toluene/heptane selectivities at 40°C and 75°C were found to be a factor of 1.5-2.5 higher as compared to those obtained with sulfolane (most industrially used solvent for the extraction of aromatic hydrocarbons) using ILs such as [3-MeBuPy][BF_4], [3-MeBuPy][CH_3SO_4], [BMIM][BF_4] (40°C) and [EMIM][Tos] (75°C). Among them, [3-MeBuPy][BF_4] was the most suitable due to a combination of a high toluene distribution coefficient ($D_{tol} = 0.44$) and high toluene/heptane selectivity ($S_{tol/hept} = 53.6$). Related extraction experiments with the same IL and other aromatic/aliphatic combinations (benzene/*n*-hexane, ethylbenzene/*n*-octane and *m*-xylene/*n*-octane) were also reported with similar selectivities.[197]

More recently, the same research group made a similar study with cyano-containing ILs having a lower density than sulfolane. Sulfolane is from a hydrodynamic point of view a better solvent than ILs for the aromatic/aliphatic extraction. The most suitable ILs for the extraction of aromatic hydrocarbons from a mixture of aromatic/aliphatic hydrocarbons are [BMIM][$C(CN)_3$], [3-MeBuPy][$N(CN)_2$], [3-MeBuPy][$C(CN)_3$], [3-MeBuPy][$B(CN)_4$] and [3-MeBuPyrr][$B(CN)_4$]. They have factors of 1.2-2.3 higher mass-based distribution coefficients than sulfolane and a similar or higher, up to a factor of 1.9 higher, aromatic/aliphatic selectivity than sulfolane. The IL [3-MeBuPy][$N(CN)_2$] is a better extractant for the separation of toluene from a mixture of toluene/*n*-heptane in a pilot plant Rotating Disc Contactor than sulfolane.[198]

A conceptual industrial process design was also proposed in which the authors concluded that the use of ILs with a high aromatic distribution coefficient (e.g. $D_{arom} = 0.6$ m/m) and a reasonable aromatic/aliphatic selectivity (e.g. $S_{arom/alif} = 40$) could reduce investment costs of such separation to about 25 to 30 € millions and the annual costs to 16 to 17 € millions with respect to total investment costs in the typically applied sulfolane extraction process. According with this study the estimated investment and variable cost for the extraction process with sulfolane and with [3-MeBuPy][BF_4] were 58.4 and 24.7 € millon, respectively.[199]

In spite of really the cost of the ILs is higher than sulfolane, the process with IL present lower cost. The key factor is the high aromatic distribution, provided aromatic/aliphatic selectivity higher enough (30 or higher) for the lower cost of IL process respect to sulfolane process.

According to these results, the implementation of a technology for dearomatization of hydrocarbons in comparison with desulfurization/denitrogenation employing ILs is much more viable than desulfurization/denitrogenation as a way to replace current technology, but special special attention to the type selected LI, in this case the proposed LI has high fluoride content which could significantly contribute to environmental pollution.

Domanska et al. reported a study of LLE in binary mixtures that contain a IL and an organic solvents including [MMIM][CH_3SO_4] or [BMIM][CH_3SO_4] with an aliphatic hydrocarbon (*n*-pentane, or *n*-hexane, or *n*-heptane, or *n*-octane, or *n*-decane), or a cyclohydrocarbon (cyclohexane, or cycloheptane), or an aromatic hydrocarbon (benzene, or toluene, or ethylbenzene, or propylbenzene, or *o*-xylene, or *m*-xylene, or *p*-xylene). Liquids curves were predicted by the COSMO-RS method. According to their results, the solubilities of [MMIM][CH_3SO_4] and [BMIM] [CH_3SO_4] in alkanes, cycloalkanes and aromatic hydrocarbons decreased with an increase of the molecular weight of the solvent and solubility differences in *o*-, *m*-, and *p*-xylene were not significant. By increasing the alkyl chain length on the cation, the upper critical solution temperature (UCST) decreased in all solvents except for the case of *n*-alkanes.[200]

