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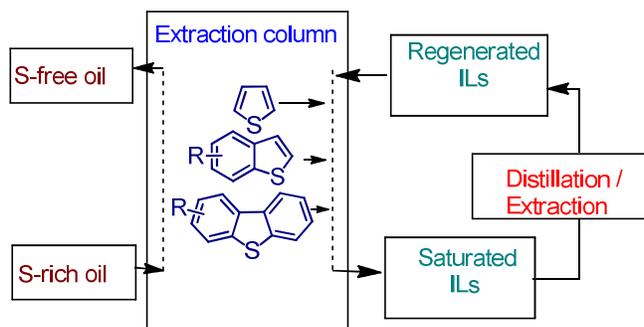


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Graphic abstract

Caption: Extractive desulfurization of fuel oils using ionic liquids as extractive reagents.



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**Xiaochun Chen**

Dr Xiaochun Chen is a Professor and Dean of College Chemical Engineering, Beijing University of Chemical Technology. He obtained his Ph.D degree in Chemical Engineering in 1998. He has an extensive research and teaching background in chemical and environmental engineering. Dr Chen is an author of more than 60 research papers and patents. His current research focuses on the design, synthesis and applications of Ionic Liquids in separation technology, industrial catalysis, membrane separation technology, process simulation and optimization.



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## A Review for Extractive Desulfurization of Fuel Oils using Ionic Liquids

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**Abstract:** Hydrodesulfurization (HDS), a widely employed method in industry for desulfurization of fuel oils such as gasoline and diesel fuel, is facing some challenges to produce lower-sulfur or sulfur-free fuel oils which are required by more and more countries; because HDS is not well effective to remove thiophenic sulfur compounds due to sterically-hindered adsorption on catalyst surface, also operated under harsh conditions such as high temperature, high pressure, noble catalyst and hydrogen requirement. Extractive desulfurization (EDS) of fuel oils using ionic liquids (ILs) has been being studied intensively in the latest decades, showing a good future as alternative or complement method to HDS. In this review, we reviewed the research results of EDS using ILs and gave comprehensive discussions on diversified factors influencing desulfurization such as ILs species, IL-oil mass ratio, initial sulfur content, temperature, time, mutual solubility, multiple extraction and regeneration where potential problem or shortcoming was also stated. Some other desulfurization methods under studying such as extraction, oxidation, adsorption and biodesulfurization were also outlined briefly. It can be inferred that ILs remain a class of ideal solvents to realize clean fuel oil in the near future because of their desirable physiochemical properties which are lacking in molecular organic solvents while there are possible challenges such as relatively high viscosity and low efficiency.

**Keywords:** Ionic liquids, clean fuel oils, thiophenic sulfur compounds, extractive desulfurization.

## 1. Introduction

Sulfur compounds (S-compounds, see Figure 1) in fuel oils such as gasoline and diesel fuel give rise to SO<sub>x</sub> emission during combustion, drop of combustion efficiency, deactivation of three-way catalyst, and increasing emission of CO and particulates. Therefore, desulfurization of fuel oils is an important process in oil refinery<sup>1,2</sup>.

Currently, hydrodesulfurization (HDS) is widely employed in industry, in which S-compounds in fuel oils react with hydrogen in presence of catalyst (mostly Co-Mo/Al<sub>2</sub>O<sub>3</sub> and Ni-Mo/ Al<sub>2</sub>O<sub>3</sub> catalysts<sup>3-4</sup>) to produce hydrogen sulfide (H<sub>2</sub>S) and H<sub>2</sub>S is removed from fuel oils. HDS, however, is facing some challenges with more countries limiting the S-content in fuel oils to lower level even to zero (e.g., the European directive on transportation fuels limited the S-content to 150 ppm for gasoline and 350 ppm for diesel in 1998, it was reduced to 50 ppm just five years later, and now it stands at <10 ppm; USA and Japan have put tax on transportation fuel exceeding 10 ppm S-content<sup>5-6</sup>; see Figures 2 and 3 for S-limitation in diesel fuel and gasoline from different countries<sup>7,8</sup>). This challenge is from the fact that HDS is effective for removal of aliphatic S-compounds such as thiols, thioethers and disulfides while not well effective for removal of heterocyclic S-compounds such as thiophene (TS), benzothiophene (BT), dibenzothiophene (DBT) and their derivatives due to the steric hindrance of adsorption on catalyst surface. To reduce S-content to a lower level in HDS, more harsh conditions are required such as higher temperature (~400<sup>0</sup>C), higher pressure (~20MPa) and more active noble catalyst, which gives rise to increasing cost and oil loss (e.g., alkene)<sup>9-11</sup>.

To this end, alternative methods such as extraction, oxidation, adsorption and biodesulfurization were studied, among which extractive desulfurization (EDS) is one preferable method because it is operated at mild and simple conditions and does not alter the chemical structure of the compounds in fuel oils and the extracted S-compounds can be re-used as raw materials. Earlier, a few molecular solvents such as polyalkylene glycol, imidazolidinone, pyrimidinone and dimethylsulfoxide were tested in EDS; the volatile nature of such molecular solvents, coupled with the limited number of suitable extractants, however, prevented the final application of EDS in industry due to volatile loss of solvent and difficult regeneration of extractant<sup>10,11</sup>.

The arising of ionic liquids (ILs) brings new chance for EDS. Different from traditional molecular solvents, ILs are entirely composed of cation and anion; as a result ILs have a

negligible vapour pressure, in other words, ILs are not volatile (the reason why ILs are called “green solvents”). In addition, ILs have high thermal/chemical stability, tunable dissolving or extracting capability for inorganic or organic compounds, wide liquidus range, non-flammability, recyclability, and so on<sup>12,13</sup>. These desirable properties favour ILs as extractant in EDS as illustrated in Figure 4, where S-compounds are extracted from oil phase to ILs phase and are removed from ILs phase (ILs regeneration) through simple distillation employing nonvolatility of ILs or other solvent re-extraction employing tunable solubility between ILs and other solvents.

In the latest decades, EDS using ILs (shortened as ILs-EDS) have been studied intensively. The research results indicate a good future for ILs-EDS as potential alternative or complement to HDS while some trivial problems possibly exist. In this work, we review the research results of ILs-EDS and give comprehensive discussions on diversified factors influencing desulfurization such as ILs species, IL-oil mass ratio, initial S-content, temperature, time, mutual solubility, multiple extraction and regeneration where potential problem was also stated. Some other desulfurization methods under studying such as extraction, oxidation, adsorption and biodesulfurization are also outlined briefly. This review is expected to contribute to not only experimental study on ILs-EDS but also their final industrial fate.

## 2. Alternative Desulfurization Methods

### 2.1. Adsorptive Desulfurization (ADS)

In ADS, S-compounds in fuel oils are removed through being adsorbed on one adsorbent that is typically positioned on non-reactive and porous substrate. ADS can be direct or reactive, depending on interaction nature between S-compound and adsorbent. The choice of adsorbent is one main factor influencing adsorptive efficiency<sup>14-15</sup>. Different types of adsorbents were investigated, e.g., activated carbon<sup>16</sup>, alumina<sup>17</sup>, zeolites<sup>18</sup>, zirconia<sup>19</sup> and silica gel<sup>20</sup>, among which activated carbon is the mostly studied because of its effective surface area with good porosity<sup>16,21-22</sup>. Lee and his co-workers investigated 10 type of activated carbon produced from different natural raw materials and observed that coconut-shell based activated carbon was more efficient than coal based and wood based activated carbon<sup>23</sup>. S-Zorb was developed by Conoco Phillips Petroleum Co., in which S-compounds were removed by reactive adsorption at high temperature and low

hydrogen pressure<sup>24-25</sup>. Table 1 shows different adsorbents.

Table 1. Different adsorbents used in ADS at optimized conditions

Adsorbents	Model oil	S-comp.	Initial S: (ppm)	Temp. (K)	Pressure (atm)	S-removal	Ref.
Activated carbon	gas oil	DBT	178	198	1	95%	16
	gas oil	TS	300	243	1.5	88%	21
Alumina	gas oil	DBT	700	393	n/a	30%	17
Zeolites from coal	hexane	TS, BT	500	303	1	63%	18
NiMoP/Al <sub>2</sub> O <sub>3</sub>	hexane	DBT	450	600	40	56%	26
Gallium +Y -zeolite	nonane	DBT	500	333	n/a	97%	27
Cu-zirconia	octane	TS	2000	180	n/a	99%	19
Ruthenium complexes	hexane	DBT	40	298	1	55%	28

One challenge in ADS is to find good adsorbents that selectively and efficiently adsorb S-compounds while not adsorb hydrocarbon and olefin; aromatic S-compounds, however, are similar to olefinic in some properties such as presence of more than two double bonds which atoms of metals can easily interact. Another challenge is the regeneration of adsorbents completely after adsorption. In addition, the adsorption efficiency of many adsorbents were found to be low, e.g., 1~4 mg S-compounds were adsorbed per g clay material which means huge amounts of adsorbent required.

