

Toward Application of Ionic Liquids to Desulfurization of Fuels: A Review

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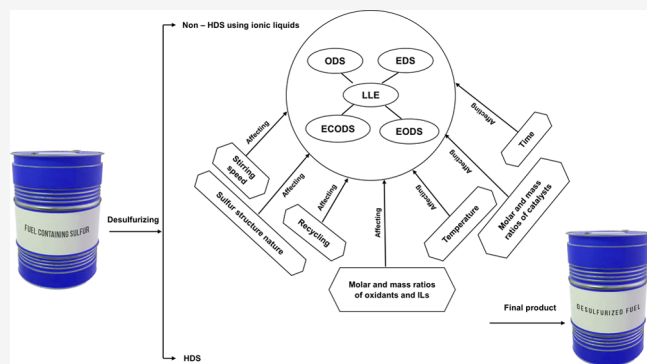


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ABSTRACT: Over the past decades, the desulfurization of fuel oils has been known as one of the most challenging processes in petroleum refineries due to economic considerations. The presence of sulfur compounds results in SO_x emissions, detrimentally affecting the equipment of refineries, the environment, and human health. In this direction, the unique features of ionic liquids have introduced them as a beneficial alternative for conventional desulfurization of fuel oils using traditional organic solvents. In this review, we aim to study ionic liquids used in different desulfurization processes of fuel oils, including hydrodesulfurization (HDS), oxidative desulfurization (ODS), extractive desulfurization (EDS), extraction combined with oxidation desulfurization (ECODS), extractive and catalytic oxidative desulfurization (LLE). Furthermore, governing factors, including temperature, mixing time, reusability of ionic liquids, stirring speed, sulfur structure nature, and molar and mass ratios of oxidants and ionic liquids, and catalysts, have been reviewed in detail.



1. INTRODUCTION

Since the advent of machines, fossil fuels (e.g., petrol, diesel, and crude oil) have been used. In some cases, such fuels contain sulfur compounds, which are highly capable of damaging facilities. Besides, when they are burnt in the combustion or even in an engine combustion, these fuels send out SO_x emissions. These emissions not only damage facilities and human health but also help to make acid rain. Therefore, environmental compliance inspectors have tried to stringently control the sulfur contents of oil fuels. In this way, the European Union had taken steps to decrease the sulfur content in diesel below 10 ppm by 2009.¹ As a result, many countries have been trying to decrease the maximum sulfur emissions by placing lower maximum sulfur limits, Figure 1a and 1b. In this figure it is shown that some countries, such as India, have succeeded in reducing sulfur. Figure 1 shows the importance of desulfurization around the world according to which countries have tried to reduce the sulfur contained in fuels.

Because of such serious effects, prior to consuming such fuels, they must be desulfurized. For this purpose, various methods have been proposed (e.g., the use of bacteria, microwaves, ultrasound, electricity, adsorption, extraction, and hydrogen gas along with catalysts at high pressures). As such methods result in difficulties, many have attempted to propose an alternative method to desulfurize fuels. In this way, ionic liquids (ILs) have shown promising results. To better understand fuels desulfurization, review articles can be useful. Table 1 presents published review articles in fuels desulfurization along with areas on which

researchers focused as well as years up to which their references covered. This table clearly shows how important ionic liquids are at desulfurizing fuels. However, most of them have only focused on a specific desulfurization process instead of comparing all available ionic liquids-based desulfurization processes together, indicating a critical gap.

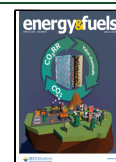
Ionic liquids are an interesting category of molten salts with low melting points, below 100 °C. This kind of chemical is generally composed of organic cations and organic or inorganic anions.^{28,29} During the past decades, ionic liquids have been increasingly developed as an environmentally friendly substitute for the instable volatile organic compounds traditionally used as industrial solvents. These “designer solvents” can be considered to produce a brilliant set of properties, while their molecular structure can be adjusted to fit the chemical process conditions.^{18,30} The main properties of ionic liquids along with the related references are tabulated in Table 2.

Anions are often comprised of inorganic compounds (AlCl_3 , BF_3 , AgBF_4 , and so forth)⁴⁶ and are often classified according to their cation type.⁷⁰ Common cations in ionic liquids include

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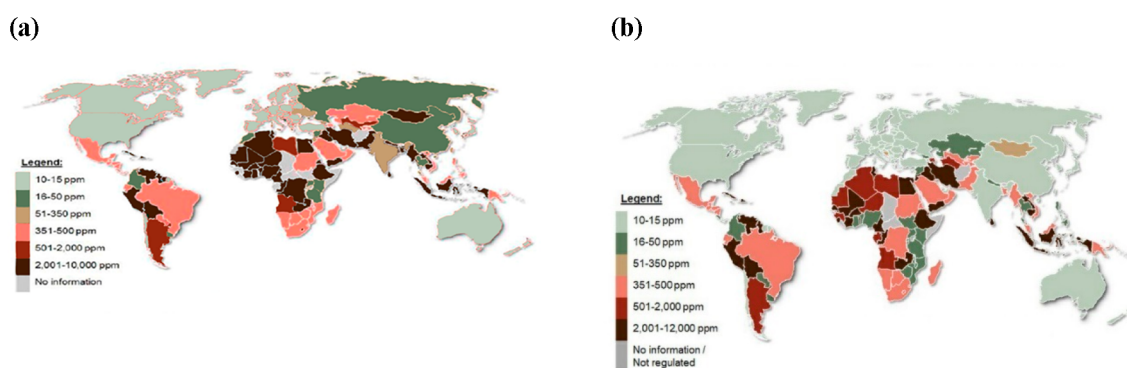


Figure 1. On-road diesel sulfur limits across the world (sourced from Stratas Advisors): October 2015 (a)² and October 2020 (b).³

Table 1. Published Review Articles Regrading Fuels Desulfurization

areas focused on	years covered (up to)	ref
investigating factors impacting oxidative desulfurization (ODS) toward liquid fuels with a focus on the use of ionic liquids (ILs)	2021	4
reviewing the use of ILs and deep eutectic solvents (DESs) in extractive desulfurization (EDS)	2021	5
sulfur removal from fuel oils through ODS with the help of homogeneous and heterogeneous polyoxometalate catalysts	2021	6
studying desulfurization and denitrogenation methods with a concentration on extraction using ILs and their regeneration and recycling	2020	7
reviewing the utility of DESs in desulfurization of transportation fuels as well as comparing that of ILs in the same process with DESs	2020	8
reviewing the performed advances in adsorptive desulfurization (ADS)	2020	9
uses of green ILs and DESs toward desulfurization, denitrification, biomass, biodiesel, bioethanol, and hydrogen fuels were reviewed	2020	10
ODS catalyst toward fuels and the effect of ILs on ODS catalyst were reviewed	2020	11
only concentrating on the utility of metal-based ILs in ODS	2020	12
reviewing the role of ILs in extractive and catalytic oxidative desulfurization (ECODS), ODS, and hydrodesulfurization (HDS)	2019	13
catalytic oxidative desulfurization method for liquid fuel oil	2019	14
use of ILs in ODS toward heavy oils containing large sulfur content was reviewed	2018	15
reviewing the use of metal-based ILs in fuel desulfurization and denitrogenation	2017	16
studying solvent extractive desulfurization using organic solvents and ILs toward straight run gas oils and other gas oils	2017	17
investigating the structural characteristics, properties, preparation, and IL applications in catalytic organic transformations	2016	18
studying ODS using ILs	2016	19
investigating desulfurization methods, containing HDS, ODS, biodesulfurization (BDS), adsorption, extractive desulfurization (EDS), and S-compound transformation using superoxide ion as well as the role of ILs in ODS and EDS	2016	20
reviewing the use of ILs as solvents, extractants, catalysts, and both catalysts and extractants toward extractive oxidative desulfurization (EODS) as well as ODS	2016	21
investigating the use of ILs in extractive and catalytic oxidation	2015	22
mainly studying the role of ILs in EDS	2014	23
reviewing the use of ILs in achieving ultralow-sulfur diesel	2010	24
developments toward oxidation catalysis with ILs as solvents	2010	25
utility of ILs as green solvents in extractive processes such as extraction of organosulfur from fuels and gases	2005	26
mainly investigating desulfurization technologies, including conventional HDS, HDS using advanced catalysts, HDS using advanced reactor designs, HDS by fuel specification recovery, and methods to convert S compounds	2001	27

imidazolium, pyrrolidinium, pyridine, ammonium, and phosphonium. In this respect, common anions are halogenated anions, such as $[\text{Cl}^-]$, $[\text{Br}^-]$, $[\text{I}^-]$, $[\text{BF}_4^-]$, $[\text{AlCl}_4^-]$, and $[\text{PF}_6^-]$,⁷¹ and basic anions, such as SCN^- , MP^- , and NTF_2^- , have high desulfurization efficiency.⁵³

The presence of aromatic rings in ionic liquid cations and the π - π interactions between the cations and the sulfur compounds can be considered to be an important reason for the higher extraction ability of imidazolium-, pyridinium-, and thiazolium-based ionic liquids. In contrast, an ammonium-based ionic liquid that does not have a ring has better performance, as opposed to some imidazolium-based ionic fluids.⁷⁰

Opting for a suitable ionic liquid is an important step for the desulfurization process, and the ability to desulfurize the ionic liquids is different, depending on the type of cation and anion.⁷² Both ionic liquid anions and cations are chosen according to the

physical properties of the melting point, viscosity, density, resolution ability, etc.^{1,34,46,61,67,68,73-76} Ionic liquids have the potential to be replaced with flammable substances, which are used in sulfur dioxide and cause environmental concerns. Besides, they are environmentally friendly,⁷⁷ known as green solvents.^{59,78,79}

Since anions play a major role in extracting sulfur compounds from ionic liquids, most researchers are working to modify anions with a larger alkyl group such as $[\text{EtSO}_4]^-$ and $[\text{DEP}]^-$ or the use of suitable metal anions with halogens such as $[\text{AlCl}_4]^-$ and $[\text{FeCl}_4]^-$ to increase the partition coefficient of sulfur.

However, both mentioned methods for anions have disadvantages. Alkyl modification increases the solubility of soluble fuels in ionic liquids, and metallic halogen-containing anions are sensitive not only to moisture but also to the aid of a coextractor and are problematic for aromatic hydrocarbon

Table 2. Key Properties of Ionic Liquids

properties	ref
fluidity at room temperature	31, 32
high temperature stability	1, 33–36
high chemical stability	37–39
very low vapor pressure	40–43
relatively inflammable	39, 43–45
low volatility	46–50
high conductivity	46, 51, 52
low toxicity	53–55
flexibility, reusability, and recoverability	45, 50, 56, 57
structure and polarity adjustability by changing cation and anion parts	58–60
hydrophobic	53, 61–63
high solubility for the gas phase	64–66
low viscosity	48, 67, 68
low surface tension	63
high polarity	52, 55, 69

compounds. Because of the problems caused by anion modification, cation correction is used as an alternative method to increase the sulfur extraction because the extraction of aromatic compounds of sulfur with different aromatic cations of ionic liquids is always positive. This comes from the π - π interaction between the aromatic structures of sulfur compounds and the aromatic cations of ionic liquids.⁸⁰

To clearly show the advantages and disadvantages of ionic liquids, Table 3 is provided. In order to overcome some of the

Table 3. Advantages and Disadvantages^{82–84} of Ionic Liquids

advantages	disadvantages
being designable and adjustable	high prices
high electrochemical range	high viscosity
good solvent capacity	difficult purification process
high extraction efficiency	contaminating and toxicizing underground water resources
widespread electrochemical application	flammability of some of ionic liquids
solubility in a wide range of organic and inorganic compounds	high precaution in use

disadvantages of ionic fluids, ionic liquids can be placed on porous surfaces, whereby less ionic liquid is used and a lower amount is paid for the purchase of these expensive compounds; also, due to the increased contact surface between the ionic liquid and the gas, the rate of absorption increases, which results in a high efficiency. For this purpose, porous silica gel can be used as an option, which has advantages, including a stable porous structure, significant contact surface, adjustable pore size, good mechanical structure, and acceptable thermal stability. Silica gel with ILs (ILs-SiO₂) has the benefits of both the IL and porous silica gel simultaneously, and the desulfurization efficiency increases.⁸¹

In this study, a thorough review on the desulfurization techniques, including oxidative desulfurization (ODS), extractive desulfurization (EDS), extractive oxidative desulfurization (EODS), extractive and catalytic oxidative desulfurization (ECODS), and liquid-liquid extraction (LLE), as well as on the factors impacting the desulfurization efficiency, such as time, temperature, stirring speed, reuse of ionic liquids, nature of the sulfur structure, molar and mass ratios of oxidants, ionic liquids, and catalysts, has been conducted. Furthermore, detailed results of the desulfurization experiments using ODS, EDS, EODS,

ECODS, and LLE have been provided in order to present a better view of the performance of ionic liquids. In doing so, the used ionic liquids, their structures, targeted sulfur compounds, operational conditions, and the obtained results have been tabulated. Due to the lack of space, some of these results have been provided as [Supporting Information](#).

To the best of our knowledge, through a comprehensive review of many available articles, there is a gap regarding a comparison of the desulfurization methods investigated in this study along with the study of factors affecting these methods. In this regard, a review to bridge this gap is crucial, which has not been done yet. Therefore, the main focus of this review is to investigate the effects of such factors on these processes and to compare these desulfurization processes to one another. Furthermore, a variety of ionic liquids in different methods has been studied, which helps researchers for future studies. These comparisons and investigation of the employed ILs as well as that of the impacts of key factors will help to identify a cost-effective, efficient, and above all environmentally friendly desulfurization process as well as to introduce optimum parameters for the identified desulfurization process. Such a thorough review will be of assistance to researchers aiming to develop desulfurization processes at the industrial scale.

2. DESULFURIZATION METHODS

2.1. Hydrodesulfurization (HDS). Generally, fuel desulfurization technology mainly involves two processes of hydrodesulfurization (HDS) and nonhydrodesulfurization (NHDS).⁸⁵ The hydrodesulfurization of petroleum is broadly experienced on an industrial scale for the production of low-sulfur clean fuels. In HDS, sulfur compounds are first converted to hydrogen sulfide and corresponding byproduct hydrocarbons. The commercial hydrodesulfurization of fuels is mainly performed using catalysts of alumina material with such catalyst supports as cobalt, nickel, and molybdenum (e.g., Co-Mo/Al₂O₃, Ni-W/Al₂O₃, or Ni-Mo/Al₂O₃ catalyst).^{53,86} Titania is also considered as a supportive catalyst due to its high desulfurization reactivity per unit surface area.⁸⁷ The produced H₂S is subsequently separated from the fuel oil through the Claus process and oxidized to elemental sulfur. Figure 2 presents a schematic representation for pathways of the HDS of dibenzothiophene at 300 °C and 102 atm in the presence of CoMo/Al₂O₃.^{88,89}

The previous studies have shown that HDS can be used for removal of thiols,^{29,90,91} sulfides,⁹¹ heterocycle sulfides,⁹² disulfides,^{29,90,91} thiosulfides,^{19,93} thioethers,^{29,90} mercaptans,^{94–96} and light thiophenic

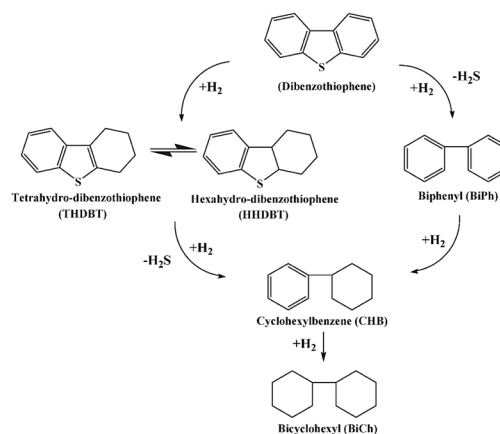


Figure 2. Schematic representation for pathways of the hydrodesulfurization of dibenzothiophene at 300 °C and 102 atm in the presence of CoMo/Al₂O₃. Reproduced with permission from ref 88. Copyright 1978 Wiley-Blackwell.

compounds.⁹⁵ Although hydrodesulfurization is extensively used to eliminate sulfur compounds from refined petroleum products such as gasoline, jet fuel, diesel, and fuel oils, it has some operating limitations. HDS is carried out at high temperatures (300 °C < T < 400 °C) and pressures of hydrogen (20 atm < P_{H_2} < 100 atm). Figure 3 shows a

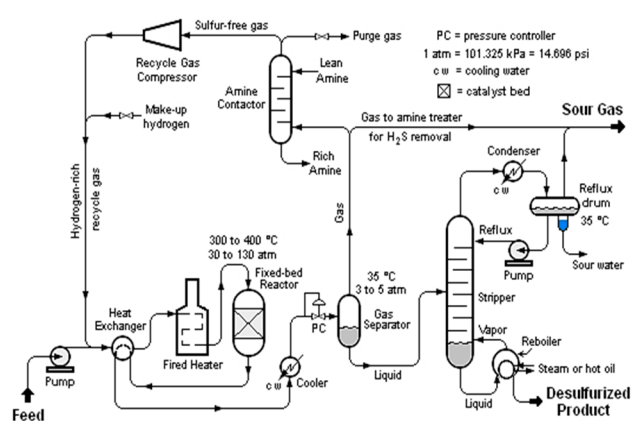


Figure 3. Schematic depiction of the equipment and process flow streams in a typical refinery HDS unit.

schematic depiction of the equipment and the process flow streams in a typical refinery HDS unit.⁹⁷ In addition, HDS shows great resistance and lower efficiency for elimination of refractory heterocyclic sulfur compounds such as benzothiophene and dibenzothiophene. Therefore, more active catalysts are consumed, and temperatures and pressures must be further increased, resulting in significant increases in investment and in operating costs, and the process becomes an environmentally unfavorable operation.