The extraction selectivity of a specific aromatic compound has been also reported to be influenced by anion volume, hydrogen bond strength between anion and cation (e.g. imidazolium) as well as the length of 1-methyl-3-alkylimidazolium alkyl side chain. The interaction of alkylbenzenes and sulfur heterocyles with IL was found to go preferentially through hydrogen bonding and the quantity of these aromatics in the IL phase decreases with an increase in steric hindrance imposed by the substituents of the aromatic nuclei. Competitive extraction experiments suggested that benzene, pyridine and DBT do not compete for the same hydrogen bond site of the IL.[201] For more detailed studies LLE (IL plus hydrocarbon) and modeling of over 150 binary systems by COSMO-RS methods, readers are kindly referred to a recent review from Ferreira et al.[202]

A systematic study about the structural influence in ILs (in terms of cations and anions) and the effect of the temperature on the selectivity and the capacity for aliphatics/aromatics and *n*-hexane/hex-1-ene separation problems was recently conducted. The analysis was made on the basis of activity coefficients at infinite dilution as a helpful parameter to characterize the behaviour of liquid mixtures, estimation of mutual solubilities, predicting the existence of an azeotrope and the development of thermodynamic models. ILs with less aliphatic character (e.g. $[MMIM]^+$, $[EMIM]^+$, $[EtPy]^+$, $[Et_3S]^+$ as well as those containing –CN groups) exhibited higher selectivity values. Unfortunately high selectivity is associated with low capacity. The highest capacity values were found for [NTf_2] and [$FeCl_4$] anions.[203] Further studies have been conducted on the extraction of benzene from aliphatic compounds using ILs containing alkylsulfate anions as solvent in ternary systems (alkane + aromatic + IL),[204-214] with two novel ILs ([BMPy][NTf_2] and [BMPy][TfO]) recently reported to have a good performance in this particular application.[215]

ILs have also been studied for the selective separation of aliphatic/aromatic hydrocarbons by pervaporation. Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. It is considered an attractive alternative to other separation methods for a variety of processes. Pervaporation is a physical process that involves the separation of two or more components across a membrane by differing rates of diffusion through a thin polymer and an evaporative phase change comparable to a simple flash step. A concentrated and vapor pressure gradient is used to allow one component to preferentially permeate across the membrane (see Figure 5). A vacuum applied to the permeate side is coupled with the immediate condensation of permeated vapors. The separation of compounds during pervaporation is based mainly on the interaction of the feed components with the membrane material combined with the gradient in a chemical potential.

The major issue associated with solute recovery by pervaporation is the compromise between selectivity and flow (residence time).[216]

Due to their high surface tension and low vapor pressure, ILs can potentially have advantages of minimum loss of membrane liquid by the dissolution/dispersion effect, as well as by evaporation. The potential of ILs in SILMs for pervaporation of solutes from aqueous mixtures was first demonstrated by Schäefer and coworkers in 2001,[217] followed by Branco[218] and Izák and coworkers.[219-221] Nevertheless, only few data about pervaporation using SILMs with potential applications for refinery feedstocks is currently available.

The application of SILMs has also been investigated in the separation of toluene from *n*-heptane, using different imidazolium ILs (1-methyl-3-octyl imidazolium chloride, 1-ethyl-3-methyl-imidazolium ethyl sulfate, 1-methylimidazole hydrogen sulfate and 1*H*-imidazolium, 1-ethyl-4,5-dihydro-3-(2-hydroxyethyl)-2-(8-heptadecenyl) ethyl sulfate). Using silver ion as a carrier in membrane phase, batch extraction experiments were also carried out and the permeation rate and separation factor were determined by varying the operating parameters: contact time, concentration of Ag^+, stirring effect, initial feed phase concentration and temperature.