## 2.2. Biodesulfurization (BDS)

BDS is considered as a green process, in which microorganisms are used to remove S-atom from organic compounds. The microorganisms have the natural ability to consume aromatic S-compounds as their energy source and metabolize organo S-compounds by reductive C–S bond cleavage, oxidative C–S bond cleavage, or oxidative C–C bond cleavage. Generally, BDS takes place by two pathways: the Kodama pathway, in which the first attack is intended against one of the carbon atoms; the 4S pathway, in which early catalysis is directed against the axis of sulfur<sup>29-33</sup>. Table 2 summarizes the results of BDS at optimized conditions.

Table 2. Biodesulfurization by different microorganisms

Microorganism	Model oil	Initial S: (ppm)	Temp (K)	S-removal	Ref.
<i>Gordonia alkanivorans RPI90A</i>	hexadecane	320	303	90%	34
<i>Mycobacterium sp. ZD-19</i>	hexadecane	92	303	100%	34

<i>Mycobacterium goodii X7B</i>	tertradecane	200	313	99%	35
<i>Rhodococcus erythropolis IGTS8</i>	hexadecane	100	303	80%	36
<i>Gordonia alkanivorans strain 1B</i>	heptane	100	308	63%	37
<i>Bacillus subtilis WU-S2B</i>	tridecane	100	323	50%	38
<i>Pseudomonas stutzeri UP-1</i>	hexadecane	500	304	74%	39
<i>Sphingomonas subarctica T7b</i>	gas oil	280	300	94%	40
<i>Bacterium, strain RIPI-22</i>	hexadecane	100	303	77%	41
<i>Pseudomonas delafieldii R-8</i>	diesel oil	591	303	47%	42

Slow biodegradation and suitability of biocatalyst are the challenges in BDS. The logistics of sanitary storage, handling, shipment, storage and use of living microbes within the refinery atmosphere are also problematic, because they are very sensitive in nature<sup>43</sup>.

### 2.3. Oxidative Desulfurization (ODS)

ODS is able to remove S-compounds from fuel oils at mild conditions<sup>44</sup>. ODS typically includes two steps. In first step, sulfides are oxidized into sulfoxides or sulfones by oxidant. In second step, these sulfoxides or sulfones are separated from fuel oils by solvent extraction on the basis of their increased polarity. The used solvent is then recovered through distillation<sup>45-46</sup>. Nitrogen dioxide (NO<sub>2</sub>) was used first time as oxidant in ODS followed by extraction with methanol<sup>47-48</sup>. However, NO<sub>2</sub> led to the formation of huge quantity of residue and waste<sup>48</sup>. Many other organic and inorganic acids such as formic, acetic and performic acids were used as catalysts in ODS technology, while hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was used commonly in ODS as an oxidant. ILs as alternative to traditional organic solvents were also used in ODS<sup>49-59</sup>. Figures 5 and 6 show general and specified ODS process.

Selectivity of oxidant, and extractive solvent are two challenges in ODS. Some oxidants resulted in unwanted side reactions that decrease the mass and quality of fuel oils. Selection of incorrect solvent may cause eliminating hydrocarbon compounds such as aromatic and olefin from the liquid<sup>60</sup>.

### 2.4. Extractive Desulfurization (EDS)

As mentioned above in the section of introduction, EDS is a desirable method where desulfurization is performed at mild and simple conditions (low temperature, low pressure) without catalyst and hydrogen required. More important, EDS selectively extract S-compounds from fuel oils while does not destruct the other compounds in fuel oils, and

the extracted compounds can be re-used as raw materials. EDS is based on different partition of S-compounds in oil phase and extractant phase. The choice of extractive solvent is one main factor in EDS. As mentioned above, there are a few problems when volatile solvents such as polyalkylene glycol, imidazolidinone, pyrimidinone and dimethylsulfoxide are used. The ideality of solvent depends on its efficiency, recyclability, and reusability, therefore the important assignment for researchers is to discover a technique of substituting volatile organic compounds with green solvents. ILs technology is attracting widespread attention in separation processes. Various types of ILs have been employed in recent studies involving as a solvent in EDS<sup>11,61-64</sup>.

### 3. ILs-EDS

ILs are composed of organic cations and inorganic/organic anions which provide unique medium for separation and chemical reaction processes. The properties of ILs depend on ionic characteristics and the combination of cation and anion<sup>65-67</sup>. Well known cations are imidazolium, pyridinium, isoquinolonium, ammonium, phosphonium and sulfonium as shown in Figure 7.

Although the first IL was synthesized as far back as 1914<sup>68</sup>, it was not until the 90's that ILs had generated much attention as a class of solvents to revolutionize chemical separation or reaction technology. ILs are considered to be ideal solvents because of their physical and chemical properties. These properties include non-volatility, non-emission, easy alteration of cation/anion structure or combination for specific applications, high thermal and chemical stability. Similarly they have high ionic conductivity and good ability to dissolve organic and inorganic compounds. Due to all these favourable properties, ILs are usually referred to as "green" and "designer" solvents<sup>69</sup>. ILs have been used in liquid-liquid extraction, nanotechnology, catalysis, electrochemistry, separation technology<sup>69-78</sup>.

EDS, which began with the use of molecular solvents such as polyalkylene glycol, imidazolidone, pyrimidinone and dimethylsulfoxide<sup>11</sup>, are recently robustly focused on ILs. In the latest decades, a number of literatures have been appearing that gave the results of ILs-EDS. These results indicated that ILs are capable of effectively extract S-compounds from fuel oils, and the main factors influencing ILs-EDS process typically include nature of ILs, IL-oil mass ratio, initial sulfur content, temperature, time, mutual

solubility, multiple extraction and regeneration. In the following sections, we will present these ILs-EDS results and discuss these factors.

### 3.1. ILs used in EDS

In 2001, A. Bosman<sup>79</sup> and his co-workers applied ILs-EDS technique to remove S-compounds in fuel oils for the first time. These ILs were acidic in nature. Since, many researchers have made use of ILs as solvents for S-compounds removal. Mostly those ILs were imidazolium and pyridinium based ILs with different anions. Table 3 shows the list of ILs, used in EDS by different researchers.

Table 3. ILs used in EDS of fuel oils

Name of IL	Formula of ILs	Ref.
N-methyl-n-methylimidazolium dimethyl phosphate	[MMIM][DMP]	80
N-ethyl-n-methylimidazolium diethyl phosphate	[EMIM][DEP]	80
N-butyl-n-methylimidazolium dibutyl phosphate	[BMIM][DBP]	80
1-ethyl-2,3-trimethyleneimidazolium chloride	[EtMIM]Cl	62
N-ethyl-N-methyl-imidazolium dimethylphosphate	[EMIM][DMP]	63
N-ethyl-N-ethyl-imidazolium diethylphosphate	[EEIM][DEP]	63
N-butyl-N-ethyl-imidazolium dibutylphosphate	[BEIM][DBP]	63
1-ethyl-3-methylimidazolium tetrafluoroborate	[EMIM][BF <sub>4</sub> ]	81
1-butyl-3-methylimidazolium hexafluorophosphate	[BMIM][PF <sub>6</sub> ]	81
1-butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF <sub>4</sub> ]	82,83
1-methyl-3- octylimidazolium tetrafluoroborate	[OMIM] [BF <sub>4</sub> ]	83
1-methyl-3-octylimidazolium bis [trifluoromethylsulfonyl]imide	[OMIM][NTf <sub>2</sub> ]	84
1-butyl-3-ethylimidazolium ethyl sulfate	[BEIMEt][SO <sub>4</sub> ]	85
1-ethyl-3-ethylimidazolium ethyl sulfate	[EIMEt][SO <sub>4</sub> ]	85
1-ethyl-3-methylimidazolium ethyl sulfate	[EMIMET][SO <sub>4</sub> ]	85
1-ethyl-3-methylimidazolium methyl sulfate	[EMIMMe][SO <sub>4</sub> ]	85
1-butyl-3-methylimidazolium methyl sulfate	[BMIMMe][SO <sub>4</sub> ]	85
1,3-dimethylimidazolium methyl sulfate	[MMIMMe][SO <sub>4</sub> ]	85
1-nbutyl- 3 methylimidazolium octylsulfate	[BMIM] [OcSO <sub>4</sub> ]	5
1-ethyl-3-methyl-imidazolium ethylsulfate	[EMIM][EtSO <sub>4</sub> ]	5
1-butyl-2,3-dimethyl imidazolium chloride	[BDMI][Cl/FeCl <sub>3</sub> ]	86
1-hexyl-2,3-dimethyl imidazolium chloride	[HDMICl][FeCl <sub>3</sub> ]	86
1-butyl-3-methylimidazolium dicyanamide	[BMI][N(CN) <sub>2</sub> ]	87
1-ethyl-3-methylimidazolium dicyanamide	[EMI][N(CN) <sub>2</sub> ]	87
Ethylated tetrahydrothiophenium dicyanamide	[S <sub>2</sub> ][N(CN) <sub>2</sub> ]	87
Ethyl dimethylsulfonium dicyanamide	[EtMe <sub>2</sub> S][N(CN) <sub>2</sub> ]	87
1-ethyl-3-methylimidazolium ethyl sulfate	[EMIM] [EtSO <sub>4</sub> ]	64
1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[PMIM] [Tf <sub>2</sub> N]	64
1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[BzMIM] [Tf <sub>2</sub> N]	64
1-heptyl-2,3-dimethylimidazoliumbis (trifluoromethylsulfonyl) imide	[HpMMIM] [Tf <sub>2</sub> N]	64
1-decyl-2,3-dimethylimidazoliumbis (trifluoromethylsulfonyl)	[OMMIM] [Tf <sub>2</sub> N]	64