Furthermore, the octane/cetane number of the fuel decreases because of unwanted side reactions, resulting in saturation of olefins. In addition, specific active catalysts are required, the consumption of hydrogen is high, and the catalyst lifetime is low, which increases the consumption of catalyst.^{45,98} To better understand the available advantages and disadvantages of HDS in comparison with other desulfurization methods, Table 4 has been prepared. Several investigations have focused on the elaboration of new catalysts or improving the activity of the existing catalysts and on modifying HDS operation conditions to solve the process challenges. On the other hand, a large number of studies have concentrated on developing new techniques for deep desulfurization of fuels such as adsorption-based processes,⁹⁹ reactive alkylation,¹⁰⁰ precipitation,¹⁰¹ distillation,¹⁰² extraction,^{103,104} photocatalytic desulfurization,^{105,106} complexation,¹⁰⁷ selective oxidation,¹⁰⁸ biodesulfurization,^{105,109} ultrasound-assisted biodesulfurization,¹¹⁰ ultrasound-accompanied oxidation,¹¹¹ and combinations of the mentioned methods.^{53,104}

2.2. Oxidative Desulfurization (ODS). As a nonhydrodesulfurization method, oxidative desulfurization (ODS) is one of the most beneficial techniques that can be conducted without any hydrogen usage under normal conditions at low temperatures (~50 °C) and atmospheric pressure. Different oxidants, such as hydrogen peroxide (H_2O_2),^{29,112} O_2 ,^{108,113} ozone (O_3),^{29,114,115} *tert*-butyl hydroperoxide,¹¹⁶ peroxy acids, and NO_2 have been used in the ODS process to diminish sulfur compounds in fuels.^{89,117} The ODS process contains two main steps. First, the sulfur compound is oxidized to its sulfone or sulfoxide derivatives in the presence of oxidizing agent. Second, the obtained oxidized sulfur compounds with more polarity are eliminated from the reaction mixtures by adsorption or liquid–liquid extraction methods.^{79,118} To view better the performance of the ODS process in comparison with the other methods, Table 4 shows the disadvantages and advantages of this process. In this new method, ionic liquids are used as extractors instead of traditional organic solvents. During this process, the sulfur compounds enter the ionic liquid phase. After oxidizing, they change to the sulfonic compounds. Eventually, sulfones are readily removed due to their higher polarity. Solvents (oxidants)

used in ODS include hydrogen peroxide (H_2O_2),^{76,119,120} *tert*-butyl hydroperoxide,^{120,121} *n*-dimethylformamide (DMF), methanol,^{79,119} acetonitrile, dimethyl sulfoxide (DMSO),^{79,119} *n*-methyl-2-pyrrolidone (NMP),¹¹⁹ *n*-methylpyrrolidone (NMP) and furfural,¹⁹ organic peroxide,¹²² deoxygen,¹²² oxygen,^{120,121,123} ozone,^{120,121,123} hydrogen peroxide, and cumene.¹²⁰

To obtain a better understanding, Table S1 presents the ionic liquids used for the ODS method along with the obtained results and the experimental conditions (see Supporting Information).

Of the investigated oxidants, hydrogen peroxide is currently the most popular one since it delivers a multitude of benefits, such as selectivity, availability, appropriateness in terms of economic and environmental considerations,¹²⁴ and being inexpensive. In addition, it is non-contaminated and commercially available.¹²⁵ However, transporting, working with, and storing this oxidant is potentially harmful, and it requires high safety measurements that are expensive. In addition, H_2O_2 is explosive, unstable, and highly corrosive. Thus, it is usually held at special conditions in which its concentration is below 52 wt %. Unfortunately, new methods are not effective toward producing H_2O_2 . In contrast, KO_2 , which is a solid oxidant, can be maintained at high concentrations and is stable and safe even at high purity.¹²⁴ Apart from the disadvantages of the oxidants, it was claimed that the rate of desulfurization could scale up by increasing the oxidant concentration.¹²⁶ Table 5 presents the effect of the use of oxidants on desulfurization.⁷⁴ Moreover, the advantages and disadvantages of the ODS method are presented in Table 4 in order to provide a better understanding.

To have a better understanding of the ODS method toward sulfur removal, Figure 4 has been prepared, which shows various mechanisms of sulfur removal using different ionic liquids in the ODS method.

Figure 4a presents the mechanism of removal of DBT using the acidic ionic liquid utilized by Ge et al. In this experiment, surfactant type octamolybdate was dispersed in the ionic liquid after mixing the system in a homogeneous way. Since H_2O_2 was a strong oxidizer in an acidic environment, octamolybdate was oxidized quickly in the H_2O_2 solvent, changing into peroxomolybdic. It is worth mentioning that it is an active connector for oxidizing many organic compounds through the use of H_2O_2 . The cation containing a long hydrocarbon chain length transferred peroxy to DBT, leading to the oxidation of DBT. It was then transformed to $DBTO_2$. Because this was of the highest polarity, it could be absorbed by the ionic liquid, resulting in desulfurization. This process would be performed again if there was extra H_2O_2 .¹⁵⁵

The mechanism of removal of DBT from *n*-heptane by Zhao et al. is presented in Figure 4b. In this regard, the ionic liquid had a catalytic role to play in segregating hydrogen peroxide and converting this into hydroxyl radicals, which are considered as strong oxidizers. The DBT, extracted from the oil phase, could become sulfone using hydroxyl radicals. Regarding the large polarity that the ionic liquid had, there were no sulfones after desulfurization.¹⁵⁶

Figure 4c presents the mechanism of oxidative desulfurization by Zhao et al. in which H_2O_2 –formic acid was the oxidative factor. Although this formulation was insoluble, it could be mixed with the ionic liquid which was soluble in water, making the reaction homogeneous. In this experiment, it could be assumed that the ionic liquid played the role of a phase transfer catalyst. According to the hydroxyl radicals produced by H_2O_2 in an acidic environment, the desulfurization efficiency was scaled up.¹⁵⁷

Oxidative desulfurization using [Hnmp]HCOO is indicated in Figure 4d. The ionic liquid was more efficient than DBT because there was a five-membered cycle. This could be justified through the similarity with intermiscibility theory. The mechanism entailed a step in which sulfur compounds entered the ionic liquid phase and reacted with it. H_2O_2 converted [Hnmp]HCOO to peracid. The obtained product changed polar sulfur compounds into sulfones. The reduced peracid in the previous step entered the cycle again. Consequently, a continuous descending trend could be seen.⁷¹

The mechanism of oxidative removal of sulfur from alkyl dibenzothiophene is presented in Figure 4e. This substance was extracted from a kind of diesel and entered the ionic liquid phase ([$(CH_2)_2COHMIM$][HSO_4]). The functional group of $-COOH$,

Table 4. Advantages and Disadvantages of Desulfurization Methods

	HDS	ODS	EDS	EODS	ECODS	LLE
advantages						
high performance of desulfurization toward nonaromatic sulfur components ¹²⁷	high desulfurization efficiency ^{6,91}	normal operating conditions ^{104,128}	able to cope with the equilibrium limitations ¹²⁹	simple ¹³⁰ and highly effective ¹³¹	normal operating conditions ¹³²	
	operating under normal conditions ^{91,133}	low cost at commercial scales ¹⁰⁴	capable of improving conversion ¹²⁹	enables more selectivity ¹³⁴	consumes less energy ¹³²	
	does not use hydrogen ^{91,135}	consumes less energy ^{128,136}	consumes less energy ¹²⁹	consumes minimal catalyst ¹³¹	economically advantageous ^{5,3}	
	less polluting ¹³⁷	no hydrogen usage ¹³⁶	uses less energy ¹²⁹	operational at ambient temperature and atmospheric pressure ¹³⁸	largely used in separation and purification processes ³⁹	
	less capital cost ⁹¹	loses lower octane number ¹⁴⁰	reduces the use of raw materials ¹²⁹	sulfur compounds react and separate simultaneously in a single unit ^{13,8}	no sulfones adsorption on catalyst ¹³⁸	
	alternative for ultra-deep desulfurization methods because of its electrophilic substitution mechanism ¹⁴¹			strong stirring and complex facilities are not required ¹³⁸		
	high selectivity ¹⁴²			desulfurizing benzo-thiophenic compounds ¹³⁴		
	high selectivity ¹⁴²					
disadvantages						
high costs ^{143,144}	needs costly oxidizing agent for large-scale applications ¹⁰⁵	limited to the selection of solvents due to sulfur solubility limitations in solvents ²⁴	coupling with H ₂ O ₂ puts limitations against the desulfurization efficiency due to the water product ¹⁴⁵	mainly limited to the selection of catalysts as for an efficient process a catalyst with high activity is needed ¹⁴⁶	using organic solvents often results in further costs and energy usage when it comes to retreating such solvents ¹³⁷	
requires high temperature ¹⁴³	lack of study on its performance toward heavy fractions ¹⁰³	oxidizing sulfur leads to higher efficiency ¹⁴⁸	phase transfer limitations in the interface ⁴⁵	production of aromatic hydrocarbons (e.g., toluene) decreases the efficiency ¹³	limited to the selection of suitable solvents ¹³² and producing organic waste ¹³²	
needs high hydrogen gas pressure ¹⁴³	requires catalyst, which is expensive, when it comes to deep desulfurizing ¹⁰³	desulfurizing fuels without extracting preferred sulfur-free hydrocarbons is challenging ²⁴	uses a large amount of oxidizing agent at the industrial scale ¹⁴⁹		slowly separating phase and produces emulsions that are stable, requiring a large surface area to transfer mass ⁵⁰	
fast deactivation of employed catalysts over desulfurization of fuels containing a high sulfur amount ¹⁵¹	when oxidizing agents react more, it might cause non-needed products, particularly when sulfuric acid is employed ⁶⁰	produces a high percentage of co-extraction of targeted hydrocarbons ²⁴			mostly uses a sulfonane process that results in huge costs due to the high boiling point of sulfonane and the solubility of sulfonane in the raffinate stream ¹⁵²	
minimally desulfurizing aromatic sulfur compounds ¹⁵³	weak to convert thiophenes ¹⁵⁴					

Table 5. Effect of H₂O₂ Oxidants on Sulfur Removal Using Different ILs^a

entry	ILs	sulfur removal (%)				
		extraction ^b	I + H ₂ O ₂	II + H ₂ O ₂	III + H ₂ O ₂	IV + H ₂ O ₂
1	[BMIM]BF ₄	19.9	90.6	19.1	19.2	21.2
2	[BMIM]PF ₆	19.8	30.2	28.3	59.9	21.8
3	[OMIM]BF ₄	34.5	82.7	41.9	52.1	34.9
4	[OMIM]PF ₆	33.9	100	97.9	95.1	36.7
5	without IL		3.3	3	1.8	2.6

^aReproduced with permission from ref 74. Copyright 2011 Elsevier. Conditions: $T = 30\text{ }^{\circ}\text{C}$, $t = 1\text{ h}$, IL = 1 mL, model oil = 5 mL, molar ratio $n(\text{H}_2\text{O}_2)/n(\text{DBT})/n(\text{Catal.}) = 480:120:1$. DBT dissolved in *n*-octane as model oil (S content = 500 ppm). ^bThe results have been taken from ref 84 (I = [MIMPS]₃PW₁₂O₄₀·2H₂O; II = [BMIM]₃PW₁₂O₄₀; III = [BMIM]₃PMo₁₂O₄₀; IV = [BMIM]₄SiW₁₂O₄₀).

which was available in the ionic liquid, reacted with H₂O₂, converting it to a peroxy-carboxylic group (–COOOH). This was capable of oxidizing sulfur compounds. Owing to the existence of H₂O₂, this process was repeated until desulfurization was completely done. In addition, [(CH₂)₂COOHMIM][HSO₄] was used as the catalyst and ionic liquid at the same time.⁹⁵

The mechanism for the removal of DBT from an oil sample is shown in Figure 4f. By absorbing DBT from the oil–ionic liquid [BMIM]-HSO₄ phase, desulfurization began. In scaling up the desulfurization rate, adding H₂O₂ played an effective role. This provided DBT with sufficient oxygen radicals to convert it into sulfones. By continuing this trend, desulfurization was gradually completed, and DBTO₂ precipitated in the ionic liquid.¹⁵⁸

Figure 4g presents a ternary system, containing oil, ionic liquid [BMIM]PF₆, and H₂O₂. To desulfurize, DBT left the oil phase, entering the ionic liquid phase. By oxidizing H₂O₂, hydroxyl radicals are produced. Since the ionic liquid included the anion, cation, and some dielectric, hydroxyl radicals entered the ionic liquid phase, increasing the concentration of the oxidant. The existence of oxidant changed DBT into DBTO₂. This trend continued until desulfurization was completed.¹⁰⁶

Figure 4h presents the process by which DBT was removed. In doing so, the ionic liquid ([BMIM]PF₆) and a catalyst ([C₁₈H₃₇N(CH₃)₃]₇[PW₁₁O₃₉]) were used. In this process, the catalyst took the role of an emulsifier and made a thin film on the solved beads of the ionic liquid. The anion part of the heteropolyanions dissolved in H₂O₂, while the cation part of the catalyst was in the oil phase. In the presence of H₂O₂, the part called [PW₁₁O₃₉]⁷⁻ was separated into several particles, oxidizing sulfur. This oxidation converted sulfur to sulfones. The generated sulfones could be then dissolved in the ionic liquid. Finally, after experiencing the desulfurization process several times, such sulfones became crystallized, leading to a clean fuel without sulfur components.¹⁵⁹

Figure 4i shows how to remove sulfur compounds and convert them into sulfones using surfactant-type polyoxometalate-based ionic liquids (SPILs). The performed reactions show the steps in which desulfurization was done. As the first step was reversible, [(*n*-C₈H₁₇)₃NCH₂]₃(PO₄[MoO(O₂)₂]₄) reproduced the catalyst and made the reaction continue.¹⁶⁰

Figure 4j presents the mechanism by which DBT was removed from an oil sample. This could be done through a system containing [BMIM]BF₄ and a catalyst TiO₂. By shining ultraviolet light on TiO₂, the created holes reacted with water and/or hydroxyl groups, which were available on the surface of TiO₂. Consequently, hydroxyl radicals were generated, oxidizing DBT. This produced DBTO₂. Desulfurization continued until DBT was transferred from the oil sample into the IL phase.⁹¹

The mechanism through which the removal of DBT was performed using graphite carbon-supported POM-IL catalyst ([PSPy]PMo/GC) is presented in Figure 4k. The water-repellent part of the catalyst dissolved in the oil sample, while the water-soluble part of it was in H₂O₂. In this way, H₂O₂ gave oxygen to Mo=O and made it active, [Mo(O₂)]. After this step, DBT was first changed into DBTO, and DBTO was eventually turned into DBTO₂. In this process, the active

[Mo(O₂)] entered a cycle in which it returned to Mo=O. This continued until there was H₂O₂.¹⁶¹

2.3. Extractive Desulfurization (EDS). Extractive desulfurization (EDS) is a promising technology and has a simple process⁷⁰ because it can be utilized at ambient temperature and pressure.^{98,126} Since the operating parameters for EDS are ambient temperature and pressure and there is no need to consume hydrogen in this method, extractive desulfurization is considered as one of the most efficient methods.^{98,139} In other words, not requiring a catalyst or any other materials during the process and needing normal circumstances to be done,^{44,78,90,162} EDS seems to be more applicable than other desulfurization methods.^{44,162,163} Thus, EDS has received a lot of attention because it needs simple and normal operating conditions. In this regard, Table 4 has been provided to indicate the advantages and disadvantages of the EDS process compared to the other investigated desulfurization methods.