This study demonstrated that the use of [OMIM]Cl as a membrane solvent enabled the bulk liquid membrane operation to be used for the separation of toluene from *n*-heptane, even at a low membrane permeation rate. Ag^+ concentration, stirring speed, initial toluene concentration in feed phase and temperature were found to have critical factors having a strong effect on permeation rate and separation factor.[222]

Aiming to prevent the loss of membrane liquids, Wang et al. proposed a novel approach of SILMs in which vapor permeation with an IL filling-type SLM replaces solvent extraction. The molecular diffusion coefficient is higher in ILs to that obtained in polymers (and the latter are often chosen as dense materials for the separation of organic liquids). Unlike solvent extraction, only a small amount of liquid was utilized to form SILMs according to the authors, and therefore the use of expensive ILs is justified, becoming economically possible. [BMIM][PF_6] was studied as a membrane liquid for the separation of a toluene/cyclohexane mixture, representative of aromatic and aliphatic hydrocarbons.

Vapor permeation through SILMs has also been employed for the dehydration of aqueous 1-propanol and aqueous ethanol mixtures.[223]

The selective separation of aromatic hydrocarbons including benzene, toluene and *p*-xylene has also been attempted using 1-*n*-butyl-3-methylimidazolium hexafluorophosphate-based SILMs. Although the permeation rates were inferior to those of water, the selectivity of aromatic hydrocarbons was greatly improved reaching a maximum to heptane using benzene in the aromatic permeation and the aforementioned IL in the liquid membrane phase.[224] The same authors also studied the vapor permeation of benzene/cyclohexane through a SILMs based on 1-alkyl-3-methylimidazolium and quaternary ammonium salts. The effects of ILs and the benzene fraction in the feed on permeation flux and separation factor, and the stability of the SILM were investigated. The sorption step mainly affected the separation factor depending on the hydrophilicity of the IL. The ammonium type IL *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate showed the highest selectivity (47.1) for the mixed solution, giving the highest separation factors (185 for 53 wt% benzene and 950 for 11 wt%

benzene), superior to previously reported values obtained by pervaporation. The SILM was found to be highly stable after 1 month under steady flux, without a significant loss in selectivity.[225]

2.9. Remotion of Naphthenic Acids from crude oil

Naphthenic acids comprise a mixture of several cyclopentyl and cyclohexyl carboxylic acids found as natural constituents in many petroleum sources, with molecular weights in the range of 120 to well over 700 atomic mass units. The main fraction contains carboxylic acids with a carbon backbone of 9 to 20 carbons. The naptha fraction of crude oil is oxidized and yields naphthenic acid. The composition differs to that of crude oil and conditions employed during refining and oxidation.[226]

The presence of naphthenic acids has a significant influence in crude oil as they tend to cause operational problems on petroleum refiners including foaming in the desalter or other units as well as carrying cations through the desalting process, which can cause deactivation of catalysts and corrosion problems. Typically naphthenic acids are effectively removed from crude fractions by aqueous base washing but serious emulsion issues arise during these cleaning processes.[227, 228] Chinese researchers proposed a novel method to separate naphthenic acids from highly acidic crude oil via *in-situ* formation of ILs. In this method, the basic character of imidazole is utilized to prepare *in-situ* Brønsted ILs by acid-base reaction between imidazole and naphthenic acids to form naphthenates ILs. Afterward, the residue was cooled to ambient temperature and then extracted by petroleum ether (60−90 °C) to remove neutral oils that were coextracted. Then, the precipitation of 2-methylimidazole could be observed, which could be separated with ionic liquids by filtration. HCl solution (aqueous) was added to the ionic liquids to make naphthenic acids generating finally (Figure 12).

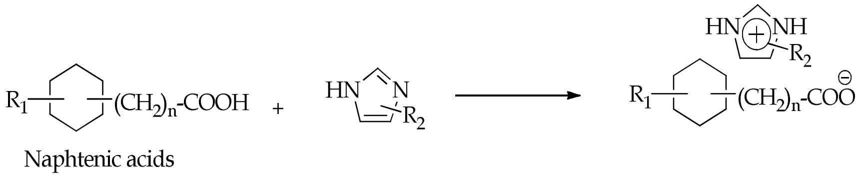


Fig. 12 ILs formation by acid-base reaction between naphtenic acids and alkylimidazole.