imide		
1-hexyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide	[HMMPy] [Tf <sub>2</sub> N]	64,88
N-butylpyridinium tetrafluoroborate	[BPy][BF <sub>4</sub> ]	89
N-hexylpyridinium tetrafluoroborate	[HPy][BF <sub>4</sub> ]	89
N-octylpyridinium tetrafluoroborate	[OPy][BF <sub>4</sub> ]	89
N-butyl-pyridinium nitrate	[BPy][NO <sub>3</sub> ]	90
N-ethyl-pyridinium nitrate	[EPy][NO <sub>3</sub> ]	90
N-butyl-pyridinium tetrafluoroborate	[BPy][BF <sub>4</sub> ]	90
N-ethyl-pyridinium tetrafluoroborate	[EPy][BF <sub>4</sub> ]	90
N-ethyl-pyridinium acetate	[EPy][Ac]	90
N-butyl-pyridinium acetate	[BPy][Ac]	90
3-methyl-N-butyl-pyridinium dicyanamide	[MBPy][N(CN) <sub>2</sub> ]	91
4-methyl-N-butyl-pyridinium dicyanamide	[MBPy][N(CN) <sub>2</sub> ]	91
4-methyl-N-butyl-pyridinium thiocyanate	[MBPy][SCN]	91
N-butyl-N-methylimidazolium tricyanomethanide	[BMIM][C(CN) <sub>3</sub> ]	91
N-butyl-N-methylimidazolium dicyanamide	[BMIM][N(CN) <sub>2</sub> ]	91
1-butyl- 3- methylimidazolium thiocyanate	[BMIM][SCN]	91,92
1-butyl- 3- methylimidazolium chloride	[BMIM]Cl/FeCl	86
1-octyl-3-methylimidazolium chloride	[OMIM]Cl/FeCl	86
3-butyl-4-methylthiazolium dicyanamide	[BMTH][DCA]	93
3-butyl-4-methylthiazolium thiocyanate	[BMTH][SCN]	93
3-butyl-4-methylthiazolium hexafluorophosphate	[BMTH][PF <sub>6</sub> ]	93
3-butyl-4-methylthiazolium tetrafluoroborate	[BMTH][BF <sub>4</sub> ]	93
1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate	[BMPYR][CF <sub>3</sub> SO]	94
1-butyl-1-methylpyrrolidinium tricyanomethanide	[BMPYR][TCM]	94
1-hexyl-3-methylimidazolium tetracyanoborate,	[HMIM][TCB]	95
1-methyl-3-methylpyrrolidone dimethyl phosphate	[MMP][DMP]	95
1-methyl-3-ethylpyrrolidone diethyl phosphate	[MEP][DEP]	95
1-hexyl-3-methylpyrrolidone dimethyl phosphate	[HMP][DMP]	95
1-hexyl-3-ethylpyrrolidone diethyl phosphate	[HEP][DEP]	95
1-butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF <sub>4</sub> ]	96
1-octyl-3-methylimidazolium tetrafluoroborate	[OMIM][BF <sub>4</sub> ]	96
1-butyl-3-methylimidazolium hexafluorophosphate,	[BMIM][PF <sub>6</sub> ]	96
1-octyl-3-methylimidazolium hexafluorophosphate	[OMIM][PF <sub>6</sub> ]	96
N-methylpiperazinium lactate	[C1 pi][Lac]	97
N-ethylpiperazinium lactate	[C2 pi][Lac]	97
N,N'-dimethylpiperazinium dilactate	[C1C1pi][lac]	97
2-2-dimethylamino ethoxy propionate	[DMEE][CO <sub>2</sub> Et <sub>2</sub> ]	98
3-dimethylamino propanenitrile propionate	[DMAPN][CO <sub>2</sub> Et]	98
1-butyl-3-methylimidazolium copper chloride	[BMIM][CuCl <sub>2</sub> ]	99
1-butyl-3-methylimidazolium tetrachloroaluminate	[BMIM]AlCl <sub>4</sub>	100
1-butyl-3-methylimidazolium octylsulfate	[BMIM][OcSO <sub>4</sub> ]	101
1-ethyl-3-methylimidazolium thiocyanate	[EMIM][SCN]	102
1-Alkyl-3-methyl Imidazolium methyl phosphate	[MMIM][MP]	103
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	[BMIM][OTf]	103
N-methylimidazolehydrogen sulfate	[HMIM][HSO <sub>4</sub> ]	104
N-methylpyrrolidonehydrogen sulfate	[HNMP][HSO <sub>4</sub> ]	104

### 3.2. Thermodynamic Extractive Equilibrium

Thermodynamics extractive equilibrium is a very important aspect of any process because short time favours high product yield or small size of contact equipment in industry. It is observed from literatures that the thermodynamics extractive equilibrium of ILs-EDS is directly related to ILs viscosity. High viscous ILs such as [BMIM][OcSO<sub>4</sub>], [BMIM][CH<sub>3</sub>CO<sub>4</sub>], [HMIM][HSO<sub>4</sub>] and [HNMP][SO<sub>4</sub>] took 30-40 minutes to achieve the equilibrium (Figures 8, 9) while low viscous ILs such as [BMIM][SCN], [BMTH][N(CN)<sub>2</sub>], [BMIM][N(CN)<sub>2</sub>] and [BMTH][SCN] took less than 10 minutes to reach at equilibrium (Figures 10, 11).

A possible reason behind these variations can be that the low viscous ILs had better dispersion in fuel oils and faster mass transfer of S-compounds from the oil phase to the IL phase<sup>105</sup>. Figures 8-11 show DBT removal efficiency verses thermodynamic extractive equilibrium and TS removal efficiency verses thermodynamics extractive equilibrium by different ILs at mild conditions.

### 3.3. IL-oil Mass Ratio

IL-oil mass ratio is one important factor for selectivity of ILs for desulfurization. As ILs' cost is high, it is preferred to utilize minimum quantity in fuel desulfurization, but it is observed from the literatures shown in Table 4 that the S-extraction efficiency decreases with decreasing IL-oil mass ratio. For instance mass ratios of [BMI][N(CN)<sub>2</sub>] to oil were tested under atmospheric conditions for 20 minutes and the order of S-extraction efficiency follows the order 1:5<1:4<1:3<1:2<1:1<2:1 (w/w) IL-oil<sup>87</sup>. Meanwhile, the S-partition coefficients did not prove very sensitive to the mass ratio. Similar results were obtained when a series of [BF<sub>4</sub>] and [MeSO<sub>4</sub>]-based ILs were used to investigate the influence of mass ratio<sup>85,106</sup>. Despite increasing behaviour of extraction efficiency with increasing IL-oil mass ratio, it is found that the extent of increase is not with same rate. This typically depends on the individual chemical nature of ILs related with their extraction abilities.