During this method, the chemical structures of the compounds in the fuel oils change slightly, having a marginal impact on the quality of the fuel oils.¹⁶⁴ Bossmann et al. first used ionic liquids as potential solvents for EDS.⁷⁰ By 2001, they presented a report on the desulfurization of diesel fuel by extracting with the help of ionic liquids.^{72,94} In doing so, they studied AlCl₃ and dialkyl imidazolium chlorides as extractive solvents.⁷⁰

It should be noted that the efficiency of ODS with respect to the removal of sulfur is between 30% and 40%, while the desulfurization efficiency in the extractive desulfurization (EDS) method reaches 90%.¹¹⁹ The efficiency of EDS is dependent upon the arrangement of the sulfur components between the fuel phase and the solvent phase, showing that choosing an appropriate solvent is of great importance. Preferably, this solvent should be physically and chemically stable and environmentally friendly.⁷⁰

Table S2 provides the ionic liquids used for EDS along with the obtained results and experimental conditions, see Supporting Information. However, briefly, it is mentioned that there are some types to which most researchers pay attention, including guanidinium-based ionic liquids, known as 1,1,3,3-trimethyl-guanidinium lactate ionic liquids,³⁶ ionic liquids containing halide metal anions such as Fe ions,¹²⁶ 4-dimethylaminopyridinium-based ionic liquids,⁸⁰ and pyridinium and thiazolium ionic liquids. The last one has provided promising results as potential solvents for EDS processes compared to other ionic liquids. It should be noted that the mechanism of extraction of sulfur aromatic compounds through the use of imidazole-based ionic liquids can be explained by the effect of a π - π possible interaction between the aromatic compounds of sulfur and the imidazole rings of the ionic liquids.⁹⁴

The use of a new solvent for EDS is important because the proposed molecular solvents have special problems when it comes to extracting sulfur components such as polyalkylene glycol, dimethyl sulfoxide, imidazolidinone, and pyrimidinone.⁸⁰

Many ionic liquids have been synthesized and studied in order to choose the best ionic liquid for the EDS process. On this basis, it has been found to be difficult to come up with an appropriate ionic liquid. Therefore, various classes of ionic liquids have been continuously studied. Besides the type of ionic liquid, the conditions under which the extraction is performed affect the efficiency of the EDS process. The

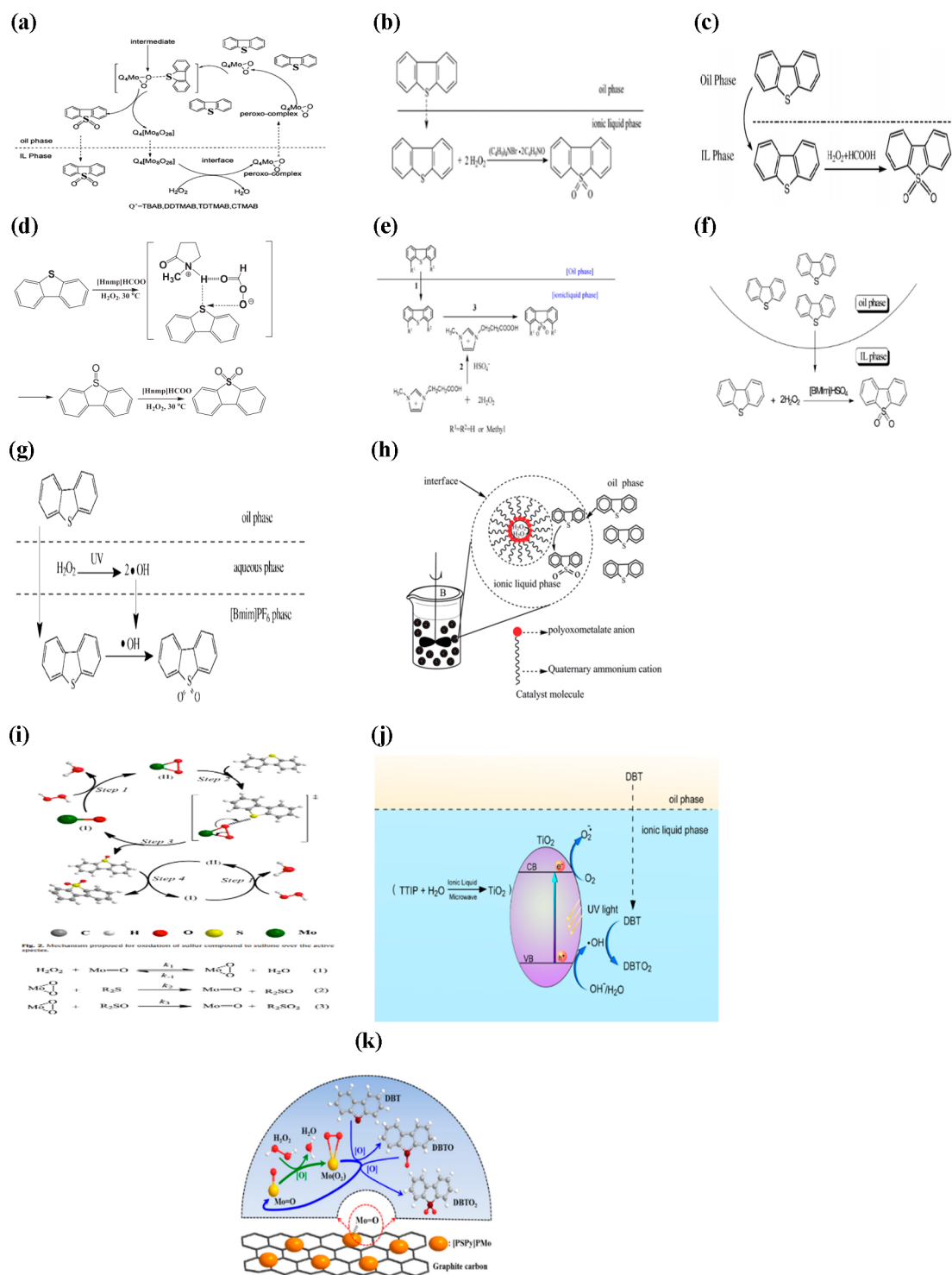


Figure 4. Mechanism of sulfur removal using various ionic liquids based on the ODS method. (a) DBT removal using $[(\text{CH}_2)_3\text{SO}_3\text{HMIM}]\text{BF}_4$. Reproduced with permission from ref 155. Copyright 2014 Taylor and Francis Ltd. (b) DBT removal using $[(\text{C}_4\text{H}_9)_4\text{NBr} \cdot 2\text{C}_6\text{H}_{11}\text{NO}]$. Reproduced with permission from ref 156. Copyright 2009 Taylor and Francis Ltd. (c) Proposed mechanism to remove DBT using the experimented ionic liquid. Reproduced with permission from ref 157. Copyright 2010 Elsevier. (d) DBT removal by $[\text{Hnmp}]\text{HCOO}$. Reproduced with permission from ref 71. Copyright 2014 Elsevier. (e) Removal of alkyl dibenzothiophene from diesel using $[(\text{CH}_2)_2\text{COOHMIM}][\text{HSO}_4]$. Reproduced with permission from ref 95. Copyright 2010 Elsevier. (f) DBT removal from an oil sample using $[\text{BMIM}]\text{HSO}_4$. Reproduced with permission from ref 158. Copyright 2010 American Chemical Society. (g) DBT removal from an oil sample using $[\text{BMIM}]\text{PF}_6$. Reproduced with permission from ref 106. Copyright 2010 American Chemical Society. (h) DBT removal using $[\text{BMIM}]\text{PF}_6$ and $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3][\text{PW}_{11}\text{O}_{39}]$ catalyst. Reproduced with permission from ref 159. Copyright 2011 American Chemical Society. (i) Desulfurization using surfactant-type polyoxometalate-based ionic liquids (SPILs). Reproduced with permission from ref 160. Copyright 2013 Elsevier. (j) DBT removal from an oil sample using a system containing $[\text{BMIM}]\text{BF}_4$ and TiO_2 catalyst. Reproduced with permission from ref 91. Copyright 2012 American Chemical Society. (k) DBT removal using graphite carbon-supported POM-IL catalyst ($[\text{PSPy}]\text{PMo}/\text{GC}$). Reproduced with permission from ref 161. Copyright 2017 Elsevier.

effects of temperature, fuel–solvent mass ratio, and time are often the main parameters studied in the EDS process.⁷⁰

Figure 5 presents the mechanism in which extracting-based desulfurization can be performed using a polyether-based IL. As it

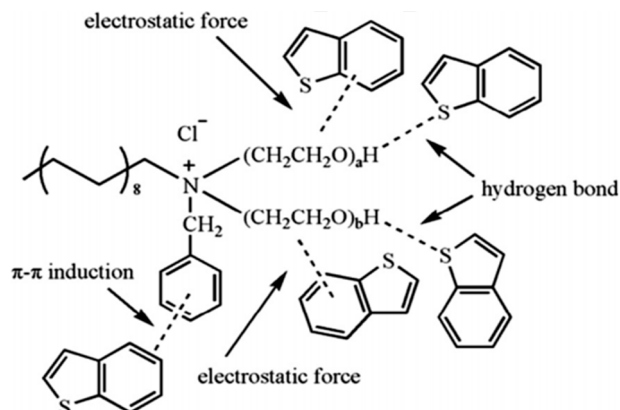


Figure 5. Mechanism of S removal using a polyether-based ionic liquid through the EDS method. Reproduced with permission from ref 165. Copyright 2016 Elsevier.

was done by Yu et al., the EDS process could be completed by a variety of bonds and attractive forces, including electrostatic force, hydrogen bond, and π - π induction. These weak attractive forces caused the ionic liquid to react highly with sulfur components, such as BT and phenyl sulfides. After several minutes, the extraction system moved toward the completed equilibrium. Adding some NaCl could help the polyether reach a higher level of equilibrium.¹⁶⁵

2.4. Extractive Oxidative Desulfurization (EODS). Extractive oxidative desulfurization (EODS) is a process by which ODS is performed by extraction, known as one of the most effective processes.^{93,166} The results showed that EODS is better than EDS.¹⁶⁶ In the world today, there is widespread use of extractive ODS in which

H_2O_2 and ionic liquids are, respectively, used as an oxidant and as extractors.¹⁶⁷ In the EODS process, the use of various oxidizing agents, including oxygen, hydrogen peroxide (H_2O_2), nitric acid (NO_2), and tetrabutyl hydroxide, has been largely studied. In such processes, sulfur compounds are oxidized and changed to the corresponding sulfones. These products can be then separated by selective extraction with the help of organic solvents.¹²⁶ To better compare the EODS process with other processes, the disadvantages and advantages of this method have been tabulated in Table 4.

To obtain a better understanding, Figure 6a–c shows the removal of DBT using EODS along with various ionic liquids. Figure 6a presents the way in which removal of DBT from an oil sample is conducted using $[\text{CH}_2\text{COOHPy}]\text{HSO}_4$, which was done by Zhang et al. By making a π bond and causing the ionic liquid to react highly with DBT, DBT simply left the oil phase and entered the ionic liquid phase. When the system reached the expected temperature and equilibrium, H_2O_2 was added. In this regard, the hydroxyl groups of the ionic liquid reacted with H_2O_2 , producing peroxycarboxyl. The obtained product could highly oxidize. This converted DBT into sulfur oxide and the concerned sulfones. Being of high polarity, these products dissolved in the ionic liquid. By continuing this process, the concentration of DBT was scaled down until the desulfurization process was completed.¹⁶⁸

Figure 6b presents a system in which H_2O_2 and Brønsted acidic ionic liquids remove DBT. In this process, the ionic liquid absorbed DBT from the oil phase. At the same time, the obtained product, $-\text{COOH}$, from the reaction between the hydroxyl groups of the ionic liquid and H_2O_2 converted this DBT into sulfur oxide and sulfones, generating highly polar products. These were accumulated in the ionic liquid phase. By continuing the process and removing DBT, the desulfurization was gradually completed.¹⁶⁹

Figure 6c shows the process by which DBT is removed. In doing so, $[\text{C}_4\text{MIM}]\text{Cl}/\text{FeCl}_3$ and H_2O_2 played a great role. As can be noticed, the ionic liquid could not be mixed with the oil phase, making a binary phase system. In this system, DBT was capable of simply leaving the oil phase. Using OH radicals, the absorbed DBT was converted to DBTO_2 . This product became accumulated in the ionic liquid phase. This process continued until the desulfurization was accomplished.¹²⁶

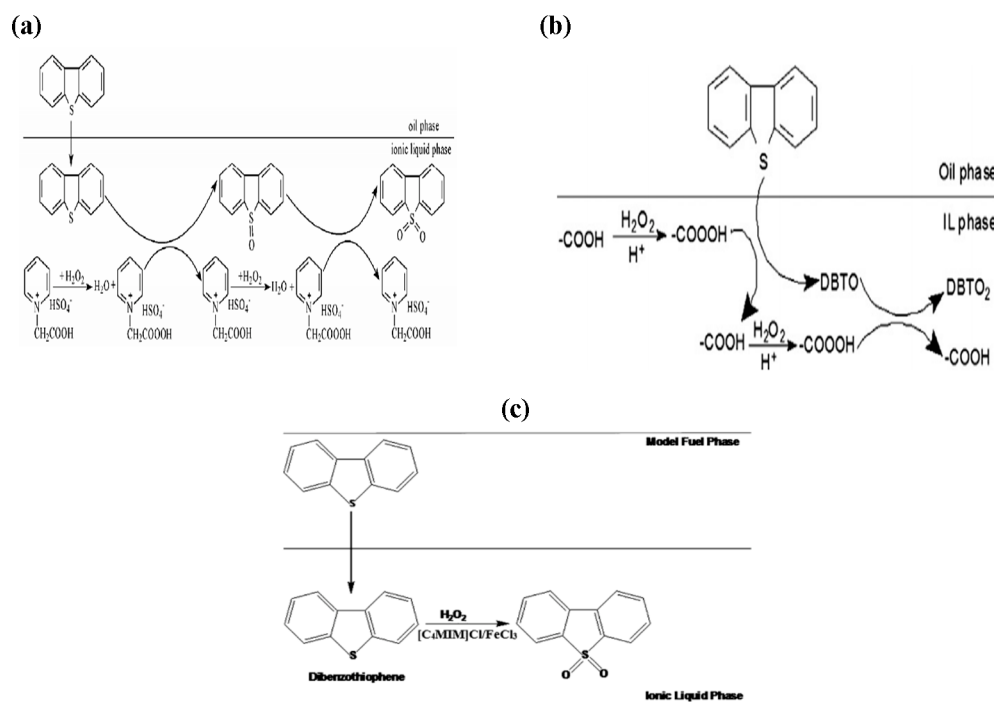


Figure 6. Sulfur removal using various ionic liquids, including (a) $[\text{CH}_2\text{COOHPy}]\text{HSO}_4$ (Reproduced with permission from ref 168. Copyright 2011 Elsevier.), (b) Brønsted acidic ionic liquids (Reproduced with permission from ref 169. Copyright 2012 Elsevier.), and (c) $[\text{C}_4\text{MIM}]\text{Cl}/\text{FeCl}_3$ (Reproduced with permission from ref 126. Copyright 2015 Springer New York.) through the EODS process.