The effect of different imidazole derivatives and polar solvents were evaluated. The acid-removal rate was influenced by the content of 2-methylimidazole, reagent/oil ratio, reaction time and reaction temperature, all of which had a positive effect on acid-removal rate. The reagent/oil ratio had a negative effect on the oil yield rate. High-purity naphthenic acids could be obtained in this process.[229]

The same approach was employed by BASF to develop the first large-scale industrial application of ILs in 2003 through the process BASIL (Biphasic Acid Scavenging ILs), in which an *N*-alkylimidazole derivative was employed to remove acid from a particular process in situ, forming ILs that could be easily removed from the reaction mixture. The excellent performances of this protocol enabled are currently used for production of multi-tone scale.[230]

2.10. Extraction of Asphaltenes from Direct Coal Liquefaction Residue

Direct coal liquefaction refers to a process in which coal is converted into liquids fuels and chemicals at high temperatures (400-470 °C) and hydrogen pressures. Direct Coal Liquefaction Residues (DCLR) generally formed as by-products account for 20-30 wt % of the coal fed into the liquefaction reactor. Such residue contains about 30 wt % heavy oil, 25 wt % asphaltenes (a highly aromatic polydisperse mixture) and other non-identified by-products as polymers and carbonaceous residues.

A series of dialkylphosphate ILs have been recently synthesized and investigated in the dissolution and extraction of asphaltenes from DCL residues. Imidazolium, pyridinium, and ammonium as IL cations were selected in order to have a better insight into the structure–function relationship of these ILs series in terms of extractive performance. Among the screened ILs, Methyltriethylammonium dimethylphosphate ([MTEtA][DMP]) exhibited an optimum extractive performance due to its low viscosity, higher asphaltenes extraction yield and good characteristics of the extract (e.g. higher number of aromatic carbons per cluster, higher SP) as well as advantages of lower ash content. The potential of dialkylphosphate ILs to manage DCL residues was proposed to be related to the ability of ILs to disrupt intermolecular interactions in asphaltenes in such a way that the structures of these ILs could be tuned (by varying the ring and substituent groups and the nature of anion) to increase their extractive performance.[231]

More recently, the same research group synthesized and evaluated alkylsulfate-based ILs as solid–liquid separation solvents to extract asphaltene-type materials from DCLR. Among the ILs employed, tetraethylammonium ethylsulfate$[Et_4N][EtSO_4]$) was proved to be a potential solvent for trapping asphaltene-type materials from DCL due to the higher extraction yield and the lower H/C atomic ratio of the extract. *N*-methyl-2-pyrrolidone (NMP) was added to reduce the viscosity of $[Et_4N][EtSO_4]$. It also increased the extraction yield and decreased H/C atomic ratio of the asphaltene-type materials. The mechanism of extraction is that the interactions are formed between ILs or $[Et_4N][EtSO_4]$/NMP mixed solvents and asphaltene-type materials, which breaks the interactions between DCL and leads to the dissolution of asphaltene-type materials into solvents. For ILs, it is postulated that the ability to trap asphaltene-type materials from DCLR is related to the interactions including hydrogen bonding, π–π interactions, and charge transfer complexes between ILs and asphaltene-type materials. For mixed solvents, it is deduced that the smaller molecule of NMP penetrate quickly into DCLR and swell DCLR, then a large number of $[Et_4N][EtSO_4]$ molecules enter into the loose DCLR and trap asphaltene-type materials as far as possible.[232]

2.11. Extraction of fluorinated compounds from alkylated gasoline

The isoparaffin-olefin alkylation process leading to alkylated gasoline (a high-quality product from the oil industry) with a high content of isooctane is one of the most important reactions in petroleum chemistry.[233] This process was industrially carried out employing a cheap and highly reactive homogeneous acid catalyst (hydrofluoric acid in most cases), usually providing rapid reactions with a high yield of alkylated gasolines.[234] However, such alkylation process is toxic and hazardous, with the final product being often impurified with fluoride traces due to an inefficient catalyst removal.[235]

HF is indeed the cause of significant concerns in this process due to its high vapor pressure and tendency to form aerosols. Fluoride anions are highly toxic and environmentally unfriendly, which lead to ecological problems when fluorides are not efficiently removed upon gasoline alkylation reactions.[236]