It is already mentioned that S-partition is not sensitive for physical extraction. However it might be sensitive for chemical extraction. Mostly the less viscous ILs such as [BMI][N(CN)<sub>2</sub>], [EMI][N(CN)<sub>2</sub>], [BMTH][N(CN)<sub>2</sub>], [BMPYR][TCM], [HMIM][TCB], [C1pi][Lac], [C2pi][Lac] and [C1C1pi][Lac] showed less sensitivity as compared to high-viscous ILs such as [OMIM][BF<sub>4</sub>], [EMI][BF<sub>4</sub>], [EMIM][MeSO<sub>4</sub>], [HEP][DEP] and

[NMP][DMP] as per in Table 4.

Apart from the positive effect of increasing ILs-oil mass ratio, IL-oil mass ratio has to be selected carefully based on a compromise between S-removal and oil recovery. Moreover the regeneration of ILs may also be considered for the process as this highly affects the overall process cost.

Table 4. S-extraction efficiency of different ILs at different mass ratio of IL-oil

ILs	Oil	S-comp.	Time (min)	Temp. (K)	S-extraction efficiency for IL-oil mass ratio					Ref.
					2:1	1:1	1:2	1:3	1:5	
[EMIM][MeSO <sub>4</sub> ]	n-hexane	DBT	20	298.1	n/a	70	40	n/a	15	85
[MMIM][MeSO <sub>4</sub> ]	n-hexane	DBT	20	298.1	n/a	40	23	n/a	10	
[BMI][N(CN) <sub>2</sub> ]	n-hexane+ toluene	TS	20	298.1	62.6	47.5	29	22	17	87
	n-hexane	DBT	20	298.1	78.9	69.5	50	44	30	
[BMTH] [N(CN) <sub>2</sub> ]	n-octane	DBT	20	298.1	66.8	49.6	30	20	15	93
	n-hexane	TS	20	298.1	60.4	39.8	30	20	18	
[BPy][BF <sub>4</sub> ]	n-heptane + xylo	DBT	30	327	n/a	45.5	28.6	16.9	n/a	90
[BPy][NO <sub>3</sub> ]	n-heptane + xylo	DBT	30	327	n/a	30.1	19	9.4	n/a	90
[BPy][Ac]	n-heptane + xylo	DBT	30	327	n/a	32.1	20.1	10.	n/a	90
[EPy][BF <sub>4</sub> ]	n-heptane + xylo	DBT	30	327	n/a	21.8	12.6	8.9	n/a	90
[EPy][NO <sub>3</sub> ]	n-heptane + xylo	DBT	30	327	n/a	27.1	17.3	13.8	n/a	90
[BPy][BF <sub>4</sub> ]	n-dodecane	TS	15	298.1	n/a	37.5	n/a	9.37	5	89
		DBT	15	298.1	n/a	40.6	n/a	18.7	12.5	
[HPy][BF <sub>4</sub> ]	n-dodacane	TS	15	298.1	n/a	41.9	n/a	17.5	6.25	89
		DBT	15	298.1	n/a	59.4	n/a	31.2	25	
[OPy][BF <sub>4</sub> ]	n-dodacane	TS	15	298.1	n/a	43.7	n/a	18.7	6.25	89
		DBT	15	298.1	n/a	62.5	n/a	37.5	31.5	
[OMIM][BF <sub>4</sub> ]	n-hexane	DBT	20	298.1	n/a	39.8	24.7	n/a	16.1	83
[PMIM][Tf <sub>2</sub> N]	n-hexane	DBT	20	298.1	n/a	52	37	n/a	20	64
[C1pi][Lac]	n-heptane	TS	30	298.1	46	16	16	11	n/a	97
	n-heptane	DBT	30	298.1	58.2	43.3	32	24	n/a	
[NMP][DMP]	n-octane	DBT	20	298.1	n/a	87.5	75.1	66.2	51.6	95
		BT	20	298.1	n/a	73.2	61.3	51.4	34.4	
		TS	20	298.1	n/a	72.1	50.2	42.5	25.3	

### 3.4. Initial S-content

For an ideal physically determined ILs-EDS technique, the initial S-content in the oil to be treated has little or no influence on the extraction efficiency. Notwithstanding, different IL systems tend to exhibit varied extraction mechanisms. For example, [BMI][N(CN)<sub>2</sub>],

[BMTH][N(CN)<sub>2</sub>] and a [BF<sub>4</sub>]-based IL showed decreasing S-extraction efficiency with increasing initial S-content in oil, although this influence was not pronounced<sup>87,93</sup>. However, when Huang, C. at al. used [BMIM][Cu<sub>2</sub>Cl<sub>3</sub>] for the desulfurization of gasoline<sup>107</sup>, increasing S-extraction efficiency with increasing initial S-content was reported, and this influence was obvious, e.g. between 950 ppm/w S-content and 196 ppm/w S-content, 16.2% and 37.4% S-extraction efficiency was realized. Table 5 demonstrates some examples of S-extraction efficiency of different ILs for different initial S-contents.

Table 5. S-extraction efficiency of different ILs for different initial S-contents

IL	Oil	S-comp.	Temp. (K)	IL-oil mass ratio	Time (min)	Initial S: (ppm)	S-extraction efficiency (%)	Ref.
[BMI][N(CN) <sub>2</sub> ]	n-hexane + toluene	TS	298	1:1	20	200	52.1	87
						500	51.4	
						800	49.8	
						1500	48.1	
						2000	45.1	
	n-hexane	DBT	298	1:1	20	200	70.9	
						500	70.3	
						800	69.2	
						1500	67.1	
						2000	67.9	
[BMIM][Cu <sub>2</sub> Cl <sub>3</sub> ]	gasoline	DBT/TS	RT	1:1	20	196	37.4	107
						410	29.1	
						680	21.6	
						950	16.2	
[BMTH][N(CN) <sub>2</sub> ]	n-octane	DBT	298	1:1	20	203	64.3	93
						557	63.9	
						944	63.1	
						1440	62.8	
						2927	61.6	
	n-hexane	TS	298	1:1	20	275	45.2	
						549	44.1	
						849	43.2	
						1546	41.1	
						2645	39.4	

Obviously, this insensitivity of S-extraction efficiency to initial S-content in fuel oils is valuable to deal with oils industrially with wide range of S-content.

### 3.5. Temperature

Studies have shown that there is very infinitesimal influence of temperature on S-extraction efficiency and the corresponding S-partition coefficients. Effect of temperature on S-removing efficiency for ILs is tabulated in Table 6. The literatures show that low viscous ILs such as [BMI][N(CN)<sub>2</sub>], [BMTH][N(CN)<sub>2</sub>] and [BMIM][SCN] have slight decreasing trend for S-extraction efficiency and corresponding S-partition coefficient with increasing temperature. On the other hand the trend becomes reversed for high viscous ILs such as [EPy][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>], where increase in temperature confirms slight increase in efficiency and partition coefficient. However, in some studies temperature has showed great effect on desulfurization such as [HNMP][HSO<sub>4</sub>] where increase in temperature from 40<sup>0</sup>C to 70<sup>0</sup>C corroborates great increase in S-extraction efficiency from 48% to 63%<sup>104</sup>.

The reason for these variations for high and low viscous ILs can be understood from the variation in viscosity of ILs on increasing temperature. With the increase of temperature for high viscous ILs the viscosity of ILs is decreased, due to which the ILs and the S-content in the oil have more possibility to interact with each other, which leads the high S-removal efficiency. However, the impact of temperature on the desulfurization is limited. The conclusive remark in this regard is that low viscous ILs has more advantages over high viscous ILs in terms of energy consumption and S-extraction efficiency at room temperature.