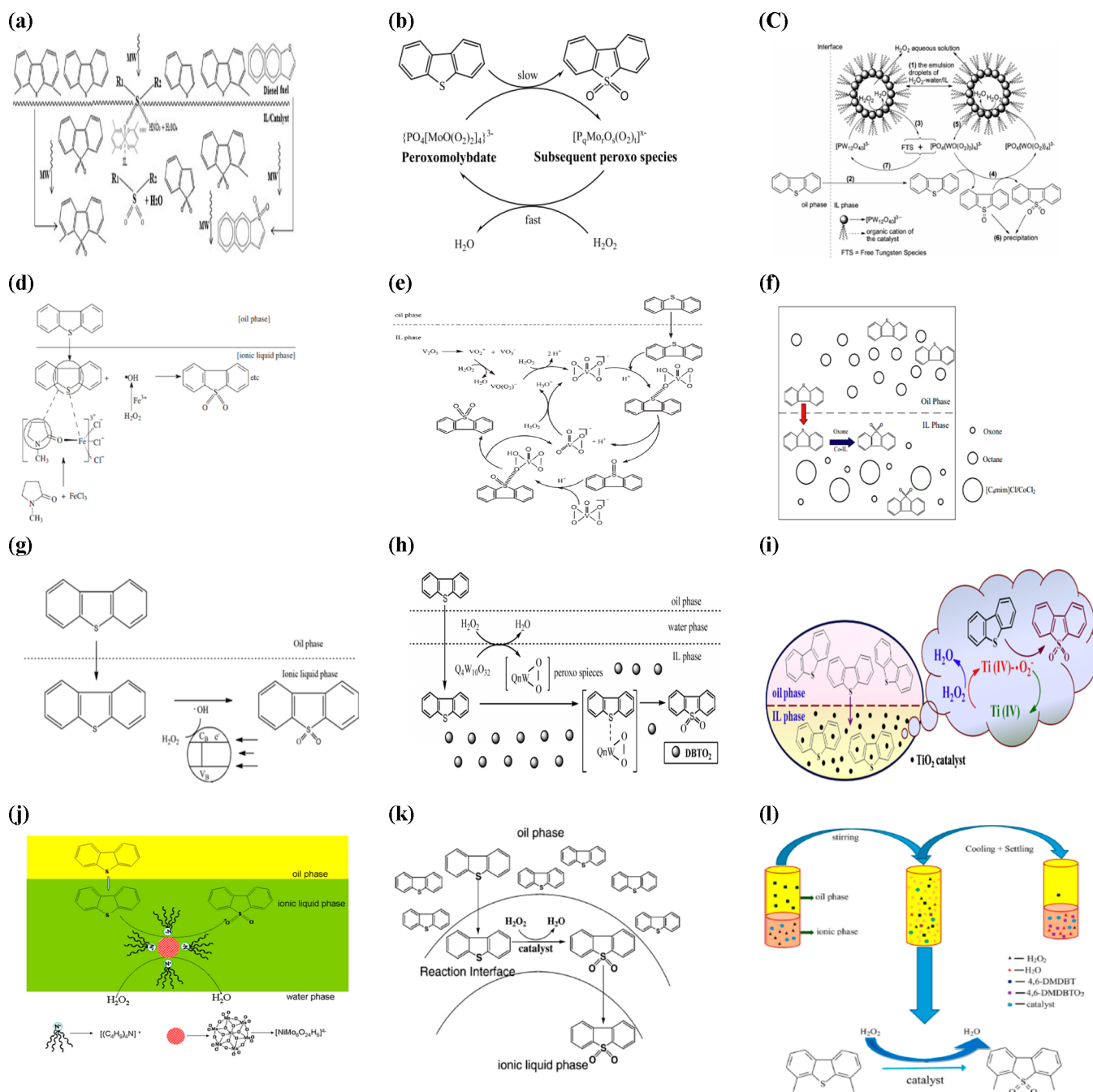


Figure 7. S-removal mechanism using various ionic liquids based on the ECODS method. (a) Sulfur compound removal by [HPy][H₂PO₄]. Reproduced with permission from ref 171. Copyright 2019 Taylor and Francis Ltd. (b) Sulfur compound removal by [BMIM]BF₄. Reproduced with permission from ref 170. Copyright 2012 Taylor and Francis Ltd. (c) Removal of thiophenic sulfur of the fuel in the presence of [MIMPS]₃PW₁₂O₄₀·2H₂O as catalyst in the [BMIM]PF₆ system. Reproduced with permission from ref 172. Copyright 2012 American Chemical Society. (d) DBT removal of a ternary system including oil, IL (C₅H₉NO·0.3FeCl₃), and H₂O₂. Reproduced with permission from ref 81. Copyright 2015 Elsevier. (e) DBT removal by V₂O₅ catalyst in [BMIM]BF₄. Reproduced with permission from ref 79. Copyright 2009 American Chemical Society. (f) DBT removal of octane by oxone as oxidizing agent in [C₄MIM]Cl/CoCl₂. Reproduced with permission from ref 173. Copyright 2017 Elsevier. (g) Desulfurization of DBT catalyzed by TiO₂ in [BMIM]BF₄. Reproduced with permission from ref 174. Copyright 2014 Springer New York. (h) DBT removal in [BMIM]PF₆, H₂O₂, and decatungstates catalyst. Reproduced with permission from ref 175. Copyright 2009 American Chemical Society. (i) DBT removal by [BMIM]BF₄ with H₂O₂ and TiO₂ catalyst. Reproduced with permission from ref 176. Copyright 2015 Elsevier. (j) DBT removal of diesel by [BMIM]PF₆ containing H₂O₂ and Anderson-type catalyst. Reproduced with permission from ref 47. Copyright 2013 Elsevier. (k) DBT removal by [BMIM]BF₄ with H₂O₂ and [(C₄H₉)₄N]₃[PO₄[MoO(O₂)₂]₄] catalyst. Reproduced with permission from ref 166. Copyright 2008 American Chemical Society. (l) 4,6-DMDBT removal by imidazolium (or phosphoric)-based ionic liquid with (NH₄)₆Mo₇O₂₄·4H₂O catalyst and H₂O₂. Reproduced with permission from ref 93. Copyright 2014 American Chemical Society.

To have a better view, Table S3 is provided which shows the ionic liquids used for the ECODS process, see the Supporting Information.

The obtained results and the experimental conditions are provided in the same table.

2.5. Extractive and Catalytic Oxidative Desulfurization (ECODS). Most of the published reports have concentrated on the removal of sulfur components by the EDS or EODS methods, and ECODS has not been given as much attention as it should be. In the ECODS system, catalysts with shorter alkyl branches have higher catalytic activity than those enjoying longer alkyl branches. To investigate the performance of the ECODS process, the advantages and disadvantages of this method have been tabulated in Table 4.

To obtain a better view of ECODS, Figure 7 presents the sulfur removal mechanisms based on ECODS using ionic liquids. Figure 7a presents the mechanism through which the sulfur components are removed from a diesel sample. This is based upon experiments by Benmabrouka. In this two-phase oxidation, the vanadium catalyst became highly oxidized by the available acid in the polar phase, producing oxohydroperoxy catalyst. This moved to the nonpolar phase due to anion transfer among the oxidants. The movement of oxygen also occurred between the peroxide and the sulfur components using the peroxidized catalyst in the contact level between the ionic liquid and the diesel.¹⁷⁰

Figure 7b shows how to remove DBT from an oil sample, which was conducted by Zhu et al.¹⁷¹ In this way, PMo_{12} and H_2O_2 were not soluble in the oil sample, while they dissolved in the ionic liquid. In this step, PMo_{12} reacted with the extra H_2O_2 , generating $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$ peroxomolybdate. The ionic liquid increased the catalytic activity and oxidation rate. During desulfurization, DBT left the oil phase and entered the ionic liquid phase. With the help of the catalyst, it was then converted into DBTO_2 .

A three-phase system containing $[\text{BMIM}]\text{PF}_6$ ionic liquid, hydrogen peroxide, and phosphotungstate catalyst is indicated in Figure 7c. In this process, a stable emulsion was generated by H_2O_2 with the help of the catalyst in the ionic liquid, extracting DBT from the oil phase and transferring it to the ionic liquid phase. The extracted DBT was changed to DBTO , and it was then converted to DBTO_2 . This product precipitated, and this precipitation could finally be separated from the oil phase.¹⁷²

Figure 7d presents the process through which NMP first reacted with FeCl_3 . This reaction led to producing $\text{C}_5\text{H}_9\text{NO}-\text{FeCl}_3$. It acted as an extraction liquid and catalyst. In the next stage, DBT moved to the ionic liquid phase. It should be mentioned that there were two theories for the extraction mechanism. The first one was based on a five-membered chain interaction whereby DBT reacted with NMP. The foundation of this was on the similarity–intermiscibility theory. The second theory was related to the reaction in which the sulfur atoms reacted with Fe^{3+} . In this process, DBT reacted with the obtained OH radicals from H_2O_2 , generating DBTO_2 or other substances. Considering this process, the desulfurization continued.⁸¹

Figure 7e shows a scheme in which the V_2O_5 catalyst is insoluble in the $[\text{BMIM}]\text{BF}_4$ ionic liquid. This experiment was performed by Xu et al.⁷⁹ By adding H_2O_2 , this catalyst could be oxidized, becoming soluble. The active oxygen atoms moved to sulfur atoms by adding the oxidized sample $\text{VO}(\text{O}_2)^{2-}$. This movement was of importance to convert DBT to sulfur oxide and the needed sulfone. Since there was extra H_2O_2 , $\text{VO}_2(\text{O}_2)^-$ was continuously changed into $\text{VO}(\text{O}_2)^{2-}$. The extracted sulfur components accumulated in the ionic liquid. This accumulation could be then extracted using a centrifuge.

In Figure 7f, Xu et al.¹⁷³ showed that DBT left octane in the first step and then entered the $[\text{C}_4\text{MIMCl}]\text{FeCl}_3$ ionic liquid. The absorbed DBT was oxidized by oxone and $[\text{C}_4\text{MIMCl}]\text{CoCl}_2$ ionic liquid. In the next stage, Co^{2+} reacted with oxone, generating sulfate radicals that could be largely oxidative, helping to convert DBT to DBTO_2 . In doing so, Co^{2+} was changed to Co^{3+} . This reacted with H_2O_2 , contributing to the production of Co^{2+} . This trend continued until the desulfurization is done.

Figure 7g shows that sulfur components could be extracted using $[\text{BMIM}]\text{BF}_4$ ionic liquid. OH radicals converted these extracted sulfur components to sulfones. The obtained product was precipitated, which could be separated using a centrifuge. In this experiment, the TiO_2 catalyst helped H_2O_2 provide the needed OH radicals in order to continue the desulfurization process.¹⁷⁴

In Figure 7h, decatungstates were used as a catalyst. By changing to peroxy components, decatungstates offered appropriate performance for desulfurization. The catalyst exposed sulfur components to oxidants and created an active system for oxidation. By continuously mixing, this catalyst dissolved in $[\text{BMIM}]\text{PF}_6$ ionic liquid. In this regard, peroxy oxidized DBT and converted it into sulfones. The obtained sulfone components were absorbed in the ionic liquid owing to the high polarity, playing a part in an acceptable desulfurization.¹⁷⁵

Figure 7i shows a heterogeneous catalyst system containing the model oil, TiO_2 , and $[\text{BMIM}]\text{BF}_4$. In this mechanism, the catalyst reacted with H_2O_2 , producing radicals to convert DBT, which left the model oil phase and entered the ionic liquid phase, to DBTO_2 . Due to the high polarity of the produced substance, it stays in the ionic liquid in a soluble way. By continuing this process, a large proportion of sulfur disappeared from the oil sample.¹⁷⁶

A process through which DBT can be extracted from a model diesel using $[\text{BMIM}]\text{PF}_6$ and an Anderson-type catalyst is indicated in Figure 7j. In this process, the oxidant continuously generated the required active oxygen for heteropolyanions, which was available in the contact level between the ionic liquid and the water phase. Heteropolyanions then oxidized the absorbed DBT and changed it to DBTO_2 . The concentration of sulfur components was scaled down in the model diesel, and the desulfurization became gradually wrapped up.^{47,177}

Figure 7k shows a desulfurization system including $[\text{BMIM}]\text{BF}_4$ ionic liquid, $[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4]$ catalyst, and H_2O_2 . It is worth mentioning that the efficiency of the desulfurization was 16.8% when the catalyst, having a short alkyl chain length, and H_2O_2 were used to desulfurize in the absence of the ionic liquid. This means that the ionic liquid has a great role to play in increasing the efficiency of the process, so much so that when this process was performed in the presence of the ionic liquid, the efficiency was up to 97.3%. This rise came from the increase of the catalytic activities to oxidize DBT. The oxidized DBT entered the ionic liquid phase in the form of DBTO_2 . This conversion accumulated in the ionic liquid and could be extracted easily.¹⁷⁸

Figure 7l presents the mechanism of 4,6-dimethyldibenzothiophene removal from a petroleum sample using imidazolium-based and phosphoric-based ionic liquids ($[\text{EMIM}]\text{DEP}$, $[\text{MMIM}]\text{DMP}$, and $[\text{BMIM}]\text{DBP}$), a catalyst $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, and H_2O_2 as an oxidant. The three ionic liquids used were insoluble in the sample. In this respect, their functions were as both extractors and reaction intermediates. They accelerated the catalytic performance. During the experiment, 4,6-dimethyldibenzothiophene was extracted from the sample and became oxidized in the IL. Oxidized sulfur compounds were accumulated in the ionic liquid as 4,6-DMDBTO₂. This accumulation could be easily separated from the system.²⁹

Also, to obtain a better view, the employed ILs during ECODS as well as the obtained results and the applied experimental conditions are tabulated in Table S4, see Supporting Information.

2.6. Liquid–Liquid Extraction (LLE). In this method, the extraction efficiency depends on the solvent selected for the separation processes.^{45,53} Common solvents used for the extraction are flammable, highly volatile, and often toxic.⁴⁵ Since the use of common organic solvents such as sulfone results in significant environmental pollution, recently, ionic liquids have been introduced as a useful alternative to liquid–liquid extraction of sulfur compounds. Having advantages, liquid–liquid extraction is widely utilized in industrial processes such as aromatic separation and purification.^{139,179} These advantages can be defined as this method has a simple operation,⁵³ the reaction conditions are normal, and liquid–liquid extraction is performed at low temperature and pressure.^{41,180} In addition, this method consumes less energy,^{45,180} has economic benefits,⁵³ and does not change the chemical structure of the fuel.¹⁸⁰ To better compare the LLE process with the other studied methods, Table 4 has been provided to show the advantages and disadvantages of this method. Table S5 also shows the various ILs used in the LLE method along with the obtained results and experimental conditions, see Supporting Information.

Some important industrial extraction processes, such as the separation of aliphatic and aromatic hydrocarbons or aliphatic alcohols and hydrocarbons, are still considered as a challenge. Because these

compounds have similar boiling points and have several azeotropic compositions,^{53,83} 1-butyl-3-methylimidazolium trifluoromethanol sulfonate ([BMIM][OTf]) ionic liquid has been used as an extractive solvent for two separations, which often bring industrial problems to the petroleum industry.⁵³ These separations are, namely, the extraction of aromatic compounds of sulfur and the removal of nitrogen from aliphatic hydrocarbons. To do this, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), 1,3-dimethylimidazolium methylphenate, and 1-butyl-3-methylimidazolium thiocyanate ionic liquids were used.⁸³

3. FACTORS IMPACTING DESULFURIZATION

3.1. Effect of Reusing Ionic Liquids on Desulfurization.

The mobility and flexibility of ionic liquids are unique properties of these compounds. This helps to recycle them easily.^{45,53} Such a process is an important feature when it comes to choosing an ionic liquid. In other words, this feature compensates for the high price of ionic liquids. The methods of recycling ionic liquids, loaded with sulfur components, are different. On the basis of the nature of the sulfur compounds and the ionic liquids, the appropriate method should be chosen.¹⁹ To remove sulfur components from an ionic liquid, there are three ways, including heating the ionic liquid,³¹ re-extracting sulfur compounds using hydrocarbons with a low boiling point (e.g., pentane and hexane),³⁸ and depositing sulfur compounds through the water dilution process.⁹⁴

Regarding the results obtained by Bhutto et al.,¹⁹ during the recycling of some ionic liquids there was a loss, resulting in a slight decrease in the removal of DBT from the oil phase with increasing number of cycles. He et al.¹⁶⁶ investigated the performance of desulfurization to remove DBT from a fuel sample using [BMIM] BF₄ ionic liquid, including [(C₄H₉)₄N]₃[PO₄[MoO(O₂)₂]₄] and H₂O₂. After the reaction, the IL phase (the bottom layer) in the oil bath was distilled at 110 °C to completely remove H₂O₂. The fresh H₂O₂ and the oil sample were then dissolved for subsequent reaction in the IL phase.

Figure 8 shows the effect of reusing [BMIM]DBP ionic liquid on desulfurization. When the recycling times increased, there

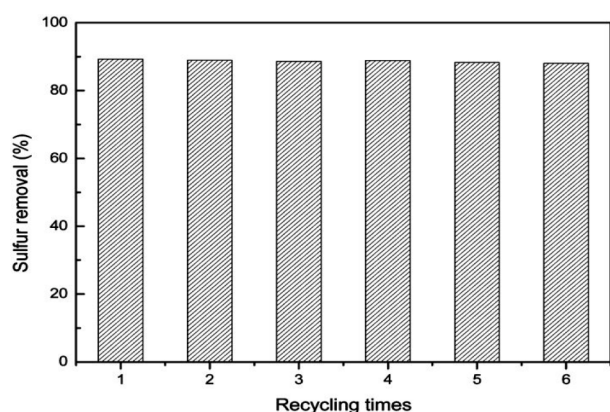


Figure 8. Effect of recycling [BMIM]DBP on desulfurization. Reproduced with permission from ref 93. Copyright 2014 American Chemical Society.

was a slight decrease in the performance of sulfur removal from the ILs. When the system was recycled 6 times, sulfur removal was scaled down by 1.93% under identical laboratory conditions. This reduction came from producing oxidation products after recycling, making a reduction in the performance of ionic

liquids. A further reason was that some of the ionic liquid was eliminated when it was separated from the oil and recycled, reducing the activity of the ionic liquid in the next stage. After recycling, the structure of the ionic liquid was similar to that of the original ionic liquid. In other words, the ionic liquid properties did not change.⁹³

Batista et al.³⁶ showed that by increasing the cycle repetition, the removal of dibenzothiophene decreased because the extraction decreased. This was the result of the saturation of oxidation products in the ionic liquid.