Alternative catalysts have been proposed and evaluated for this process. These include solid acid materials such as zeolites as well as Lewis and Brönsted acid in different solid supports,[237-242] heteropolyacids,[243] Nafion silica nanocomposites,[244] and both supported and unsupported ILs.[245-248]

A mentioned before, the largest commercial usage of ILs reported to date relates in fact to the alkylation of isobutene carried out in a strongly Lewis acidic IL based on aluminium (III) chloride. This process known as "Ionikylation" has been tested at pilot plant scale and retrofitted into an existing 65,000 tonne per year sulfuric acid alkylation unit at PetroChina.[249]

Years later, Aschauer and coworkers reported the isobutane/butene-alkylation using promoted Lewis-acidic IL-catalysts in a batch reactor using 1-octyl-3-methylimidazolium bromide-aluminium chloride ([OMIM]Br/$AlCl_3$) pure, and in a mixture with compounds containing SO_3H-groups. The acidity of the IL was modified by the addition of acid cation exchange resins (dry or with a small amount of water), or by the addition of a second IL ([(HO_3SBu)MIM][HSO_4]). A high content of the desired trimethylpentanes (up to 64%) was reported, with a high octane (RON up to 96) in the alkylate.[250] The effect of different promoters on activity and selectivity of these catalysts was subsequently studied number under both batch and continuous flow conditions. *Tert*-butyl halides exhibited a higher activity as compared to sulfuric acid or protic additives, significantly speeding up rates of reaction with a selectivity shift towards the desired high-octane trimethylpentanes (TMPs) under both batch and continuously operated liquid phase alkylation reactors. However, secondary reactions including oligomerization and cracking could not be suppressed and high deactivation rates were observed under continuous operation. Since alkylation acceleration in haloalkane supported IL-catalysis leads to a rapid formation of C_8^+-carbocations, the slow hydride shift from isobutane to the C_8^+-cation is not able to quench the C_8^+-cations. Further addition of olefins, results in a product distribution dominated by high ends (C_9 and C_{10+}).[251]

The application of ILs to remove fluorinated compounds from alkylated gasoline has also been reported. A series of twenty nine ILs were synthesized and evaluated for fluorinated-compounds removal by liquid-liquid extraction at IL:alkylated gasoline 1:10 ratios. Some of these ILs exhibited good extracting properties for these types of contaminants. Fluorinated compounds were removed almost completely, with 90-99 % removal efficiencies.[252]

ILs evaluated in this study were selected in base of following empirical criteria:

- ILs containing halogens as anion (i.e. Cl and Br), due to is known that halogens can react with HF through metathesis reaction forming a polyfluoride [$X(HF)_n$] anion (X = halogen).
- ILs containing fluorine in the anion structure, such as [PF_6], [BF_4], [CF_3CO_2] and [$N(Tf)_2$], because presumably these ILs could be good chemical affinity by fluorinated species and the specially [$N(Tf)_2$]-containing ILs are very low viscosity ILs, which favors a better liquid-liquid extraction.
- ILs containing non-saturated chain in the cation that could react with HF (reactive extraction).
- ILs containing organic basic anions (i.e. acetate and benzoate), to favor acid-basic interaction between HF and the IL.

According with this studies ILs showing a good performance to removed not only HF traces but also organofluorinated compounds presents in the alkylated gasoline by liquid-liquid extraction at room temperature. The best results were obtained with [OMIM][N(Tf)$_2$], but taking in account the cost and efficiency, ILs containing chloride anion (I.E. [OMIM]Cl) could be the best alternate for industrial application.[253]

2.12. Ionic liquids as desemulsifier of crude oil.

Crude oil is invariably accompanied by water and formations of stable water-in-oil (W/O) emulsions are frequently encountered in the oil industry. This emulsified water contains important quantities of contaminants, salts and other corrosive compounds.