Table 6. S-extraction efficiency of different ILs at different temperatures

IL	Oil	S-comp.	Time (min)	S-extraction efficiency for temperatures (%)					Ref.
				20 <sup>0</sup> C	25 <sup>0</sup> C	35 <sup>0</sup> C	45 <sup>0</sup> C	55 <sup>0</sup> C	
[BMI][N(CN) <sub>2</sub> ]	n-hexane + toluene	TS	20	46.7	46.2	45.3	43.2	40.6	87
	n-hexane	DBT	20	66.8	65.4	63.5	61.7	59.9	
[BMTH][N(CN) <sub>2</sub> ]	n-octane	DBT	20	55.3	55.1	53.3	52.8	51.9	93
	n-hexane	TS	20	38.5	38.4	37.8	36.1	35.4	
[BMI][SCN]	dodacane	DBT	20	n/a	n/a	64	62	60	92
[EMI][N(CN) <sub>2</sub> ]	Gasoline	DBT	20	41	40.7	38.9	37.4	36.2	
[BPy][BF <sub>4</sub> ]	n-heptane + xylol	DBT	30	n/a	45.5	45.9	46.5	47	90
[C <sub>1</sub> pi][Lac]	n-heptane	DBT	30	21	20	19	18	18	97
	n-heptane	TS	30	39	40	43	40	39	
[NMP][DMP]	n-octane	DBT	20	n/a	87	86	86	856	95
		BT	20	n/a	73.2	72.1	71.1	70.2	
		TS	20	n/a	72.1	71.7	71.1	70.8	
[HNMP][HSO <sub>4</sub> ]	n-octane	TS	20	n/a	n/a	47.1	53.2	60.1	104

### 3.6. Regeneration

Regeneration of ILs after extraction is a significant feature for selectivity of ILs. Regeneration and recyclability can compensate for the high cost of ILs. The methods of regeneration of S-loaded ILs may vary on the basis of nature of ILs and S-compounds. Mostly regeneration of hydrophobic ILs is done by distillation followed by adsorption, and regeneration of hydrophilic ILs by dilution process with water followed by distillation. Original structure of ILs mostly found unchanged after regeneration, which is best sign for ILs. During regeneration, S-compounds in the vicinity of solvent molecules are repelled; after regeneration, ILs are reused without a noticeable decline in efficiency for model oils as demonstrated in the literatures<sup>62,76</sup>. Many ILs such as [BMI][N(CN)<sub>2</sub>], [BMTH][N(CN)<sub>2</sub>], [EMI][N(CN)<sub>2</sub>], [MBPy][N(CN)<sub>2</sub>], [NMP][DMP], [C1pi][Lac], [MMIM][DMP], [EMIM][DEP] and [BMIM][DBP] showed remarkable results after their regeneration but it was also found in the literatures that the low viscous ILs such as [BMI][N(CN)<sub>2</sub>], [BMTH][N(CN)<sub>2</sub>], [EMI][N(CN)<sub>2</sub>] and [MBPy][N(CN)<sub>2</sub>] can more easily be regenerated as compared to high viscous ILs such as [NMP][DMP], [HNMP][SO<sub>4</sub>], [BMIM][DMP] and [BEIM][DEP]. Table 7 shows S-removal efficiency verses regeneration cycle by different ILs at mild conditions.

Table 7. S-extraction efficiency vs regeneration cycle by different ILs at mild conditions

ILs	Oil	S-comp.	Time (min)	Temp. (K)	IL-oil mass ratio	S-extraction efficiency for regeneration cycles				Ref.
						1	2	3	4	
[BMI][N(CN) <sub>2</sub> ]	n-hexane + toluene	TS	20	298	1:1	47.5	47.2	46.4	45.2	87
	n-hexane	DBT	20	298	1:1	69.5	68	67	65.8	
[BMTH][N(CN) <sub>2</sub> ]	n-octane	DBT	20	298	1:1	69.5	69.4	69.3	69	93
	n-hexane	TS	20	298	1:1	49.6	49.5	49.5	49.5	
[EMIM][N(CN) <sub>2</sub> ]	n-hexane	TS	20	298	1:1	43	42.9	42.8	42.7	87
Et <sub>3</sub> NHCl-AlCl <sub>3</sub>	benzene	DBT	20	293	1:1	40.2	39.1	n/a	n/a	61
	toluene	TS	20	293	1:1	25.	25.0	n/a	n/a	

### 3.7. Multiple Extractions

In a single-step extraction, it is very difficult to reduce the S-content in oil to the statutory limit (say, 10ppm), a fact that has necessitated multiple extractions<sup>104</sup>. This may be due to S-compounds partition between fuel oils and ILs which makes a complete removal of S-

compounds in a single extraction rather impossible. [EMIM][N(CN)<sub>2</sub>] reduced thiophenic sulfur in model gasoline from ~500ppm to ~300 ppm (41.7% efficiency) in a single extraction at 1:1(w/w) IL-oil, 25°C for 20 minutes, and to ~15 ppm (about 97% efficiency) after five extraction cycles. In the same token, [BMI][N(CN)<sub>2</sub>] realized an almost 100% S-removal after five cycles as opposed to a mere 49.2% in a single extraction<sup>87</sup>. [EMIM][SCN] removed DBT completely from model diesel in the third step and removed 96% TS after three stages. These studies suggest that the multiple-extractive process is a remarkable way to reduce S-content to near or below the required limit as shown in table 8.

As it is already discussed that it is not possible to reduce S-content to the legislative limit in a single extraction step, but when we consider performances of different ILs for only single step extraction, low viscous ILs such as [BTH][N(CN)<sub>2</sub>], [EMI][N(CN)<sub>2</sub>] and [BMI][N(CN)<sub>2</sub>] shows highest results for both S-content compounds *i.e.* DBT and TS at mild conditions. However, some high viscous ILs also showed good results for S-content in single step at high temperature such as [NMP][DMP] and [HNMP][HSO<sub>4</sub>].

Table 8. S-extraction efficiency of different ILs at multiple extraction steps

ILs	Oil	S-comp.	Temp. (K)	IL-oil mass ratio	Time (min)	S-extraction efficiency for multiple steps (%)				Ref.
						1	2	3	4	
[DMIM][Tf <sub>2</sub> N]	diesel	DBT	RT	1:1	20	36.3	56.3	69.7	77.2	64
	gasoline	TS	RT	1:1	20	17.1	29.8	40.9	50.5	
[HpMMIM][Tf <sub>2</sub> N]	diesel	DBT	RT	1:1	20	31.9	53.7	59.1	70.4	64
	gasoline	TS	RT	1:1	20	12.7	26.1	35.2	40.5	
[HMMPy][Tf <sub>2</sub> N]	diesel	DBT	RT	1:1	20	35.6	59.1	71.3	92.6	64
	gasoline	TS	RT	1:1	20	12.0	24.4	40.1	50.5	
[BMTH][N(CN) <sub>2</sub> ]	diesel	DBT	293	1:1	20	50.3	81.8	94.5	99.1	93
	gasoline	TS	293	1:1	20	58.1	61.8	79.1	90	
[BMI][N(CN) <sub>2</sub> ]	diesel	DBT	298	1:1	20	66.6	90	98.3	n/a	87
	gasoline	TS	298	1:1	20	49.9	83.3	89.9	95.8	
[EMIM][N(CN) <sub>2</sub> ]	gasoline	TS	298	1:1	20	41.1	66	81.2	90.1	87
[NMP][DMP]	n-octane	TS	298	1:1	30	71	89.6	96	98	95

### 3.8. Mutual Solubility

The mutual solubility of ILs and fuel oils is an important factor to consider in ILs-EDS process mainly for two reasons: conspicuous dissolution of ILs in fuel oil causes ILs loss and contamination of fuel oils (this might change the quality and composition of fuel oils);

solubility of fuel oils in ILs leads to an increase in separation cost and loss of fuel oils<sup>80</sup>. Gravimetric methods such as gas chromatography, liquid chromatography and vacuum drying oven have been employed to measure the mutual solubility; literature in this area is relatively scarce. Nie et al. conducted solubility experiments of gasoline in ILs at 298.15K for [MMIM][DMP], [EMIM][DEP] and [BMIM][DBP], and the results were 1.12, 4.25 and 20.6 wt% respectively. Also, solubility values of gasoline in [EMIM][DMP], [EEIM][DEP], [BEIM][DBP], [BMIM][DMP] and [BEIM][DEP] were found to be 2.06, 5.81, 26.69, 3.53 and 10.26 wt % respectively<sup>80</sup>. When the solubility of model oil (comprising hexane, toluene and droplets of thiophenic S-compound) in [BMI][N(CN)<sub>2</sub>] and [EMI][N(CN)<sub>2</sub>] was tested, the result showed a slight solubility with respect to a low content of toluene but the solubility increased with increasing toluene content in oil (e.g., for [BMI][N(CN)<sub>2</sub>], 6.7 wt % for 20% mass fraction of toluene; for [EM][N(CN)<sub>2</sub>], 3.08 wt% for 15% mass fraction of toluene)<sup>87</sup>. The solubility of different ILs with different organic compounds has also been studied in the literatures. It is found that most of ILs are soluble in different organic compounds such as acetone, ethanol, methanol, and water, but not too much in hexane, toluene or heptane<sup>112</sup>. The literature regarding mutual solubility of ILs and liquid fuels suggest that the mutual solubility of ILs with fuel oils have to be more studied and optimized for future applications.

#### 4. Real fuel Oil Check

As opposed to model fuel oils, ILs-EDS technique for real fuel oils is complicated due to the presence of wide-ranging amount of heterocyclic and polycyclic compounds, which are derivatives of thiophene and mercaptans. Only a limited number of literatures reported the results for real fuel oils. Table 9 summarizes the results of ILs-EDS for real fuel oils at optimized conditions.