When the ionic liquid was used 5 times, there was a slight decrease in the activity of the desulfurization system. The repeated use of ionic liquids had a negligible impact on the H₂S solubility. In addition, ionic liquids could be used up to 6 times without reducing their absorption capacity.²⁸

The sulfur removal capacity was slowly reduced, and ionic liquids could be reused up to 5 times; this capacity did not decrease significantly. Thus, ionic liquids had excellent reuse performance in the adsorption and oxidation of H₂S since the ionic liquid used had appropriate temperature stability.⁵³ The ionic liquid was recycled 5 times with a negligible decrease in the extraction efficiency at room temperature. However, when the sixth cycle was completed, the desulfurization performance slightly decreased because when the number of cycles increased, benzene thiophene was produced more along with the ionic liquid, decreasing the extraction performance and the desulfurization efficiency.¹²⁶

The research conducted by Chen et al.¹⁸¹ showed that after 7 cycles, the desulfurization efficiency decreased slightly due to the accumulation of oxidation products (such as DBTO₂). Likewise, Yao et al.¹⁶⁴ found that the desulfurization efficiency decreased slightly after the ionic liquids were used 7 times. The possible reason for this was that some of the ionic liquid was lost during the recycling process. In another study performed by Wang et al.,⁹⁴ when ionic liquids were used 7 times, their performance experienced only a slight reduction.

Zhu et al.'s studies⁷⁴ showed that the percentage of DBT removal stood at 93.1% after the ionic liquid was utilized 7 times, whereas when it was used again, the performance decreased to 89.7%.

The results of the experiment carried out by Shao et al.⁹³ showed that when the ionic liquid was used 6 times, the proportion of desulfurization declined from 89.21% to 87.98%. This decrease came from a large number of oxidation products after recycling, contributing to the decrease of the ionic liquids' performance. Another reason was that some ionic liquid was lost after the ionic liquids were separated from the oil and recycled. This reduced the activity in the next step.

The percentage of sulfur removal decreased from 93.3% to 89.5% when the ionic liquids were used 5 times.⁹⁵ Similarly, when ethanolamine lactate ILs were used 5 times, the efficiency decreased from 97.7% to 84%.¹⁸² Ren et al.⁶⁶ found that the mass ratio of sulfur to ionic liquid dropped by 0.073 after the ionic liquid had been utilized 10 times. In a study by Enayati and Faghiani,¹⁸³ the efficiency decreased from 94.8% to 90.6% after using the ionic liquid 5 times. In a study by Zhu et al.,⁷⁴ when the ionic liquid was used 8 times to desulfurize, the efficiency dropped from 99.5% to 94.6%.

By the same token, in recent years, many have studied the reuse of different ionic liquids. Their usages have been reported to be between 2 and 64 times in various studies.^{29,44,61,63,75,78,79,91,165,184–186}

Table 6. ILs Used in ODS, EDS, EODS, ECODS, and LLE over Various Temperatures along with Their Structures, Removed Sulfur Components, and Obtained Optimum Temperature

ILs	Structure	Sulfur compounds removed	Temperatures range [°C]	To [°C]	Ref
ODS					
1-butyl-3-methyl-1-imidazolium tetrafluoroborate [(CH ₂) ₃ SO ₃ HMIM]BF ₄		DBT	30 - 70	60	192
quateryary ammonium-coordinated ionic liquid [(C ₄ H ₉) ₄ NBr. 2C ₆ H ₁₁ NO]		DBT	20 - 70	50	156
1-(4-sulfonic acid) butyl-3-methylimidazolium p-toluenesulfonate [(CH ₂) ₄ SO ₃ HMIM] [TOS]		DBT	1.85 - 71.85	49.85	193
carboxylate-anion-based protic ionic liquid [HNMP]HCOO		BT, DBT, 4,6-DMDBT	30 - 80	50	71
N-methylpyrrolidonium zinc chloride [HNMP]Cl/ZnCl ₂		TS	30 - 75	75	119
1-Butyl-3-methyl-imidazolium Trifluoroacetic Acid ([C ₄ MIM]TFA)		TS	40 - 80	70	167
[BPy]BF ₄ [BPy]SCN [BPy]HSO ₄ [BPy]H ₂ PO ₄		DBT	20 - 80	60	157
1-Hexyl-3-methylimidazolium tetrafluoroborate ([HMIM]BF ₄)		TS, BT, DBT	60 - 100	90	184
ammonium oxidative-thermoregulated bifunctional ionic liquids		TS	40 - 60	60	185
1-ethyl-3-methylimidazolium acetate ([BMIM]CH ₃ COO)		TS, BT, DBT, 4,6-DMDBT	25 - 80	25	194
[PNBIM]CH ₃ COO [HXBIM]CH ₃ COO [HPBIM]CH ₃ COO [OTBIM]CH ₃ COO		TS	40 - 70	70	195
[C ₄₃ MPy]FeCl ₄ [C ₆₃ MPy]FeCl ₄ [C ₈₃ MPy]FeCl ₄		DBT	25, 35, 50	25	196
C ₅ H ₉ NO 0.1ZnCl ₂ C ₅ H ₉ NO 0.3ZnCl ₂ C ₅ H ₉ NO 0.1FeCl ₃ C ₅ H ₉ NO 0.3FeCl ₃		DBT	30 - 50	30	81
[C ₄ MIM]Cl/MCl ₂ (M = Zn, Fe, Cu, Mg, Sn, Co)		DBT	30 - 60	45	69
1-(2-carboxylic acid) ethyl-3-methylimidazolium bisulfate ((CH ₂) ₂ COOHMIM][HSO ₄)		DBT, 4-MDB, 4,6-DMDBT	24.85 - 61.85	24.85	197
SBA-15 supported silicotungstic acid ionic liquid (HSiW-IL/SBA-15)		BT, DBT, 4,6-DMDBT	40 - 60	60	96

Table 6. continued

ILs	Structure	Sulfur compounds removed	Temperatures range [°C]	T ₀ [°C]	Ref
ODS					
[C ₁₆ MIM] ₂ [W ₂ O ₅ (O ₂) ₄]		DBT, 4,6-DMDBT	50 - 70	60	198
N-butyl-N-methylimidazolium hydrogen sulfate ([BMIM][HSO ₄])		DBT	50 - 80	60	158
Phosphotungstic Acid Immobilized on Ionic Liquid-modified mesoporous silica SBA-15 (HPW-IL-SBA-15)		BT, DBT, 4,6-DMDBT	30 - 60	60	199
tungsten-based IL (IL/G-h-BN)		DBT, 4,6-DMDBT	20 - 50	30	200
[HNMP][ZnCl ₃] [HNMP][HSO ₄] [(CH ₂) ₄ SO ₃ HMIM][ZnCl ₃] [(CH ₂) ₄ SO ₃ HMIM][TOS]		thiophenic sulfur	25-70	70	201
NMP·FeCl ₃ (NMP=N-methyl-2-pyrrolidone, C ₅ H ₉ NO)		BT, DBT, 4,6-DMDBT	25 - 55	40	135
N,N-dimethyl-dodecyl-(4-vinylbenzyl) ammonium chloride (DDVAC) and Divinylbenzene (DVB) (co-monomers)		BT, DBT	30 - 60	50	202
EDS					
1-Butylpyridinium tetrafluoroborate [BPy] ⁺ BF ₄ ⁻		TS	30 - 70	50	203
3-butyl-4-methylthiazolium dicyanamide [BMTH][DCA]		TS and DBT	20 - 55	25	204
1-butyl-3-methylimidazolium dicyanamide ([C ₄ MIM][N(CN) ₂]) 1-ethyl-3-methylimidazolium dicyanamide ([C ₂ MIM][N(CN) ₂])		Sulfur	20 - 55	25	205

Table 6. continued

ILs	Structure	Sulfur compounds removed	Temperatures range [°C]	To [°C]	Ref
triethyl(tetradecyl)phosphonium hexafluorophosphate ([THTDP][PF ₆])		EDS TS, BT, DBT, 3-MT, 4-MDBT, 4,6-DMDBT	20 - 55	35	206
1-butyl-3-methylimidazolium dicyano(nitroso)methanide ([C ₄ MIM][denm]) 1-ethyl-3-methylimidazolium dicyano(nitroso)methanide ([C ₂ MIM][denm]) N-ethyl-N-methylpyrrolidinium dicyano(nitroso)methanide ([C ₂ MPYR][denm]) N-butyl-N-methylpyrrolidinium dicyano(nitroso)methanide ([C ₄ MPYR][denm])		TS and DBT	20 - 65	25	207
1-butyl-3-methyl-imidazolium chloride-FeCl ₃ [BMIM]Cl/FeCl ₃ , [BMIM]Cl/ZnCl ₂ , [BMIM]Cl/SnCl ₄ , T ₄ Cl/FeCl ₃ , D ₁₀ Cl/FeCl ₃ , Et ₃ NHCl/FeCl ₃		BT, DBT, 4,6-DMDBT	30 - 80	30	208
N-methylpiperazinium lactate ([C1PI][Lac]) N-ethylpiperazinium lactate ([C ₂ PI][Lac]) N,N'-dimethylpiperazinium dilactate ([C ₁ C1PI][Lac] ₂) 1,1,3,3-tetramethylguanidinium lactate ([TMG][Lac])		TS, BT, DBT, 4-MDBT	10 - 60	30	58
NMP·FeCl ₃ (NMP=N-methyl-2-pyrrolidone, C ₅ H ₉ NO)		BT, DBT, 4,6-DMDBT	25 - 55	40	135
N,N-dimethyl-dodecyl-(4-vinylbenzyl) ammonium chloride (DDVAC) and Divinylbenzene (DVB) (co-monomers)		BT, DBT	30 - 60	50	202
1-Butylpyridinium tetrafluoroborate [BPy]BF ₄		TS	30 - 70	50	203
3-butyl-4-methylthiazolium dicyanamide [BMTH][DCA]		TS and DBT	20 - 55	25	204
1-butyl-3-methylimidazolium dicyanamide ([C ₄ MIM][N(CN) ₂]) 1-ethyl-3-methylimidazolium dicyanamide ([C ₂ MIM][N(CN) ₂])		Sulfur	20 - 55	25	205

Table 6. continued

ILs	Structure	Sulfur compounds removed	Temperatures range [°C]	To [°C]	Ref
EDS					
1-ethyl-3-methylimidazolium tricyanomethanide ([EMIM][TCM])		TS, BT	25 - 35	25	40
[OMIM]Cl. xFeCl ₃ (x= 0.5, 1, 1.5, 2 and 2.5)	-	BT, DBT, 4,6 DMDBT	25 - 60	25	209
([BPy][NO ₃])/([EPy][NO ₃]) ([BPy][BF ₄])/([EPy][BF ₄]) ([EPy]Ac)/([BPy]Ac)		TS, BT	25 - 60	25	56
tributyl(carboxymethyl)phosphonium bromide ([TBCMP][Br])		BT, DBT, DMDBT	15 - 35	25	33
polyether-based ionic liquids		BT, DBT, 3-MT, 4,6 DMDBT	30 - 70	30	165
1-butyl-3-methylimidazolium chloride/ZnCl ₂ ([BMIM]Cl/ZnCl ₂ & [BMIM]Cl ₂ ZnCl ₂) 1-Butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO ₄) 1-methylimidazolium hydrogen sulfate ([HMIM]HSO ₄)		TS, DBT	20 - 55	25	210
N-butyl-N-methylpiperidinium tetrachloroferrate ([C ₄ MPIP]FeCl ₄)		BT, DBT, 4,6 DMDBT	45 - 80	45	180
1-Butyl-3-methylimidazolium nitrate ([BMIM][NO ₃]) 1-Octyl-3-methylimidazolium nitrate ([OMIM][NO ₃]) 1-Butylpyridinium nitrate ([BPy][NO ₃]) 1-Octylpyridinium nitrate ([OPy][NO ₃])		DBT	25 - 90	25	55
1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN)		TS, BT, DBT, 3-MT, 4-MDBT, 4,6-DMDBT	20 - 40	30	52
3-butyl-4-methylthiazolium thiocyanate ([BMTH]SCN)		TS, BT, DBT, 3-MT, 4-MDBT, 4,6-DMDBT	20 - 40	30	211
Trihexyl(tetradecyl)phosphonium Chloride ([THTDP]Cl)		TS, BT, DBT, 3-MT, 4-MDBT, 4,6-DMDBT	20 - 40	30	98
[HNMP]Cl/ZnCl ₂ [HNMP]HSO ₄ [(CH ₂) ₄ SO ₃ HMIM]ZnCl ₃ [(CH ₂) ₄ SO ₃ HMIM]TOS		thiophenic sulfur	25 - 60	25	201

Table 6. continued

ILs	Structure	Sulfur compounds removed	Temperatures range [°C]	To [°C]	Ref
EDS					
ester functionalized imidazolium ionic liquids [C ₂ COOCH ₃ IMC ₂ H ₃][N(CN) ₂] [C ₂ COOCH ₃ IMC ₃ H ₇][N(CN) ₂] [C ₂ COOCH ₃ IMC ₄ H ₉][N(CN) ₂] [C ₂ COOCH ₃ IMC ₅ H ₁₁][N(CN) ₂] [C ₂ COOCH ₃ IMC ₆ H ₁₃][N(CN) ₂]		DBT	25 - 90	25	212
Tributyl(2,3-dihydroxypropyl)phosphonium chloride ([TBHPP][Cl])		DBT	15 - 35	25	213
EODS					
1-Butyl-3-methylimidazolium chloride iron chloride ([C ₄ MIM]Cl/FeCl ₃) 1-Octyl-3-methylimidazolium chloride iron chloride ([OMIM]Cl/FeCl ₃) Didecyl dimethyl ammonium chloride iron chloride (D ₁₀ Cl/FeCl ₃) Ammonium tri-butyl-methyl chloride iron chloride (T ₄ Cl/FeCl ₃) Tri-octyl-methyl ammonium chloride iron chloride (T ₈ Cl/FeCl ₃)		TS, BT, DBT, 3-MT 4,6-DMDBT	20 - 55	30	126
N-carboxymethylpyridine hydrosulphate ([CH ₂ COOHPy][HSO ₄])		DBT	30 - 60	50	168
C ₅ H ₉ NO · xSnCl ₂ (x = 0.6, 0.8, 1, 1.2 and 1.5)		DBT	30 - 50	50	214
EODS					
[(CH ₂) ₄ SO ₃ HMIM][TOS] [(CH ₂) ₄ SO ₃ HMIM][ZnCl ₃] [(CH ₂) ₄ SO ₃ HMIM][HSO ₄] [(CH ₂) ₄ SO ₃ HMIM][H ₂ PO ₄] [(CH ₂) ₄ SO ₃ HMIM][FeCl ₄]		TS, BT, DBT	For [(CH ₂) ₄ SO ₃ HMIM][ZnCl ₃] = 30 - 75 For [(CH ₂) ₄ SO ₃ HMIM][TOS] = 45 - 90	For [(CH ₂) ₄ SO ₃ HMIM][TOS] = 75 and For [(CH ₂) ₄ SO ₃ HMIM][ZnCl ₃] = 60	181
1-octyl-3-methylimidazolium persulfate ([OMIM] ₂ [S ₂ O ₈])		DBT	40 - 60	60	215
ECODS					
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄)		DBT	40 - 50	30	216
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄)		BT, DBT, 4,6-DMDBT	50 - 70	70	166
N-methyl-N-methylimidazolium dimethyl phosphate ([MMIM]DMP) N-ethyl-N-methylimidazolium diethyl phosphate ([EMIM]DEP) N-butyl-N-methylimidazolium dibutyl phosphate ([BMIM]DBP)		4,6-DMDBT	20 - 50	50	93