The dispersion of water droplets in oil is facilitated by the presence of interfacial active agents in the crude oil including asphaltenes, waxes, resins and naphthenic acid.[254] The content of these natural emulsifiers is more abundant in heavy crude oils as compared to light crude oils and thus more stable emulsions are present in such heavy oils.[255]

Destabilization of emulsions is an important step to obtain water-free oils. The formation of emulsion during oil production is a costly problem resulting in the demand of expensive chemical products and equipments and sometimes inefficient separations. Hence, chemical demulsification by adding surfactant demulsifiers is still one of the most frequently applied industrial methods to break crude oil emulsions. This process can be very difficult and non-efficient to demulsify water-in-oil emulsions of heavy viscous crude oils, being also time consuming.[256]

The application of modified resins for oil-in-water emulsion treatments showed that emulsion breaking was accelerated by the addition of a polystyrene resin grafted with cetyltrimethylammonium bromide.[257] The potential to use a cationic surfactant modified resin to coalesce fine oil droplets in stable oily emulsions is significant.[258]

An innovative study about water-in-crude oil demulsification for three types of Mexican crude oils was recently reported to be conducted by various surface-active ILs analogues. The efficiency of these surface-active agents was studied using emulsions of medium, heavy and ultra-heavy crude oils under conventional heating. Some of these surfactants were able to break water in oil emulsion in heavy and ultra-heavy crude oils. The effect of microwave irradiation as non-conventional energy source to accelerate and increase the efficiency of demulsification for heavy crude oil was also demonstrated (Fig. 13).[259, 260]

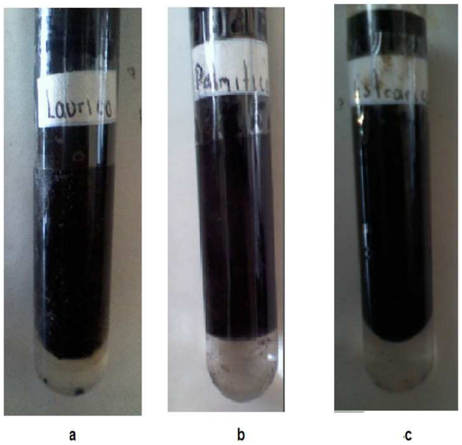


Fig. 13 Photographs of the tubes showing the results of the irradiation of the emulsion after 21 minutes of microwave irradiation for a) choline laurate, b) choline palmitate and c) choline estearate (1000 ppm).

Very recently, Mexican researchers also showed the potential of ILs analogues synthesized from aminoacids by means microwave irradiation,[261] as demulsifiers of oil-in-water emulsions previously prepared from heavy crude oil as a way to ensure the transportation through pipelines.[262] Microwave was also used to accelerated the demulsification process.[263]

3. Ionic liquids toxicity

An important consideration for large-scale application of ILs is their toxicity. The optimization of the technological properties of chemicals should be investigated in parallel with the minimization of their (eco)toxicological hazard potential. Commonly mentioned that ILs are compounds of low toxicity and in the literature these compounds have often been referred to as environmentally friendly but actually this stigma has spread grounded due to the ILs generally have negligible low vapor pressure and therefore not volatile as are most common organic solvents. In recent years the perception of their greenness dramatically changed as the scientific community began to proactively assess the risk of their application based on the entire life-cycle.

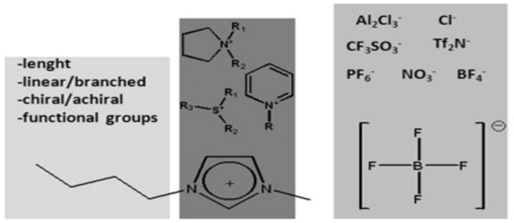
When considering the possible industrial application of ionic ILs is necessary to know about important aspect as biodegradation in the environment, migration in groundwater, bioaccumulation, aquatic toxicity, terrestrial and mammalian toxicity of ILs since all these aspects play a very important role in their environmental impact and fate.[264]