Table 9. ILs-EDS of real fuel oils at optimized conditions

ILs	Oil	Initial S: (ppm)	IL-oil mass ratio	Temp. (K)	Time (min)	S-extraction efficiency (%)	Ref.
[BMIM][N(CN) <sub>2</sub> ]	gasoline	300	1:1	298	20	18.63	108
[BMIM][N(CN) <sub>2</sub> ]	diesel	380	1:1	298	20	32.82	108
[HPy][BF <sub>4</sub> ]	diesel	83.2	1:1	RT	15	16.7	61
[OPy][BF <sub>4</sub> ]	diesel	83.2	1:1	RT	15	24.3	61
[BMIM][BF <sub>4</sub> ]	diesel	1572	1:5	RT	20	8.23	111
[C <sub>4</sub> Py][BF <sub>4</sub> ]	diesel	1572	1:5	RT	20	7	111

[C <sub>8</sub> Py][BF <sub>4</sub> ]	diesel	1710	1:5	RT	20	8.16	111
[BMIM][BF <sub>4</sub> ]	diesel	385	1:1	303	30	55.8	82
			1:3	303	30	40.1	
			1:5	303	30	27.7	
[BMIM][BF <sub>4</sub> ]	gasoline	180	1:1	303	30	70	82
			1:3	303	30	59.2	
			1:5	303	30	44.8	
[EMIM][OAc]	gasoline	240	1:1	298	20	38.7	110
	diesel	1000	1:1	298	20	12	
[HMpy][NTf <sub>2</sub> ]	gasoline	240	1:1	298	20	30	110
	diesel	1000	1:1	298	20	37.8	

#### 4.1.Extractive Equilibrium Time

It is already discussed that the extractive equilibrium time is a promising factor for generating high yield. The extractive equilibrium time of different ILs for real fuel oils was determined by some researchers. It was found that the extraction equilibrium for low viscous ILs such as [BMI][N(CN)<sub>2</sub>] and [EMI][N(CN)<sub>2</sub>] is about ~10 minutes while for high viscous ILs ([BMIM][BF<sub>4</sub>], [BPy][BF<sub>4</sub>], [OPy][NO<sub>3</sub>] and [BMIM/Cl][FeCl<sub>3</sub>], [HNMP][HSO<sub>4</sub>] is slightly high (~ 30 minutes), as shown in the Figures 12 and 13. This difference is mainly because of the viscosities of ILs, the low viscous ILs cause efficient mass transfer between ILs and fuel oils.

#### 4.2.IL-oil Mass Ratio

According to literatures of ILs-EDS, ILs-oil mass ratio has proven to be a desirable factor to improve the desulfurization efficiency for both gasoline and diesel fuel oils. As per data of S-extraction efficiency of different ILs at different IL-oil mass ratio for real fuel oils in table 10, desulfurization for real fuel oils is maximum at 2:1 and lowest at 1:5 mass ratios for both high viscous and low viscous ILs. However, the rate of increase in S-extraction efficiency is not same. Less viscous ILs such as [BMI][N(CN)<sub>2</sub>] and [EMI][N(CN)<sub>2</sub>] showed less sensitivity as compared to high viscous such as [OMIM][BF<sub>4</sub>], [OPy][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>]. This should be the case because the more the IL extractants, the better the extractive performance. Of course, the high, sometimes prohibitive, cost of ILs needs to be taken into account.

Table 10. S-extraction efficiency of different ILs at different mass ratio of IL-oil for real fuel oils

ILs	Oil	Initial S: (ppm)	Time (min)	Temp. (K)	S-extraction efficiency for IL- oil mass ratio					Ref.
					2:1	1:1	1:2	1:3	1:5	
[BMIM][N(CN) <sub>2</sub> ]	gasoline	300	20	298	22	21.5	11	10.3	9.4	108
	diesel	380	20	298	45	30	27	19	19	
[OMIM][BF <sub>4</sub> ]	diesel	711	20	298	n/a	29.9	18.1	n/a	10.1	111
		1572	20	298	n/a	39.8	24.7	n/a	16.1	
[OPy][BF <sub>4</sub> ]	diesel	711	20	298	n/a	16.2	18.1	n/a	10.1	111
		1572	20	298	n/a	39.1	25.7	n/a	15.8	
[BMIM][BF <sub>4</sub> ]	diesel	1572	20	298	n/a	n/a	12.6	n/a	8.2	111

### 4.3. Temperature

Efficiency of desulfurization of real fuel oils by low viscous ILs such as [EMIM][N(CN)<sub>2</sub>] and [BMIM][N(CN)<sub>2</sub>] is found maximum at mild conditions just like EDS of model fuels oils, where increases in temperature leads decrease in the desulfurization efficiency. On the other hand the trend becomes reverse for high viscous ILs such as [EPy][BF<sub>4</sub>], [HMMPY][NTf<sub>2</sub>] and [EMIM][NTf<sub>2</sub>] where increase in temperature confirms great increase in efficiency (as shown in the table 11). So, higher temperature will have little or no influence on desulfurization efficiency. On the industrial scale, desulfurization under ambient temperature is desirable as less energy is required.

Table 11. S-extraction efficiency of different ILs at different temperatures for real fuel oils

ILs	Oil	Initial S: (ppm)	IL-oil mass ratio	S-extraction efficiency for temperatures (%)					Ref.
				20 <sup>0</sup> C	25 <sup>0</sup> C	35 <sup>0</sup> C	45 <sup>0</sup> C	50 <sup>0</sup> C	
[HMMPY][NTf <sub>2</sub> ]	diesel	10000	1:1	n/a	24	n/a	n/a	62.2	110
[EMIM][NTf <sub>2</sub> ]	diesel	10000	1:1	n/a	11	n/a	n/a	50	
[EMI][OAc]	diesel	10000	1:1	n/a	10.6	n/a	n/a	13	
[EMI][Et <sub>2</sub> PO <sub>4</sub> ]	diesel	10000	1:1	n/a	13.5	n/a	n/a	17	
[BMIM][N(CN) <sub>2</sub> ]	gasoline	300	1:1	18	12.1	12	11.1	11	108
	diesel	400	1:1	31.8	28.1	27.5	27	27	

### 4.4. Regeneration

As it is already mentioned, regeneration of ILs after extraction is a significant feature for selectivity of ILs. The excessive use of ILs as extractants can be compensated by the

good recyclability of ILs. It was found in the literatures that the low viscous ILs showed remarkable results after their regeneration (see Figure 14 for S-removal efficiency verses regeneration cycle by [BMIM][N(CN)<sub>2</sub>] at mild conditions). Also low viscous ILs can easily be regenerated by simple water dilution and vacuum distillation process.

#### 4.5. Multiple Extractions

As indicated above, desulfurization by multiple extractions is an effective way to reduce the content of heterocyclic compounds in fuel oils. Even though, some ILs ([BMIM][N(CN)<sub>2</sub>], [OPy][BF<sub>4</sub>] and [EMIM][OAc] ) showed good results of S-compound removal efficiency in a single extraction step (as shown in Table 12). However, the final S-compound in fuel oil could not meet the requirement (e.g., <10–50 ppm). For desulfurization of gasoline by [BMI][N(CN)<sub>2</sub>], less than 20% efficiency was noticed after a single extraction step while it was 60% after six extractions; for desulfurization of diesel fuel by [BMI][N(CN)<sub>2</sub>], less than 40% desulfurization efficiency was realized after a single extraction while up to 70% was obtained after six cycles<sup>108</sup>. Chu et al. performed extraction on diesel fuel at 298.15K, initial S-content = 1572 ppm, mass ratio = 1:2(w/w) IL-oil with [OMIM][BF<sub>4</sub>] and the S-content was extracted to 701 ppm after four extraction cycles<sup>111</sup>. Considering performances of different ILs for only single step extraction at mild conditions, [EMI][N(CN)<sub>2</sub>] and [BMI][N(CN)<sub>2</sub>] shows the highest results for S-extraction efficiency in real fuel oils.

In dealing with real fuel oils, desulfurization by multiple extractions is recommended to realize ultra-low S-content. The excessive use of ILs can be compensated by their good recyclability.