Table 6. continued

ILs	Structure	Sulfur compounds removed	Temperatures range [°C]	To [°C]	Ref
ECODS					
1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄) 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF ₆) 1-Methyl-3-octylimidazolium hexafluorophosphate ([OMIM]PF ₆)		BT, DBT, 5-MBT, 4-MDBT, 4,6-DMDBT	20 - 70	30	47
1-(3-sulfonic group) propyl-3-methyl imidazolium phosphotungstate ([MIMPS] ₃ PW ₁₂ O ₄₀ ·2H ₂ O) 1-butyl 3-methyl imidazolium phosphotungstate ([BMIM] ₃ PW ₁₂ O ₄₀) 1-butyl 3-methyl imidazolium phosphomolybdate ([BMIM] ₃ PMo ₁₂ O ₄₀) 1-butyl-3-methyl imidazolium silicotungstate ([BMIM] ₄ SiW ₁₂ O ₄₀)		DBT, 4,6-DMDBT	30 - 50	30	74
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄) 1-Methyl-3-octylimidazolium tetrafluoroborate ([OMIM]BF ₄) 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF ₆) 1-Methyl-3-octylimidazolium hexafluorophosphate ([OMIM]PF ₆) 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄) 1-Methyl-3-octylimidazolium tetrafluoroborate ([OMIM]BF ₄) 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF ₆) 1-Methyl-3-octylimidazolium hexafluorophosphate ([OMIM]PF ₆)		BT, DBT, 4,6-DMDBT	30 - 60	40	176
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄) 1-Methyl-3-octylimidazolium tetrafluoroborate ([OMIM]BF ₄) 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF ₆) 1-Methyl-3-octylimidazolium hexafluorophosphate ([OMIM]PF ₆)		BT, DBT, DT	30 - 50	30	121
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄) 1-Methyl-3-octylimidazolium tetrafluoroborate ([OMIM]BF ₄)		BT, DBT, 4,6-DMDBT	30 - 50	30	217
heteropolyanion-based ionic liquid ([PSPy] ₃ PW)		BT, DBT, 4,6-DMDBT	30 - 50	30	84
1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF ₆)		BT, DBT, 4-MDBT, 4,6-DMDBT	30 - 60	50	177
1-butyl-3-methylimidazolium tetrafluoroborate ([C ₄ MIM]BF ₄) 1-n-octyl-3-methylimidazolium tetrafluoroborate ([C ₈ MIM]BF ₄) 1-butyl-3-methylimidazolium hexafluorophosphate ([C ₄ MIM]PF ₆) 1-n-octyl-3-methylimidazolium hexafluorophosphate [C ₈ MIM]PF ₆		BT, DBT, 4,6-DMDBT	30 - 50	30	218

Table 6. continued

ILs	Structure	Sulfur compounds removed	Temperatures range [°C]	To [°C]	Ref
ECODS					
Lewis acidic ionic liquids [C ₄₃ MPy]Cl/nZnCl ₂ (n=1, 1.5, 2, 3)		TS, BT, DBT	24.85 - 59.85	49.85	219
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄)		BT, DBT, 4,6-DMDBT	30 - 50	30	79
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄)		DBT	30 - 70	40	172
1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF ₆)					
1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF ₆)		DBT	20 - 30	30	159
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF ₄)		BT, DBT, 4,6-DMDBT	20 - 50	30	220
1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF ₆)		BT, 4,6-DMDBT	40 - 60	60	175
Lewis acidic ionic liquids [ODBU]Cl/nZnCl ₂ (n = 1, 2, 3, 4 and 5)		BT, DBT, 4,6-DMDBT	30 - 60	50	221
1-n-butyl-3-methylimidazolium cobalt chloride ([C ₄ MIMCl]CoCl ₂)		BT, DBT, 4,6-DMDBT	30 - 60	40 - 50	173
superbase-derived Lewis acidic ionic liquids [HDBN]Cl/nZnCl ₂ (n = 1, 2 and 3)		TS, BT, DBT, 4,6-DMDBT	40 - 60	60	222
LLE					
1-butyl-4-methylpyridinium tricyanomethanide [4BMPY][TCM]		TS, Benzene	30.05 - 50.05	40.05	223
[(BMIM][BF ₄]), [(BMIM][PF ₆]), [(CH ₂) ₄ SO ₃ HMIM][HSO ₄], [(CH ₂) ₄ SO ₃ HPy][HSO ₄], [(CH ₂) ₄ SO ₃ HTEA][HSO ₄], [(CH ₂) ₄ SO ₃ HMIM][TOS], [(CH ₂) ₄ SO ₃ HPy][TOS], [(CH ₂) ₄ SO ₃ HTEA][TOS]		TS, BT, DBT, 4,6-DMDBT	40 - 120	80	224

3.2. Impact of Temperature on the Reaction. It has been shown that temperatures can strongly affect the desulfurization process.⁷¹ At lower temperatures, the reaction rate is low.¹⁹ Besides, at lower temperatures, the ionic liquid viscosity is relatively high, preventing phases from mixing and transferring

mass. Also, after H₂O₂ is decomposed, it cannot be used as efficiently as it was in the original process.¹⁸¹ On the other hand, raising the temperature does not always help to have a higher desulfurization efficiency.³⁶ By increasing the temperature, the ionic liquid viscosity decreases. This increases the catalytic

activity, which is beneficial to thiophene removal.¹⁶⁷ Choosing higher temperatures also can negatively affect the desulfurization process as it causes H₂O₂ to decompose faster. Furthermore, at higher temperatures, the risk of explosion increases. Thus, higher temperatures should not be chosen for the desulfurization process.¹⁸¹

To better investigate the effect of temperature upon the studied desulfurization methods, Table 6 has been provided to show the ILs used and their structures along with the temperature ranges and the introduced optimum temperatures. According to the obtained results from this table and tables in the Supporting Information, it seems that EDS has the potential to be commercially established and can be an alternative candidate for replacement of the HDS process compared to other investigated desulfurization methods. This is because EDS has met economic concerns, and many ILs could deliver a reasonable and reliable desulfurization efficiency during this process at 25 °C, which is a low temperature at operating scale. It should be noted that higher temperatures are not reasonable as such a situation not only increases the possibility of decomposition of materials but also scales up operating costs.

As shown in Table 6, in the ECODS process, the maximum and minimum optimum temperatures are 70 and 30 °C, respectively. By investigating the employed ILs during the ECODS process, it can be seen that some ILs, including [BMIM]BF₄, [BMIM]PF₆, [C₈MIM]PF₆, [C₄MIM]PF₆, [C₈MIM]BF₄, [C₄MIM]BF₄, [PSPy]₃PW, [OMIM]BF₄, [OMIM]PF₆, [BMIM]₃PW₁₂O₄₀, [BMIM]₃PMo₁₂O₄₀, and [BMIM]₄SiW₁₂O₄₀, lead to an optimum temperature of 30 °C. As mentioned before, one of ILs' features is that cations and anions in their structure determine how catalytic they can be. By investigating these ILs, it seems that the existence of some cations, such as [BMIM], [OMIM], [C₄MIM], and [C₈MIM], as well as of some anions, including BF₄ and PF₆, result in a lower optimum temperature. As can be seen from Table 6, the lowest and highest optimum temperatures, respectively, are 75 and 30 °C during the EODS process. By investigating the ILs used, containing [C₄MIM]Cl/FeCl₃, [OMIM]Cl/FeCl₃, D10Cl/FeCl₃, T4Cl/FeCl₃, and T8Cl/FeCl₃, which led to an optimum temperature of 30 °C, it can be understood that the anion part, which is FeCl₃, could be considered as the main reason to have the lowest optimum temperature. Unlike the EODS and ECODS processes, in the ODS process, the highest and lowest optimum temperatures stand at 90 and 25 °C, respectively.

In a study by Guo et al.,²⁸ CPL-TBAB ionic liquid was used with a temperature range of 303.15–363.15 K. As the solubility of H₂S in the ionic liquid gradually decreased with increasing temperature, 303.15 K was suggested as the optimum temperature.

In a study by Yu and Zhen,¹⁸⁷ removal of naphthenic acids by 2-ethylimidazole ionic liquid was performed in a temperature range of 50–90 °C. At low temperatures, the acid removal rate was low while the possibility of contact between the agent of acid removal and naphthenic acids increased due to a reduction of the diesel viscosity caused by raising the temperature, playing a part in scaling up the efficiency. Higher temperatures emulsified the diesel, hydrolyzed sodium naphthenate, and reproduced naphthenic acid, reducing the efficiency. Therefore, the optimum temperature was 80 °C.

Wu et al. studied¹⁸⁸ the PSMIMHSO₄ ionic liquid within a temperature range of 313–373 K. The ionic liquid highly desulfurized the sample when the temperature was increased.

Since the efficiency did not change after 353 K, the optimum temperature was 353 K.

In a study by Heintz et al.,⁵⁹ the reaction efficiency was reduced by decreasing the gas solubility in the TEGO IL KS ionic liquid, caused by increasing the temperature from 300 to 500 K.

In a study by Zhai et al.,¹⁸² the efficiency dropped from 93% to 70% by increasing the temperature from 298 to 338 K. This came from the decrease of SO₂ absorption by ionic liquids based on hydroxyl ammonium. In a study by Xie et al.,⁶⁴ the efficiency for [BMIM]FeCl₄ ionic liquid at different temperatures, including 30, 40, and 50 °C, was the same. Meanwhile, the efficiency sharply dropped when the temperature reached 60 °C. This means that although the increase of temperature scaled up the catalytic reaction, it reduced the solubility of O₂ and SO₂.

Tang et al. studied the [BPY]HSO₄ ionic liquid within a temperature range of 50–80 °C.¹⁸⁹ By increasing temperature, ionic liquid liquidity and viscosity were enhanced, scaling up the efficiency. At temperatures above 65 °C, the number of olefins available for thiophene alkylation was reduced due to olefin polymerization. Therefore, increasing the temperature to more than 65 °C reduced the efficiency. In this way, excessive olefin oligomerization reduced the alkylation desulfurization and efficiency. Consequently, 50 °C was suggested as the optimum temperature.

Han et al.¹⁹⁰ used a temperature range of 20–50 °C for CH₃CH₂Br liquid. When the temperature increased from 20 to 30 °C, there was an increase in efficiency. By pyrolyzing sulfonium salt at temperatures above 30 °C, the efficiency was largely reduced, proposing that the optimum temperature should be 30 °C.

In a study by Shirani et al.,⁴⁸ a temperature range of 20.2–53.8 °C was considered for [BMIM]Cl/FeCl₃ ionic liquid. In this experiment, as the temperature increased, the efficiency decreased gradually regarding the vaporization of the DBT compound in *n*-hexane and the adsorption process of zeolites. This vaporization was the result of the volatile property and high vapor pressure of DBT. Consequently, 23.2 °C was suggested as the optimum temperature. Wu et al. studied the PSMIMHSO₄ ionic liquid within a temperature range of 313–373 K.¹⁸⁸ By increasing the temperature from 313 to 353 K, the efficiency increased. At temperatures above 353 K, the efficiency leveled off. Thus, 353 K was selected as the optimum temperature.

A study by Li et al.⁷⁷ used a temperature range of 25–50 °C for the ionic liquid. The high viscosity of polymeric ionic liquids at low temperatures prevented the diffusion of sulfur compounds, decreasing the efficiency. As the temperature increased to 45 °C, the viscosity decreased and the efficiency increased. Since the ionic liquid at 50 °C did not have a desirable desulfurization efficiency, the temperature was considered to be 45 °C.

3.3. Effect of Stirring Speed. Technically, the mass transfer rate between phases is of importance when it comes to the desulfurization efficiency. Thus, the effect of stirring speed emerges as the more homogeneous a system is, the higher the mass transfer rate becomes, leading to higher desulfurization efficiencies. Depending on the system that wants to be desulfurized, there is an optimum stirring speed above which emulsion droplets could be damaged.

In a study by Benmabrouka et al.,¹⁷⁰ a stirring speed range of 200–500 rpm was set. By scaling up the stirring speed, smaller droplets were formed and the mass transfer rate increased between the aqueous and the organic phases, raising the

desulfurization. However, the increase of stirring speed caused the formation of stable emulsions and a cream in the aqueous phase. Therefore, the optimum stirring speed was considered to be 400 rpm. In a study by Zhu et al.,^{191,192} a stirring rate within the range of 100–1000 rpm was utilized for the $[(\text{CH}_3)_3\text{N}(\text{nC}_8\text{H}_{17})_3]_2[\text{Mo}_2\text{O}_{11}]$ ionic liquid toward the removal of DBT. When the stirring speed reached 500 rpm, the desulfurization rate increased, while at higher speeds it fluctuated due to the damage of the formed emulsion droplets. This damage came from the situation where the magnet hit the enclosure. Therefore, they considered 500 rpm as the optimum stirring speed. In a study by Ahmed et al.,⁷⁰ the ionic liquid [HMPyrr][TFSI] was used to remove thiophene (T), benzothiophene (BT), and DBT. In doing so, the stirring speeds were set at 600, 800, and 1000 rpm. Since the desulfurization efficiency depended on the contact level between the sample and the ionic liquid, the efficiency experienced an increase by increasing the stirring speed. Because the efficiency was the same for both 800 and 1000 rpm, the optimum speed was 800 rpm. In the experiment on [DMEE][CO₂Et] and [DMAPN][CO₂Et] carried out by Li et al.,⁷⁸ the stirring speed was considered to be between 300 and 1100 rpm. In contrast to the [DMAPN][CO₂Et] ionic liquid, the increase of stirring speed reduced the rate of desulfurization. Therefore, 500 rpm was taken as the optimum speed for the system consisting of these two ionic liquids.

In a study by Zhu et al.,¹⁶⁰ the stirring rate was assumed to be in the range of 100–1000 rpm for the $[(\text{nC}_8\text{H}_{17})_3\text{NCH}_3]_3(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)$ ionic liquid. By increasing the speed from 100 to 500 rpm, the efficiency reached nearly 100%. By keeping the speed increasing from 500 to 750 rpm, no appreciable changes occurred in the efficiency due to the nature of the ammonium quaternary cations (surfactant used) which played an important role in the formation and stability of the emulsion. Therefore, 500 rpm was deemed as the optimum speed.

3.4. Sulfur Structure Nature Affecting Desulfurization Using Ionic Liquids. To desulfurize a system, containing various sulfur compounds, one of factors that comes to attention is the structure of the sulfurs. The structure impacts the desulfurization efficiency and has been largely investigated in terms of the electron density and steric hindrance, which are connected to the catalytic oxidation reactivity.

Lü et al. investigated the reactivity of various sulfur components, including benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene, in the diesel sample. They desulfurized the system using the [Hnmp]HCOO ionic liquid.⁷¹ The catalytic oxidation reactivity of the sulfur components was DBT > 4,6-DMDBT > BT. The proposed reactivity of the sulfur components was mainly related to the electron density of the sulfur atom and the steric hindrance between the atoms.

The minimum electron density for sulfur in benzothiophene (5.696) resulted in the lowest reactivity compared to the other two sulfur components. The difference in electron density between dimethylbenzothiophene and 4,6-dimethyldibenzothiophene (5.758 for dimethylbenzothiophene and 5.76 mmol for 4,6-dimethyldibenzothiophene) was negligible and could be ignored. In refs 125 and 126, the effect of the nature of the sulfur compounds on desulfurization with the help of ionic liquids has also been investigated.

The results obtained by Dharaskar showed that due to the electron density and lower oxidation reactivity, the removal of benzothiophene, thiophene, and 3-methylthiophene had the

lowest amount. However, considering 4,6-dimethyldibenzothiophene, the steric hindrance of methyl substitution at positions 4 and 6 of dibenzothiophene significantly reduced the performance of the ionic liquid at desulfurizing. Moreover, the results showed that dibenzothiophene was more reactive than when dibenzothiophenes were replaced with methyls during the oxidation process. In addition, dibenzothiophene was more reactive in comparison with thiophene, benzothiophene, 3-methylthiophene, and 4,6-dimethyldibenzothiophene during the oxidation process.¹²⁶ The strength of desulfurization is presented in Table 7. As is illustrated by the table, a variety of researchers have studied the strength of desulfurization based on the nature of the sulfur components.