In 2008 Zhang showed for the first time the life cycle of [BMIM][BF_4] applied to large scale synthesis of cyclohexane and in a Diels-Alder reaction was assessed. For cyclohexane synthesis, the industrial gas phase process is the greenest, but the three solvents compared for the Diels–Alder reaction showed comparable life cycle impact. Although ILs are not the most attractive alternatives, because in comparison with traditional indicated that ILs can move the pollution associated with the early stages of the life cycle of some common organic solvents and can cause even more serious pollution. According with Zhang the result may change if their separation efficiency, stability and recyclability are improved.[265]

The effect of ILs structure on biodegradation potential have been much studied and it was concluded that the degree of degradation is strongly affected by the length of the alkyl side-chain, core ring structure and by the presence of functionalized groups,[266] while the impact of the anion structure is less pronounced,[267] in spite of this group in 2008 showed that fluoroorganic and cyano-based ILs anion present a high ecotoxicity which increased with increasing hydrophobicity.[268]

Stolte et al. studied the effect of different head groups and functionalized side chains and the anion type on the cytotoxicity of ILs. Their results showed that most of the tested 100 ILs generally exhibit a low cytotoxicity compared to other ILs previously investigated ILs containing polar ether, hydroxyl and nitrile functional groups within the side chains. The results confirm the general dependency between IL cation lipophilicity and cytotoxicity.[269] For the case of the anion, results show an anion effect in ILs on cytotoxicity for 10 of 27 tested anions. For the remaining 17 anions from our test kit no significant effect was found. With respect to structure-activity relationships, lipophilicity and/or vulnerability to hydrolytic cleavage seem to be the key structural features leading to the observed anion cytotoxicity.[270]

In an excellent 2014 overview of Bubalo et al. present some general guideline for the synthesis of greener ILs and proposed future directions in designing inherently safer ILs (Figure 14). According to these authors conventional ILs, though not benign, could become part of sustainable products and processes due to their excellent technological properties, but it is necessary to ensure the safety of employees handling these solvents and to ensure IL removal from processing effluents *via* the described regenerative methods. Drastic changes in toxicity/degradability, depending on heterocyclic moiety, attached substituents and/or the anionic part have been established, which leads us to believe that it should be possible to manipulate their chemical architecture in order to design “readily” or “ultimately” biodegradable ILs with low toxicity, thus, novel ILs originating from natural products could possibly be the future direction in IL design. The authors of this review proposed creating a database of environmentally benign structure moieties of ILs and deep eutectic solvents, based on their toxicological and biodegradation data, would be of practical use as a guideline for manufacturers and regulators to properly develop and regulate the use of these novel, truly *green* solvents.[271]



Guidelines for designing greener ionic liquids

	Substituent	"Core"	Anion
TOXICITY	***Recommended*** - introduction of short polar side-chains ***Not recommended*** - introduction of long hydrophobic alkyl chains	***Recommended*** - use of morpholinium and pyridinium ILs ***Not recommended*** -use of imidazolium ILs	***Recommended*** -use of anions like alkyl sulphates, alkyl sulphonatesalkyl benzene sulphonates, and salts of organic acids ***Not recommended*** - fluorine-containing ionic liquid anions
BIODEGRADIBILITY	***Recommended*** - introduction of long hydrophobic alkyl chains ***Not recommended*** - intorduction of polar functional groups (e.g. ether, hydroxyl or nitrile functions) into side-chain	***Recommended*** - use of pyridinium ILs ***Not recommended*** -use of imidazolium ILs	***Recommended*** -use of anions like alkyl sulphates, alkyl sulphonatesalkyl benzene sulphonates, and salts of organic acids ***Not recommended*** - fluorine-containing ionic liquid anions

Fig. 14 General guideline for the synthesis of greener ILs and proposed future directions in designing inherently safer ILs according with ref. 271.

In conclusion, to consider the application of an IL at high-scale it is very important to taking in account their toxicity in their wider context.

4. Future Perspectives

An overview of the potential of ILs to remove contaminants from refinery feeds have been compiled ion this contribution. With a staggering range of applications, and a wide diversity, ILs feature very attractive properties and composition for their application in Petroleum Industry and have a good chance to become the process of choice in future applications. However, these applications are still in an early stage and require further developments for a potential industrial implementation.