Table 12. S-extraction efficiency of different ILs at multiple extraction steps

ILs	Oil	Initial S: (ppm)	Temp. (K)	IL-oil mass ratio	Time (min)	S-extraction efficiency for multiple steps (%)				Ref.
						1	2	3	4	
[HMMPY][NTf <sub>2</sub> ]	diesel	10000	298	1:1	n/a	24	32	41	n/a	110
	diesel	10000	323	1:1	n/a	37.8	90	98	n/a	
	gasoline	240	298	1:1	n/a	20	25	26.7	n/a	
[EMIM][OAc]	diesel	10000	298	1:1	n/a	11	12.8	13	n/a	110
	Gasoline	240	298	1:1	n/a	38.7	38.9	38.2	n/a	
[BMIM][N(CN) <sub>2</sub> ]	diesel	400	298	1:1	20	32	45	52.5	60	108

	gasoline	300	298	1:1	20	17.1	23.3	36.7	58.6	
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#### 4.6. Mutual Solubility

Mutual solubility of real fuels in different ILs is analyzed by the weight variation of a quantity of IL saturated with the real fuel oils after and before ILs removal. It is concluded from different results that the diesel oil is less soluble in ILs than gasoline. Solubility of gasoline and diesel fuel oil in [BMI][N(CN)<sub>2</sub>] were reported 6.66 and 1.97 w% respectively while solubility of gasoline and diesel fuel in [EMI][N(CN)<sub>2</sub>] were 5.64 and 1.93% respectively. The solubility of diesel in [OPy][BF<sub>4</sub>] is also reported 1.97% by Gao H. et al<sup>89</sup>. To our knowledge, the solubility of ILs in real fuel oils was not reported.

#### 5. Prospects and Challenges

As the demand for cleaner oils continues to rise, legislations to lower S-content limit in fuel oils will be introduced. Thus these aforementioned alternative techniques will continue to be fully studied because of the inability of the traditional HDS technology to meet growing demands. The non-molecular novelty and ideality of ILs over traditional polar/non-polar organic solvents have won burgeoning global interest. More practical uses of ILs are likely to be intensified, evident from the colossal number of publications.

In the current studies, the S-extraction efficiency is not very satisfactory for high viscous ILs. They usually requires about ~5 extraction steps with longer thermal equilibrium time (eg., 30 minutes) at higher temperatures to lower the S-content to ≤10ppm. Low viscous ILs are proven to be desired solvents in heterogeneous liquid-liquid systems because they facilitate faster mass, require less equilibrium time and lower temperature, and offer the necessary and limited power requirements for mixing and regeneration.

Due to the fact that ILs are very expensive, a number of factors need to be considered during the selection. These factors include their thermal/chemical stability, ability to be regenerated and recycled, mutual solubility with oils, etc. In as much as ILs are welcome as a medium for green processing, more attentions need to be directed towards rationally designing task-specific ILs especially for producing cleaner fuels.

In the literature, ILs were often tested with model oils, which was necessary for simple analysis. More real fuel oils need to be investigated because in addition to S-compounds found in oils, there are many other species that may complicate the extractive process.

This is necessary for a transition from small, laboratory scale to a large, pilot plant scale production.

## 6. Remarks

In this review, we summarize the published results of IL extractive desulfurization for both model oils and real fuel oils. These include IL species, IL-oil mass ratio, multiple extractions, initial S-content, mutual solubility, temperature, extractive equilibrium time and ILs regeneration. In this review it is concluded that, 1) the ILs are limited to those imidazolium, pyridinium and thiazolium species, and more species are worthy of testing; 2) higher ILs-oil mass ratio gives a higher S-removal in one cycle, and does not change the partition coefficients, which should be compromised between cost and single S-removal; 3) multiple extraction can realize a complete S-removal, and initial S-content give a unremarkable effect; 4) solubility of IL in fuel oil is negligible and fuel oil in IL is affected by oil nature; 5) desulfurization is not dominated by temperature and equilibrium time when low viscosity ILs are used; 6) ILs are regenerable with neglectable activity loss after a limited cycles. In real fuel oils check, similar conclusions are obtained; while the S-removal efficiency is lowered, which is ascribed to a complex composition of real fuel oil. Due to the fact that extraction of S-compounds from oils by ILs is not a pure physical interaction process, ILs can be tailored to give better desulfurization performance for real fuel oils in future. ILs extractive desulfurization is potential preferable method to remove thiophenic S-compounds than traditional HDS technology. More studies such as expanding IL species, more check of real fuel oils and desulfurization mechanism are waiting for us to do for promoting their final industrial fate.

## 5. Acknowledgements

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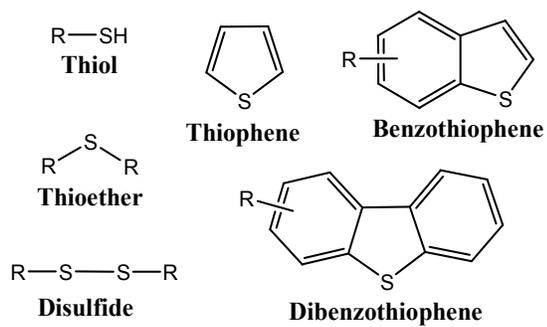
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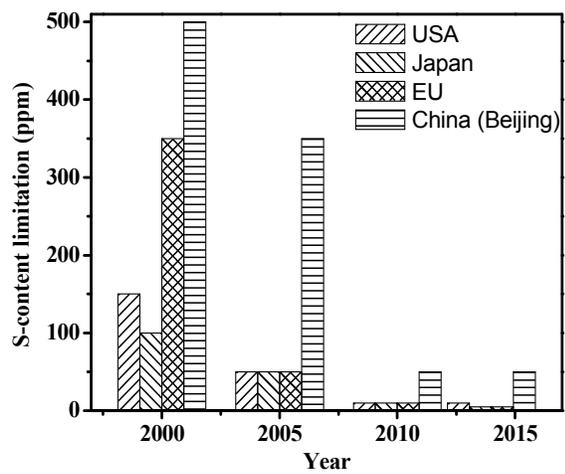
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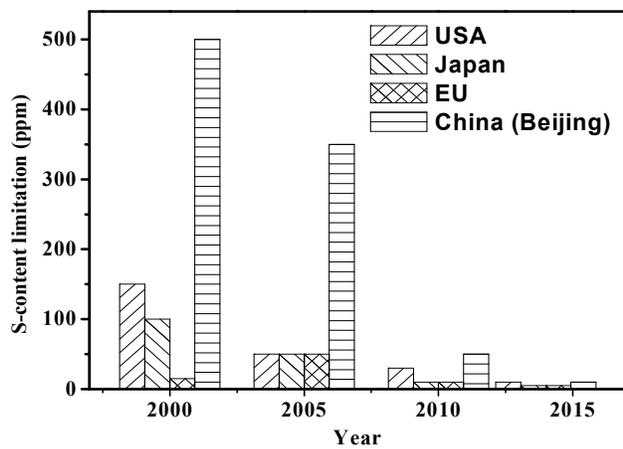
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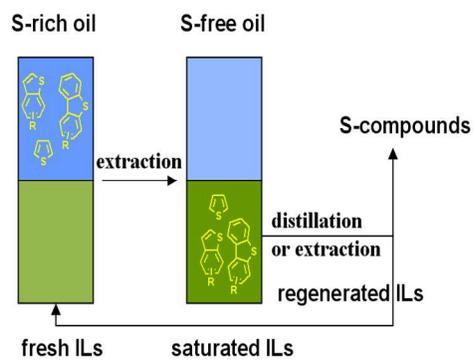
**Figure 1.** Sulfur compounds in fuel oils.



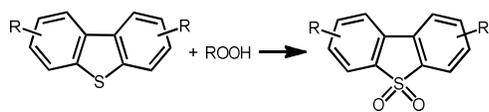
**Figure 2.** Previous, current and proposed sulfur limitations in diesel in different countries.<sup>7,8</sup>



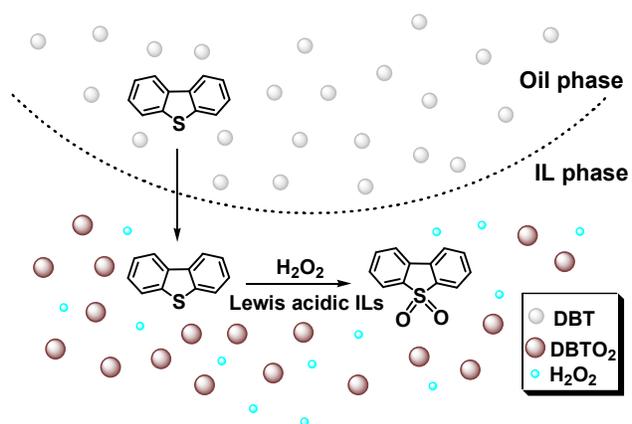
**Figure 3.** Previous, current and proposed sulfur limitations in gasoline in different countries.<sup>7,8</sup>



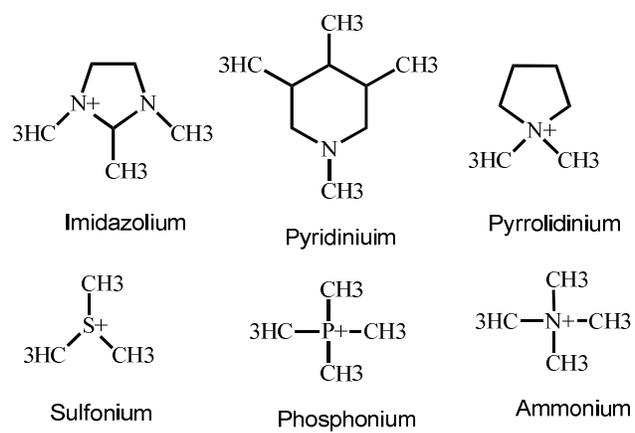
**Figure 4.** Extractive desulfurization of fuel oils using ILs.