Table 7. Strength of Desulfurization for Different Systems Containing Sulfur Components

name of researchers	strength of desulfurization	ref
Lü et al.	DBT > 4-MDBT > 4,6-DMDBT > BT > 5-MBT	47
Lu et al.	DBT > benzothiophene > thiophene	184
Ma et al.	TS > BT ≫ DBT > 4,6-DMDBT	114, 194
Jiang et al.	DBT > BT > 3-MT	38
Zhu et al.	DBT > 4,6-DMDBT > BT	74
Li et al.	DBT > 4-MDBT > 4,6-DMDBT	214
Zhang et al.	4,6-DMDBT > DBT > BT	169
Ban et al.	DBT > 4,6-DMDBT > BT	209
Zheng et al.	DBT > BT > 4,6-DMDBT	176
Kianpour et al.	DBT > BT > DMDBT	33
Yu et al.	BTO2 > DBTO2 > DBT > BT > diphenyl sulfide > methyl phenyl sulfide > 4,6-DMDBT > thiophene > 3-MT > ethyl sulfide > n-butyl mercaptan	165
Jiang et al.	DBT > BT > 4,6-DMDBT	180
Jian et al.	DBT > BT > 4,6-DMDBT	217
Xun et al.	DBT > BT > 4,6-DMDBT	76
Zhang et al.	4,6-DMDBT > DBT > BT > DT	178
Gao et al.	TS < BT < DBT	54
Huang et al.	DBT > 4,6-DMDBT > BT	84
Li et al.	DBT > BT > 2-MTS	77
Zhao et al.	DBT > 4,6-DMDBT > BT > TS > 3-MT	157
Nie et al.	DBT > BT > 3-MT	162
Xiong et al.	DMDBT > DBT > BT	199
Xu et al.	DBT > BT > 4,6-DMDBT	79

3.5. Influence of Time. To evaluate if a desulfurization process meets economic concerns, one of the determinative factors is the desulfurization time. In effect, when it comes to the effect of time, a lower desulfurization time becomes advantageous as the lower the time is, the smaller the amount of contact is between all employed equipment and the solution, leading a higher efficiency. This is favorable at the industrial scale. Therefore, many have tried to propose a desulfurization method with a lower optimum time. To understand this effect better, the obtained results from the sulfur removal processes, including ODS, EDS, EODS, ECODS, and LLE, along with the ILs used, the removed sulfur components, time ranges, and optimum times have been tabulated in Table 8. Overall, it seems that the EDS process can be conducted at a shorter optimum time, t_0 , compared to others (t_0 : EDS < ECODS < EODS < ODS). This table shows that in the EDS process, polyether-based IL and [TBHPP][Cl] IL helped to have a minimum optimum time. It seems that the [THTDP] cation had better performance to

Table 8. continued

ILs	removed sulfur component	time range [min]	t_0 [min]	ref
EDS				
$[C_2COOCH_3]_m[C_6H_{11}]_n[CN(CN)]_z$				
$[C_2COOCH_3]_m[C_6H_{13}]_n[CN(CN)]_z$				
tributyl (2,3-dihydroxypropyl) phosphonium chloride ([TBHPP][Cl])				
1-butyl-3-methylimidazolium tetrahalogenofosphate (III) ([BMIM][FeCl ₄]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF ₆]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF ₄])	DBT DBT	0–33.33 5–30	5 10	213 226
trihexyl(tetradecyl)phosphonium hexafluorophosphate ([THTDP][PF ₆])	TS, BT, DBT, 3-MT, 4-MDBT, 4,6-DMDBT	5–35	30	206
<i>N</i> -methyl- <i>N</i> -methylimidazolium dimethyl phosphate ([MMIM][DMP])	DMS	0–120	for [MMIM][DMP] and [BMIM][DBP] = 10 for [EMIM][DEP] = 60	31
<i>N</i> -ethyl- <i>N</i> -methylimidazolium diethyl phosphate ([EMIM][DEP])				
<i>N</i> -butyl- <i>N</i> -methylimidazolium dibutyl phosphate ([BMIM][DBP])				
EODS				
<i>N</i> -carboxymethylpyridine hydrogensulfate ([CH ₂ COOHpy]HSO ₄)	DBT	20–40	40	168
1-butyl-3-methylimidazolium chloride iron chloride ([C ₄ MIM][Cl/FeCl ₃])	TS, BT, DBT, 3-MT, 4,6-DMDBT	5–40	40	126
1-octyl-3-methylimidazolium chloride iron chloride ([OMIM][Cl/FeCl ₃])				
dicyclidimethyl ammonium chloride iron chloride (D ₁₀ Cl/FeCl ₃)				
ammonium tributyl-methyl chloride iron chloride (T ₄ Cl/FeCl ₃)				
1-octyl-3-methylimidazolium persulfate ([OMIM] ₂ [S ₂ O ₈])	DBT	15–180	180	215, 216
ECODS				
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF ₄])	BT, DBT, 5-MBT, 4-MDBT, 4,6-DMDBT	0–180	180	47
1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF ₆])				
1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM][PF ₆])				
1-(3-sulfonic group)propyl-3-methylimidazolium phosphotungstate ([MIMPS] ₃ PW ₁₂ O ₄₀ ·2H ₂ O)	DBT, 4,6-DMDBT	10–60	60	74
1-butyl 3-methylimidazolium phosphotungstate ([BMIM] ₃ PW ₁₂ O ₄₀)				
1-butyl 3-methylimidazolium phosphomolybdate ([BMIM] ₃ PMO ₁₂ O ₄₀)				
1-butyl-3-methylimidazolium silicotungstate ([BMIM] ₄ SiW ₁₂ O ₄₀)	BT, DBT, 4,6-DMDBT	0–90	40	176
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF ₄])				
1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM][BF ₄])				
1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF ₆])				
1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM][PF ₆])				
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF ₄])	BT, DBT, DT	10–90	90	121
1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM][BF ₄])				
1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF ₆])				
1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM][PF ₆])	BT, DBT, 4,6-DMDBT	5–30	30	217
1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF ₄])				
1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM][BF ₄])				

Table 8. continued

ECODS	ILs	removed sulfur component	time range [min]	t_0 [min]	ref
1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{MIM}][\text{BF}_4]$)		BT, DBT, 4,6-DMDBT	10–60	60	218
1- <i>n</i> -octyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_8\text{MIM}][\text{BF}_4]$)					
1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{MIM}][\text{PF}_6]$)					
1- <i>n</i> -octyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_8\text{MIM}][\text{PF}_6]$)		BT, DBT, 3-MDBT, NTH, 4,6-DMDBT	0.5–3	1.5	227
<i>N</i> -carboxymethylpyridine hydrogensulfate ionic liquid ($[(\text{CH}_3\text{COOHpy})][\text{HSO}_4]$)		4,6-DMDBT	0–180	180	93
<i>N</i> -methyl- <i>N</i> -methylimidazolium dimethyl phosphate ($[\text{MMIM}][\text{DMP}]$)					
<i>N</i> -ethyl- <i>N</i> -methylimidazolium diethyl phosphate ($[\text{EMIM}][\text{DEP}]$)					
<i>N</i> -butyl- <i>N</i> -methylimidazolium dibutyl phosphate ($[\text{BMIM}][\text{DBP}]$)					
LLC					
($[\text{BMIM}][\text{BF}_4]$), ($[\text{BMIM}][\text{PF}_6]$), ($[(\text{CH}_2)_4\text{SO}_3\text{HMIM}][\text{HSO}_4]$), ($[(\text{CH}_2)_4\text{SO}_3\text{HPy}][\text{HSO}_4]$), ($[(\text{CH}_2)_4\text{SO}_3\text{HTEA}][\text{HSO}_4]$), ($[(\text{CH}_2)_4\text{SO}_3\text{HMIM}][\text{Tos}]$), ($[(\text{CH}_2)_4\text{SO}_3\text{HPy}][\text{Tos}]$), ($[(\text{CH}_2)_4\text{SO}_3\text{HTEA}][\text{Tos}]$)		TS, BT, DBT, 4-MDBT, 4,6-DMDBT	5–30	25	224

remove a variety of sulfur compounds, including TS, BT, DBT, 3-MT, 4-MDBT, and 4,6-DMDBT. Furthermore, Table 6 clearly shows the role of the anion and cation in the structure of the ILs toward the ECODS process, so much so that anion-based ILs, such as BF_4 and PF_6 , had relatively satisfactory results in terms of the optimum time and the variety of sulfur components, including BT, DBT, DT, 5-MBT, 4-MDBT, and 4,6-DMDBT. In the case of cation-based ILs, $[\text{BMIM}]$ - and $[\text{OMIM}]$ -based ILs could deliver reliable results. When it comes to the ECODS process, it appears that FeCl_3 -based ILs could perform better, as opposed to the other employed ILs in this process. In contrast, the ODS process seems to have a different performance. If the variety of the removed sulfur compounds is considered, it can be seen that the effectiveness was in the order 1-ethyl-3-methylimidazolium acetate ($[\text{BMIM}]\text{CH}_3\text{COO}$) > $\text{NMP}\cdot\text{FeCl}_3$ ($\text{NMP} = \text{N-methyl-2-pyrrolidone}$, $\text{C}_5\text{H}_9\text{NO}$) > 1-(2-carboxylic acid) ethyl-3-methylimidazolium bisulfate ($[(\text{CH}_2)_2\text{COOHMIM}][\text{HSO}_4]$).

Yu and Zhen studied¹⁸⁷ the removal of naphthenic acids using 2-ethylimidazole ionic liquid within a time range of 5–25 min. After 5 min, due to the hydrolysis of sodium naphthenate, the reaction equilibrium shifts toward producing naphthenic acids, moving the acid from the ionic liquid phase to the oil phase, reducing the efficiency. Thus, the optimum time should be 5 min.

In Wang and Zhang's experiment,⁶³ when the molar ratio of $\text{FeCl}_3\cdot\text{H}_2\text{O}/[\text{BMIM}]\text{Cl}$ was $M = 0.5$, the absorption of H_2S scaled up after 60 min, and when the time reached 70 min, the absorption trend saw a gradual increase. However, considering $M = 2$, the time for H_2S absorption increased to 170 min. Meanwhile, after this time, the absorption process decreased due to the production of HCl.

In a study by Tang et al.,¹⁸⁹ a time range of 60–110 min was chosen for the $[\text{BPY}]\text{HSO}_4$ ionic liquid. As the amount of sulfur in the sample gradually decreased over time, 90 min was considered as the optimum time. Wu et al.¹⁸⁸ studied the PSMIMHSO_4 ionic liquid. To do so, the experiment was conducted between 5 and 30 min. Initially, the reaction rate was high and the desulfurization rate was the highest. However, after 25 min, the efficiency did not change much. Therefore, 25 min was chosen as the optimum time.

3.6. Effect of Molar Ratio of Oxidant. Since the advent of oxidation-based desulfurization methods, one of the factors that always has been investigated is the amount of oxidizing agent. Thus, a variety of oxidizing agents has been investigated over the years to find an effective one for desulfurization-based purposes. Generally, the increase of oxidants leads to higher efficiencies as more oxidants can remove more sulfur compounds.

Bhutto et al.'s research showed that the H_2O_2 concentration had a significant effect on the desulfurization efficiency. In most cases, the efficiency of desulfurization increased by raising the molar ratio of oxidant to sulfur compound (O/S).¹⁹ Chen et al.¹¹⁹ investigated the amount of oxidant. In doing so, they aimed at oxidizing DBT through a system containing H_2O_2 – $[\text{H}_{\text{tmp}}]\text{Cl}/\text{ZnCl}_2$ at different oxidant to sulfur molar ratios. As shown in Figure 9, the molar ratio of oxidant to sulfur had a considerable impact on desulfurization. There was a slight increase in the efficiency when the molar ratio of oxidant to sulfur changed from 2 to 3 over 30 min, so much so that the efficiency increased from 93.5% to 99.3%. Unbelievably, when the molar ratio of oxidant to sulfur was 4, the DBT removal rate reached 99.9%.

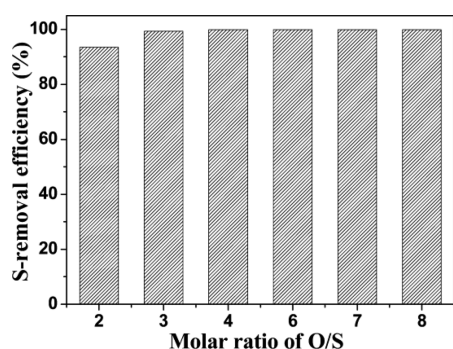


Figure 9. Effect of molar ratio of H_2O_2 to sulfur on desulfurization by $[\text{Hnmp}]\text{Cl}/\text{ZnCl}_2$. Reproduced with permission from ref 119. Copyright 2015 American Chemical Society.

It was expected that if there was much hydrogen peroxide, more sulfur components would be removed. To reach the corresponding sulfur components regarding the ODS reaction stoichiometry basis, 2 mol of H_2O_2 should be considered for 1 mol of DBT. It was anticipated that the molar ratio of oxidant to sulfur was 2. However, the highest sulfur removal rate was 99.9% when the molar ratio of oxidant to sulfur was 4 rather than 2, indicating that a stoichiometric amount of H_2O_2 was needed to remove additional sulfur. This may be attributed to the rate of decomposition and loss of H_2O_2 during the ODS process. Arguably, the desulfurization efficiency was not sensitive when the molar ratio was greater than 4, and the high doses of hydrogen peroxide were economically meaningless. Therefore, the molar ratio of oxidant to sulfur was decided to be 4 as the optimal ratio in this report.¹¹⁹

Table 9. Performance of Desulfurization Methods, Including ODS, EDS, EODS, and ECODS, at Various IL/Oil Ratios

ILs	model oil	removed S components	S-removal efficiency at various IL/oil mass ratios								ref	
			3:1	2:1	1:1	1:2	1:3	1:4	1:5	1:10		
ODS												
$[\text{C}_4\text{MQUIN}][\text{N}(\text{CN})_2]$	dodecane + diesel	DBT	N/A	N/A	100	100	N/A	N/A	95.7	71.9	228	
$[\text{C}_3^3\text{MPy}]\text{FeCl}_4$	<i>n</i> -octane	DBT	N/A	N/A	89	N/A	73.4	N/A	N/A	N/A	196	
$[\text{C}_6^3\text{MPy}]\text{FeCl}_4$	<i>n</i> -octane	DBT	N/A	N/A	88.6	N/A	70.6	N/A	N/A	N/A	196	
$[\text{C}_4^3\text{MPy}]\text{FeCl}_4$	<i>n</i> -octane	DBT	N/A	N/A	86	N/A	68.2	N/A	N/A	N/A	196	
$[\text{C}_4\text{MIM}]\text{Cl}/3\text{ZnCl}_2$	<i>n</i> -octane	DBT	N/A	N/A	87.90	99.99	96.09	57.65	49.1	N/A	69	
EDS												
$[\text{BMTH}][\text{DCA}]$	<i>n</i> -octane	DBT	N/A	66.80	48.00	24.21	17.14	9.43	N/A	N/A	204	
$[\text{BMTH}][\text{DCA}]$	<i>n</i> -hexane + toluene	TS	N/A	60.40	37.29	25.50	16.71	13.71	N/A	N/A	204	
$[\text{BMIM}]\text{PF}_6$	<i>n</i> -octane	DBT	N/A	N/A	32.90	N/A	19.70	N/A	14.2	N/A	226	
$[\text{BMIM}]\text{BF}_4$	<i>n</i> -octane	DBT	N/A	N/A	35.90	N/A	22.40	N/A	17.9	N/A	226	
$[\text{BMIM}]\text{FeCl}_4$	<i>n</i> -octane	DBT	N/A	N/A	69.8	N/A	48.4	N/A	32.1	N/A	226	
$[\text{C}_4\text{MIN}][\text{dcm}]$	<i>n</i> -hexane	DBT	N/A	81.0	65.2	50.5	38.9	26.0	23.5	N/A	207	
$[\text{C}_4\text{MIN}][\text{dcm}]$	<i>n</i> -hexane + toluene	TS	N/A	65.5	48.7	25.0	20.9	18.1	15.7	N/A	207	
$[\text{BMIM}]\text{Cl}/\text{FeCl}_3$	<i>n</i> -octane	DBT	N/A	90	81.3	72.5	67.5	N/A	58.8	N/A	208	
$[\text{C}_1\text{pi}][\text{Lac}]$	<i>n</i> -heptane	DBT	67.0	56.4	41.1	31.1	23.1	N/A	N/A	N/A	58	
$[\text{C}_1\text{pi}][\text{Lac}]$	<i>n</i> -heptane	BT	64.3	54.5	39.4	21.8	12.1	N/A	N/A	N/A	58	
$[\text{C}_1\text{pi}][\text{Lac}]$	<i>n</i> -heptane	TS	47.2	35.4	18.6	15.4	10.3	N/A	N/A	N/A	58	
$[\text{C}_1\text{pi}][\text{Lac}]$	<i>n</i> -heptane	4-MDBT	57.6	48.3	32.2	26.3	20.5	N/A	N/A	N/A	58	
$[\text{BPy}]\text{BF}_4$	<i>n</i> -heptane + xylol	T	N/A	N/A	45.5	28.6	16.9	N/A	N/A	N/A	56	
$[\text{BPy}]\text{NO}_3$	<i>n</i> -heptane + xylol	T	N/A	N/A	30.1	19.1	9.4	N/A	N/A	N/A	56	
$[\text{BPy}]\text{Ac}$	<i>n</i> -heptane + xylol	T	N/A	N/A	32.1	20.3	10.2	N/A	N/A	N/A	56	
$[\text{EPy}]\text{BF}_4$	<i>n</i> -heptane + xylol	T	N/A	N/A	21.8	12.6	8.9	N/A	N/A	N/A	56	
$[\text{EPy}]\text{NO}_3$	<i>n</i> -heptane + xylol	T	N/A	N/A	27.1	17.3	13.8	N/A	N/A	N/A	56	
$[\text{EPy}]\text{Ac}$	<i>n</i> -heptane + xylol	T	N/A	N/A	23	15.7	9.7	N/A	N/A	N/A	56	
$[\text{BMIM}]\text{Cl}/\text{ZnCl}_2$	<i>n</i> -octane	DBT	N/A	54.6	36.4	22.1	15.3	11.5	9.1	N/A	210	
$[\text{BMIM}]\text{Cl}/\text{ZnCl}_2$	<i>n</i> -hexane + toluene	TS	N/A	47.1	32.8	18.6	12.9	10.3	8.1	N/A	210	
$[\text{C}_{20}\text{COOCH}_3\text{ImC}_6\text{H}_{13}][\text{N}(\text{CN})_2]$	<i>n</i> -dodecane	DBT	N/A	80.3	61.9	N/A	N/A	N/A	N/A	N/A	212	
$[\text{EMIM}][\text{MeSO}_4]$	<i>n</i> -hexane	DBT	N/A	N/A	70	40	N/A	N/A	15	N/A	229	
$[\text{MMIM}][\text{MeSO}_4]$	<i>n</i> -hexane	DBT	N/A	N/A	40	23	N/A	N/A	10	N/A	229	
$[\text{BMI}][\text{N}(\text{CN})_2]$	<i>n</i> -hexane + toluene	TS	N/A	62.6	47.5	29	22	N/A	17	N/A	230	
EDS												
$[\text{BMI}][\text{N}(\text{CN})_2]$	<i>n</i> -hexane	DBT	N/A	78.9	69.5	50	44	N/A	30	N/A	230	
$[\text{OMIM}][\text{BF}_4]$	<i>n</i> -hexane	DBT	N/A	N/A	39.8	24.7	N/A	N/A	16.1	N/A	231	
$[\text{PMIM}][\text{Tf}_2\text{N}]$	<i>n</i> -hexane	DBT	N/A	N/A	52	37	N/A	N/A	20	N/A	232	
EODS												
$[\text{C}_4\text{MIM}]\text{Cl}/\text{FeCl}_3$	<i>n</i> -dodecane	DBT	N/A	N/A	92	N/A	86.5	N/A	69.3	N/A	126	
$[\text{OMIM}]_2[\text{S}_2\text{O}_8]$	<i>n</i> -dodecane	DBT	N/A	N/A	97.8	68.9	44.4	22.5	N/A	N/A	215	
ECODS												
$[\text{C}_4\text{MIM}]\text{Cl}/2\text{ZnCl}_2$	<i>n</i> -octane	DBT	N/A	N/A	98.1	96.7	95.4	94.5	93.8	N/A	221	
$[\text{HSO}_3\text{-C}_4\text{MIM}]\text{HSO}_4$	<i>n</i> -octane	DBT	N/A	N/A	99.96	98.88	97.09	95.98	92.23	N/A	221	