From an academic point of view, many applications using ILs result in very attractive processes and technologies useful at lab scale. In practice, several factors have made difficult their implementation as novel technology due to the requirements of new equipments and significant process engine changes plus the fact that the economic and technological competitiveness of ILs have not generally been proven at large scale. For the industrial use of ILs, some major issues must be addressed including IL synthesis scale-up, purity, stability, toxicity, recycling, disposal and price and may constitute barriers to IL process commercialization. The price of ILs must be related to process performance and to overall economy as only economically competitive as well as reliable processes will be implemented in industry, no matter the environmentally friendly or safe nature of this new technology.

In order to integrate ILs into existing industrial processes, a thorough understanding of their true capabilities and limitations is firstly needed. While the unique properties of ILs make them undoubtedly amazing materials, their performances should not be expected to exceed conventional methodologies in every application. Issues as product availability, ILs stability, and loss of activity during recycling and additional equipments required should also be resolved. An important consideration for large-scale application of ILs is their toxicity in their wider context.

Desulfurization, dearomatization and defluorination of feeds by liquid-liquid extractions might not be alternatives to substitute conventional technologies by ILs for the reasons stated in section 3.3. Nevertheless, we believe that ILs have the potential to become an environmental benign pre-treatment alternative for denitrogenation or post-treatment to traditional HDS for ultra-deep desulfurization in a near future.

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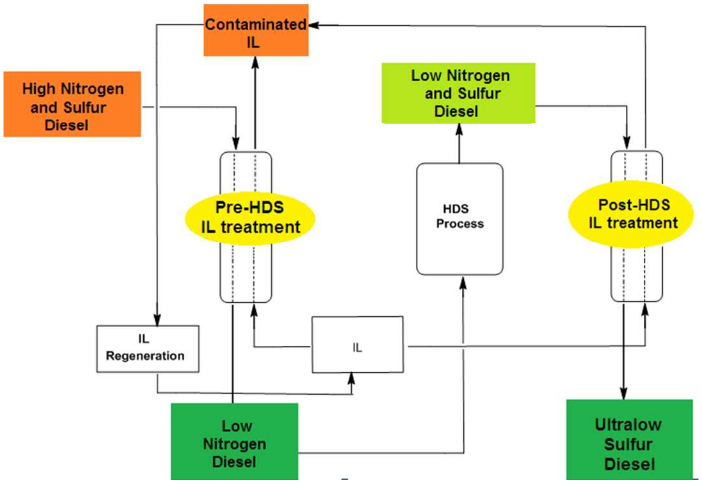
Color graphic



Text:

Ionics liquids are novel, green and efficient compounds to remove contaminants from refinery feedstocks

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Broader context box

This contribution is aimed to provide an account of chemical research to date on the use of novel and environmental technologies based on ionic liquids for removing various pollutants pollutants from refinery feedstocks including the removal of sulfur-, nitrogen- and fluorine-containing compounds, aromatics, naphthenic acids and asphaltenes, with a special emphasis on the industrial potential of applications of these processes.

Biography and photography

Rafael Martínez Palou works as a scientific research and professor at Mexican Petroleum Institute since 2002. His is involved on the development of new organic compounds for chemical treatments in the Oil Industry. His research is also focused on the study of new applications of ionic liquids and microwave energy in the area of oil/petroleum feedstocks.

Rafael Luque has a significant experience on biomass and waste valorisation practises to materials, fuels and chemicals as well as nanoscale chemistry, significantly contributing to the development of innovative greener technologies in heterogeneous catalysis, materials engineering and multidisciplinary sciences in recent years. Rafael is currently Ramon y Cajal Fellow at Universidad de Cordoba and 2014 Chinese Academy of Sciences Visiting Senior Scientist at the CAS Institute of Applied Chemistry in Changchun (China).He has been recipient of several recent awards including the RSC Environment, Sustainability and Energy Early Career Award (2013) from the Royal Society of Chemistry UK and Distinguished Engineering Fellowship from CBME at Hong Kong University of Science and Technology in Hong Kong.