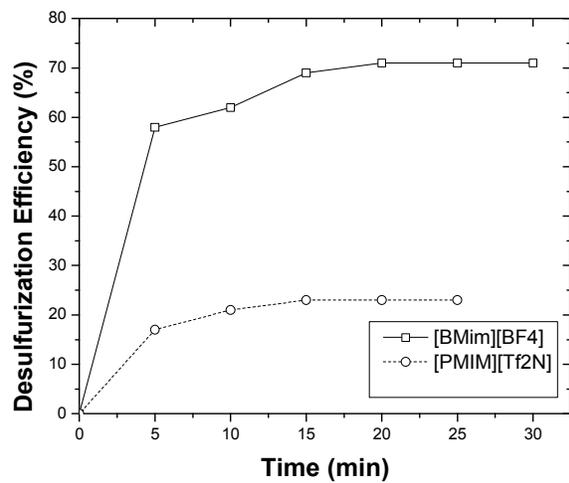
**Figure 5.** General reaction of oxidative desulfurization (ODS).



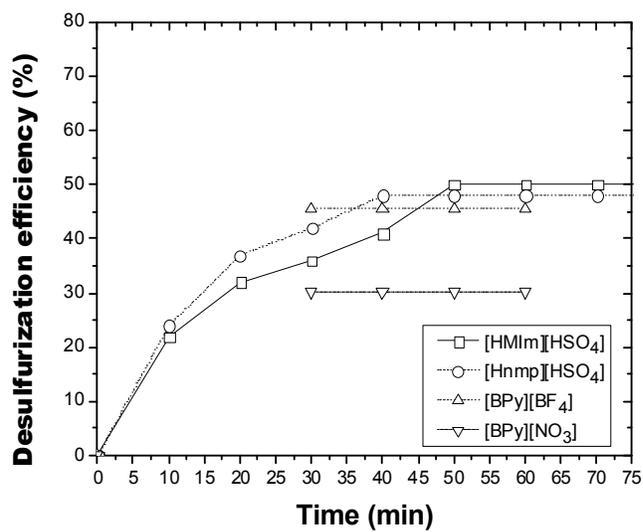
**Figure 6.** Oxidation of S-component using  $\text{H}_2\text{O}_2$  and ILs.<sup>52</sup>



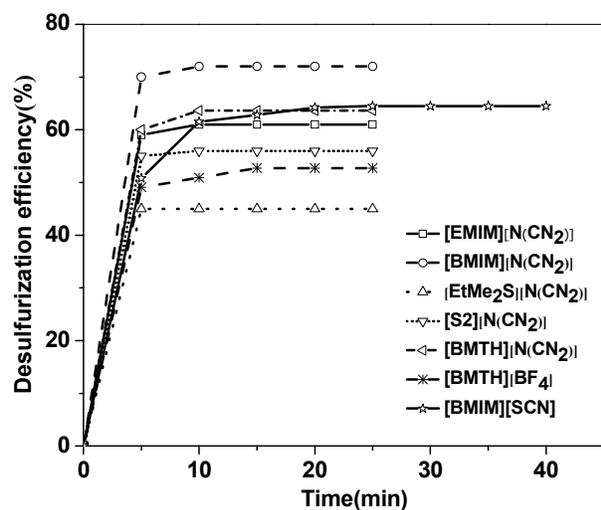
**Figure 7.** Different structures for ILs cation.



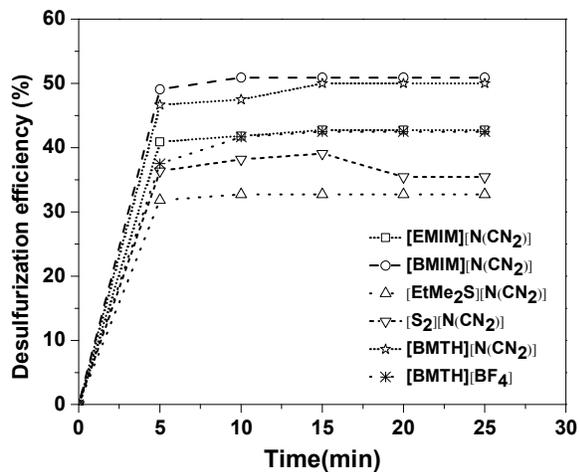
**Figure 8.** DBT vs extraction time for the desulfurization of model oil using high viscous ILs, where line indicates the trend. <sup>64,82</sup>



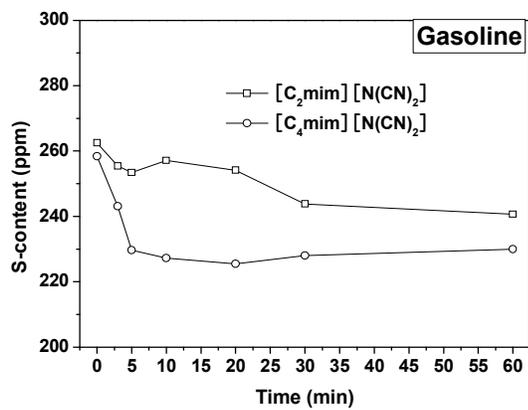
**Figure 9.** TS vs extraction time for the desulfurization of model oil using high viscous ILs, where line indicates the trend. <sup>90,104</sup>



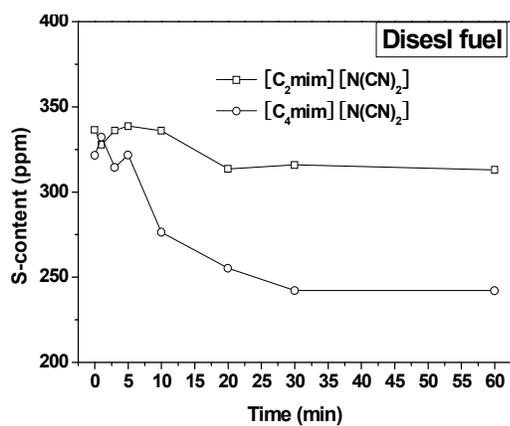
**Figure 10.** DBT vs extraction time for the desulfurization of model oil using low viscous ILs, where line indicates the trend. <sup>87,93</sup>



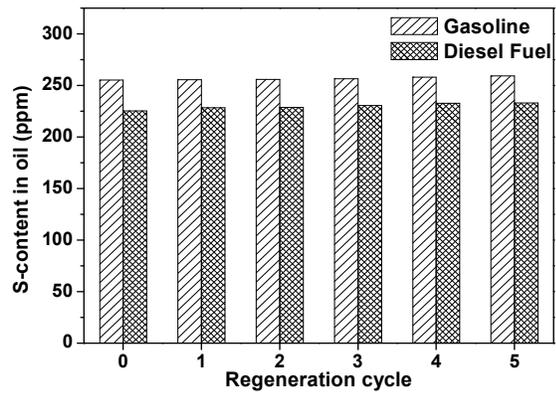
**Figure 11.** TS vs extraction time for the desulfurization of model oil using low viscous ILs, where line indicates the trend. <sup>87, 93</sup>



**Figure 12.** S-content vs extraction time for the desulfurization of real gasoline fuel, where line indicates the trend. <sup>108</sup>



**Figure 13.** S-content vs extraction time for the desulfurization of real diesel fuel, where line indicates the trend.<sup>108</sup>



**Figure 14.** S-content vs regeneration cycle for [BMI][N(CN)<sub>2</sub>] for real fuel oils<sup>108</sup>.