3.7. Effect of Mass Ratio of Ionic Liquids. During desulfurization of fuels using ionic liquids, an essential factor is the amount of the ionic liquid due to the high cost of it. Therefore, a lower amount of ionic liquids for a desulfurization system is favorable. Consequently, investigation of the mass ratio of ILs to oils comes to attention. To better understand the performance of the studied desulfurization systems, including ODS, EDS, EODS, and ECODS, at various IL:oil mass ratios, Table 9 is presented. As shown in this table, as a general trend, an increasing amount of ionic liquids (from 1:10 to 3:1) serves to have a higher desulfurization efficiency. By reviewing the tabulated data in Table 9, it was found that the mass ratio did not largely affect the sulfur partition coefficients when it came to physical extraction. However, in the case of chemical extraction, this factor might impact the partition coefficients. Generally, those ILs that have a lower viscosity could make the sulfur partition coefficients less sensitive, unlike higher viscosity ILs. In the ODS process, the system had the highest desulfurization efficiency at an IL:oil mass ratio of 1:1, except for the system using $[C_4MIM]Cl/3ZnCl_2$. This can be justified due to a reduction in the oxidant:sulfur molar ratio. Ideally, a reduction of the oxidant:sulfur molar ratio results in less oxidization of the sulfur components.⁶⁹ It was claimed that the IL phase can extract more DBT when the IL:oil mass ratio scales up.²²⁴ In contrast to the ODS process, it seems that the EDS process depends more upon the amount of ILs. From Table 9, it can be seen that higher desulfurization efficiencies mostly can be grouped in an IL:oil mass ratio of 2:1. However, when it comes to the EODS and ECODS processes, the desulfurization efficiencies are at the maximum when an IL:oil mass ratio of 1:1 is employed. By having an in-depth view to Table 9, it could be realized that those ILs with the anion part of $FeCl_3$ could show better performance compared to those with $FeCl_4$.

3.8. Molar and Mass Ratios of Catalysts Influencing Desulfurization. At an industrial scale, a serious concern is the cost of the process. As is mentioned before, use of a catalyst has proven to be effective in terms of fuels desulfurization, justifying why researchers have employed a variety of catalysts in different desulfurization methods. However, catalysts are usually expensive, emphasizing for the need to find an optimum ratio of catalysts toward fuels desulfurization.

In the literature,¹⁶⁶ the effect of the molar ratio of DBT to catalyst has been investigated. Table 10 shows the removal of

Table 10. Influence of DBT/Catalyst (Molar Ratio) On Desulfurization^a

entry	1	2	3	4
$n(\text{sulfur})/n(\text{catalyst})$	200:1	150:1	100:1	50:1
sulfur removal percent	86.7	90.6	97.3	98.3

^aReproduced with permission from ref 166. Copyright 2008 American Chemical Society. Reaction conditions: $T = 70\text{ }^\circ\text{C}$, $t = 3\text{ h}$, model oil = 5 mL, $[BMIM]BF_4 = 1\text{ mL}$, $[n(H_2O_2)/n(DBT)] = 2:1$

DBT from an oil sample after catalytic oxidation and extraction. When the molar ratio of DBT to catalyst dropped from 200:1 to 50:1, the desulfurization efficiency increased from 86.7 to 98.3%. As the amount of catalyst in the ECODS system increased, desulfurization saw an increase. This experiment proved that the catalyst had a great role to play in affecting the reaction activity.

Shao et al. studied the influence of the catalyst:oil (from 0.0025 to 0.03) mass ratio to remove 4,6-dimethyldibenzothiophene through a system containing $[BMIM]DBP$,

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and H_2O_2 . According to Figure 10, when the mass ratio reached from 0.0025 to 0.02, the sulfur

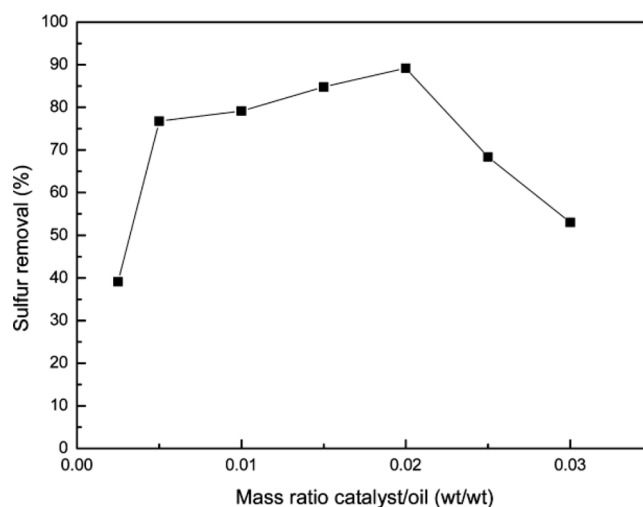


Figure 10. Effect of catalyst/oil mass ratio on 4,6-DMDBT removal by $[BMIM]DBP$. Reproduced with permission from ref 93. Copyright 2014 American Chemical Society.

removal rate increased. However, against the expectations, by increasing the mass ratio to 0.03, the rate of desulfurization increased. This behavior may come from the situation in which the additional catalyst was not completely dissolved in the $[BMIM]DBP$ ionic liquid.⁹³

4. SUMMARY OF CHALLENGES AND PERSPECTIVES

Over the years, desulfurization of fossil fuels has become an important subject due to environmental and economic concerns. In this way, HDS was introduced as an initial stage toward reaching the goal. However, it has several disadvantages (e.g., higher operating conditions). Such drawbacks have persuaded and motivated researchers to develop new methods, such as ODS, EDS, EODS, ECODS, and LLE. Each of these methods reaches a high efficiency if their key parameters are optimized. In this respect, ionic liquids have found a promising place when they are used in these methods, even though they have some disadvantages, such as high viscosity and high prices. In previous sections, they were reviewed in detail, including key factors affecting them. The ODS process has been introduced as a promising applicable method to the industry where fossil fuels can be economically and environmentally desulfurized. However, the ODS process suffers do not have an effective oxidant agent and ionic liquid. In other words, there should be research performed to find a new oxidant that should have high selectivity and availability as well as meet economic and environmental concerns. Apart from such features, it should be free of any harm when it comes to storage, transport, and use. A further parameter affecting the operating conditions of the ODS process is the ionic liquids used. Currently, the most investigated ionic liquids can bring high efficiency at relatively high temperatures ($T > 50\text{ }^\circ\text{C}$) over a relatively long period of time ($t > 100\text{ min}$). This means a new ionic liquid should be introduced that can be used in the ODS process while it helps to have lower temperatures and shorter operating times. Over the past few years, the EDS process has exceeded ODS as it has a simple procedure. It also has normal operating conditions (ambient temperature and atmospheric pressure) and marginal

effects on the quality of fuels. There is a critical parameter impacting the EDS process which is the extractant, even though there are other factors, such as temperature, mass ratio (fuel:solvent), and time. Basically, the used extractant plays a great role in increasing the desulfurization efficiency. Apart from many investigations, the absence of a new ionic liquid as an extractant is being sensed as the introduced molecular solvents have special issues. A new ionic liquid in the EDS process is required to compensate for three main features, namely, being physically and chemically stable and environmentally friendly. Facing difficulties in the HDS process, a further desulfurization process has been proposed based on the combination of the ODS and EDS processes, known as the ECODS process. It was claimed that it performs better than EDS; however, it has a higher operating temperature and a relatively long operating time compared to EDS. Since it is based on ODS and EDS, there are also the same gaps in ECODS. In the competitive way of developing new methods toward fuels desulfurization, the ECODS process was proposed. It seemed that the key factor governing the efficiency of ECODS was the type of catalyst apart from the kind of ionic liquid, meaning that higher catalytic activities are of high importance. This can be achieved using shorter alkyl branches. However, using a new ionic liquid that increases the catalytic activity and the oxidation rate is necessary. Apart from these gaps, as the ECODS process is somehow built on the EDS and ODS processes, the same gaps also should be bridged in ECODS. A further desulfurization method that has not been studied largely is the LLE process in which the type of solvent has a great role to play in scaling up the desulfurization efficiency. Since common solvents are often flammable, highly volatile, and toxic, ionic liquids have been introduced as an alternative in this process. Furthermore, it seems that this method uses less energy compared to others. However, it suffers from an effective solvent that helps to easily separate aliphatic and aromatic hydrocarbons or aliphatic alcohols and hydrocarbons when it comes to challenges, such as having almost similar boiling points and azeotropes. Although the use of ionic liquids has helped to cope with some common problems in the industry, opting for an appropriate ionic liquid is still challenging as the chosen ionic liquid should rise to some challenges (e.g., stability, corrosion damage, and cost).

Apart from the mentioned factors affecting the studied desulfurization methods, there are still other elements, including reusing ionic liquids, stirring speed, sulfur structure, molar and mass ratios of oxidants, ionic liquids, and catalysts, that have a role to play in optimizing such methods. Undoubtedly, the reuse of ionic liquids is a feature to minimize the high costs. In other words, the more times the ionic liquids are recycled, the lower the costs the industry will face. Technically, challenges of recycling ionic liquids appear when they are recycled more as their performance decreases due to the increase of oxidation products and loss of ionic liquids during separation compared to their original state. In addition, when it comes to choosing an ionic liquid for the desulfurization methods, high mobility and flexibility should be considered, which need much time and effort to select as other parameters affecting desulfurization also should be considered. Since desulfurization also depends upon the mass transfer rate, the emulsion stability and formation, and the contact level between fuels and ionic liquids, stirring speed enters into the set of factors impacting the desulfurization efficiency. This means that an optimum stirring speed should be considered at which there is a high mass transfer rate, large contact level, and minimum damage to the formation and

stability of the emulsion. This is yet challenging as proposing an optimum stirring speed is strongly dependent on the type of sulfur, the employed ionic liquid, the desulfurization method, and other investigated parameters. A further parameter that cannot be changed is the sulfur structure contained in the fuels. The nature of sulfur determines the type of ionic liquid, the desulfurization method, and so forth. Before choosing a desulfurization method and the related components engaged in it, it is wise to understand what sulfur is contained in the fuels and is needs to be desulfurized. Basically, three features of sulfur compounds dominate the desulfurization efficiency, the catalytic oxidation reactivity, the electron density, and the steric hindrance. Generally, higher catalytic oxidation reactivities and greater electron densities lead to a higher desulfurization efficiency. Moreover, the molar ratio of oxidant is directly connected to the desulfurization efficiency, meaning a higher ratio brings greater efficiency. However, as discussed earlier, commonly used oxidants have disadvantages, which motivate researchers to synthesize new oxidants. Another factor affecting desulfurization is the volume ratio of ionic liquids to fuels. A high volume ratio of ionic liquids to fuels could decrease the desulfurization efficiency as a sufficiently mixed mixture cannot be achieved. When it comes to the mass ratio of ionic liquids to fuels, desulfurization experiences a maximum level at a favorable amount of ionic liquid, depending on the molar ratio of oxidants to sulfur components, the type of ionic liquid, and other investigated factors. Thus, finding an optimum mass ratio of ionic liquids to fuels not only takes long time but also costs more.

In the ECODS process, decreasing the molar ratio of sulfur compounds to catalysts could positively impact the desulfurization efficiency, whereas increasing the mass ratio of catalysts to fuels could decrease the desulfurization efficiency as excess catalyst cannot be well dissolved. Although this shows a relatively high amount of catalyst should be in the process, exceeding an optimum level results in decreasing the desulfurization efficiency.

5. CONCLUSION

In this work, a comprehensive review of desulfurization methods, including hydrodesulfurization, oxidative desulfurization, extractive desulfurization, extractive oxidative desulfurization, extractive and catalytic oxidative desulfurization, and liquid–liquid extraction, was performed to provide future researchers with optimized conditions. By doing so, a variety of factors affecting desulfurization using ionic liquids were identified, temperature, time, stirring speed, recycling ionic liquids, sulfur structure nature, molar and mass ratios of oxidant, ionic liquids, and catalysts.

Regarding time and temperature factors, EDS performed better than ODS as the temperature and time conditions could be better controlled during the EDS method as opposed to ODS. Regarding the same factors, ECODS was better, unlike ODS (EDS > ECODS > ODS). Comparisons also showed that the optimized operational conditions of ECODS were closely connected with those of ODS. By reviewing the effect of time, it was also understood that when a system reached the equilibrium state, the efficiency could not increase significantly.

The stirring speed was investigated as a further factor in the desulfurization efficiency, showing that there should be an optimum stirring rate to reach a high efficiency. In this regard, it was shown that a high stirring speed could damage the formed emulsion droplets. For a better understanding of the factors governing the desulfurization process, the sulfur structure nature

also was investigated through reviewing the literature. It was shown that the time needed and the efficiency for the desulfurization process depended upon the structure as the sulfur structure could affect the performance of the ionic liquids.

According to economic considerations, recycling ionic liquids also was studied by reviewing the related literature, indicating that it was a key to justifying the use of ionic liquids in the desulfurization process as they could be used several times. However, it was also found that there could be a decrease in the efficiency as the number of times of recycling increased mainly because oxidation products increased and the employed ionic liquids were lost during the used separation methods.

By reviewing the literature on the molar ratio of oxidants to sulfur, it was found that there was a direct relationship between this ratio and the desulfurization efficiency. It was also shown that the optimum ratio should be 4. Furthermore, it was shown that the mass ratio of the ionic liquids as well as that of the catalyst had a limited effect upon the desulfurization efficiency, meaning that exceeding an optimum amount could result in a decrease in the efficiency rate. In this direction, the impact of the IL:oil mass ratio was studied in detail, which showed a direct impact on the desulfurization efficiency. In this regard, it was indicated that the EDS process was more dependent on this ratio. By reviewing the results from the literature on the effect of the mass and molar ratios of catalysts on the desulfurization efficiency, it was found that an increase of catalyst decreased the desulfurization efficiency as a general trend. However, an excess amount of catalyst led to a reduction in the efficiency as extra catalyst could not be effectively dissolved.

This review revealed that ionic liquids had high capability to be employed for desulfurization as they had not only high performance but also could be used several times compared to catalysts.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.1c03974>.

Used ionic liquids in ODS along with experimental conditions and obtained results; use of ionic liquids in EDS with the applied experimental conditions and their results; EODS using ionic liquids along with experimental conditions and obtained results; ECODS using ionic liquids with experimental conditions and their results; use of ionic liquids in LLE along with experimental conditions and their results (PDF)

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Notes

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