



Review article

Deep eutectic solvents as alternative green solvents for the efficient desulfurization of liquid fuel: A comprehensive review

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ABSTRACT

Increase in the requirement of energy consumption has been followed by a consistent rise in sulfur emission with economic and health issues. Moreover, it considerably decreases the efficacy of developed emission control systems of diesel engines, thus ultimately harms the atmosphere. It leads to a strict sulfur discharge limit to approximately 15 ppm and sequentially served as a goal for investigating different desulfurization technologies. Hydrodesulfurization, a conventional refinery desulfurization process is operated at higher pressure and temperature, employing expensive catalysts and hydrogen gas. This review aims to consider the merits and demerits of main areas of the substitute desulfurization processes, comprising adsorptive, extractive, oxidative, and biodesulfurization and comprehensively discuss the role of DESs emphasizing on the factors affecting in extractive and oxidative desulfurization. Different factors such as DESs selection, extraction temperature, extraction time, DESs regeneration, and multistage extractions are considered that affect the desulfurization efficiency. Deep eutectic solvents explored in 2001, a less toxic solvent have been keenly investigated as an alternative solvent for extractive desulfurization since 2013. DESs showed a higher capability for sulfur elimination. Low synthetic cost and economical raw materials, less solvent to feed ratio, and valuable green characteristics show DESs suitable for the desulfurization process.

1. Introduction

Sulfur compounds are mostly produced from the utilization of fossil fuels such as diesel, gasoline, and kerosene, which establishes great threats to the environment and human health. During combustion, various oxides of sulfur are produced. It is well-known that SO_x causes considerable challenges to an environment such as acid rain, agricultural production, and on human beings, such as cancer and respiratory diseases. Petroleum refining industries are facing many technical problems in pumping, pipelines, and refining equipment due to the occurrence of sulfur compounds in fuels. Sulfur oxides, mainly, sulfur dioxide are among the most hazardous acidic gases and air contaminating pollutants. Extreme contact with SO₂ could result in lung diseases for instance chronic bronchitis, emphysema, and asthma, and can cause neurological ailments as well [1].

Moreover, SO₂ reacts with vapor which leads to acid rain and fog and causes erosion of buildings, varies pH of water (ocean), and soil which badly disturbs marine life. In other words, sulfur dioxide as acid rain has irreversible outcomes on environmental stability. Among the major contributors of SO₂ emissions are crude petroleum refineries, industrial boilers, smelting industries, automobiles, volcanic activity, and electricity production by coal power plants [2]. Sulfur is present in various forms in fuel such as thiophene, sulfides, and disulfides [3]. Hence, monitoring bodies are enforcing progressively strict guidelines with concern to the extreme level of sulfur compounds in transportation fuel [4]. The process by which sulfur compounds are eliminated from the fuel is termed as desulfurization. Hydrodesulfurization (HDS), the traditional method includes the reaction of hydrogen gas with sulfur compounds at elevated temperature and pressure, with the consumption of costly catalysts [5]. Moreover, it lessens the octane grade of the gasoline

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and discharges poisonous H₂S gas [6].

Recalcitrant sulfur compounds such as dibenzothiophene are especially difficult to eliminate by this process. Using HDS, to further reduce the sulfur content would need more extreme conditions and high operating costs than those which are currently employed. Hence, there is an intense demand to find a substitute for desulfurization methods. Different organosulfur compounds present in the fuel are shown in Fig. 1. Various approaches have been investigated comprising microwave, ultrasound, adsorption, extraction, bacterial use, and electrical energy [7].

Deep eutectic solvents (DESs), analogues to ILs, were first proposed by Abbott and are composed of the hydrogen-bond acceptor (HBA) and hydrogen-bond donor (HBD), which formed a eutectic mixture [8]. DESs have been gaining a lot of attention due to their versatility, simple and quick preparation without any requirement of purification. Hydrogen bonding is responsible for the formation of DES (room temperature liquid phase), while the less lattice energies of HBAs and HBDs huge asymmetric ions result in less melting temperatures [9]. DESs have the potential of selectively removing organosulfur compounds from fuel to achieve deep desulfurization with low melting points and vapor pressure [10]. From an environmental and economic aspect, it's significant to reduce solvent utilization, in the case of DESs, the interesting feature is its reusability.

2. Overview of fuels desulfurization technologies

The desulfurization of fuels has turned out to be a part of huge concern for investigators in current years. It is because of progressively strict regulations enforced by monitoring organizations and a drop in the grade of extracted fuel owing to the reduction of fuel resources. The most easily accessible sweet (low sulfur) crude reservoirs have been exhausted. Hence, the increase in demand for sour (high sulfur) crude extraction has become crucial [11]. The ancient remains of animals and plants formed the black or brown flammable liquid, crude oil (petroleum) which is a complicated mixture of various chemical compounds [12]. It consists of 85–89% carbon, 10–13% hydrogen, sulfur 0.25–4% along with oxygen and nitrogen (combined less than 1%), and also a little quantity of metals [13].

Sulfur is present inherently in raw fuel in form of organosulfur compounds or free elemental sulfur. The level of sulfur in crude fuel differs with the place from which it is obtained (depending on the site,

almost zero to 8 wt%) [14]. Then petroleum is distilled into various fractions corresponding to the difference in their boiling point constituents, denser cuts include the higher proportion of sulfur. A diverse class of S-compounds is expected to be present in various fractions [15]. Hydrodesulfurization, as a traditional process [16] is not appropriate to encounter the progressively strict guidelines. Thus, for making clean fuel, substitute desulfurization technologies are required. Presently, oxidative, biodesulfurization, extractive, and adsorptive desulfurization as alternative technologies are used [17]. These processes may be utilized as complementary methods in addition to HDS or as a replacement of HDS.

2.1. Hydrodesulfurization

In petroleum industries, the most traditional and well-studied technique used is hydrodesulfurization (HDS) [18]. At least, three HDS units are required in usual western oil refineries to process several diverse feeds. In 1950, hydrodesulfurization was firstly patented by Raymond Fleck and Paul Nahin of Union Oil and sustained to be the leading process of desulfurization in fuel processing plants [19]. HDS includes the reaction of H₂ gas with S-compounds to produce hydrocarbons (HC) and H₂S, which is eliminated through amine washing employing the Claus method. The reaction conditions in HDS are 20–130 atmospheric pressure and temperature of 300–400 °C. Hence, severe conditions are required for heavier feeds. The catalysts commonly used are NiMo/γ-alumina and CoMo/γ-alumina, which are initiated through sulfiding [20].

Typically HDS is supported in a trickle-bed reactor (TBR) [21]. By escalating the harshness of HDS conditions, increased desulfurization is possible, though the higher temperature may increase the coke generation affecting the catalyst inactivation and higher pressure may result in increasing the olefin saturation, which ultimately declines the octane grade of gasoline. However, the HDS unit design limits the severity of the process [22]. S-compounds present in fuel are generally sulfides, mercaptans, H₂S, disulfides, benzothiophene (BT) and its derivative, and thiophene and its derivative. The following sequence regarding the reactivity of sulfur compounds [23]:

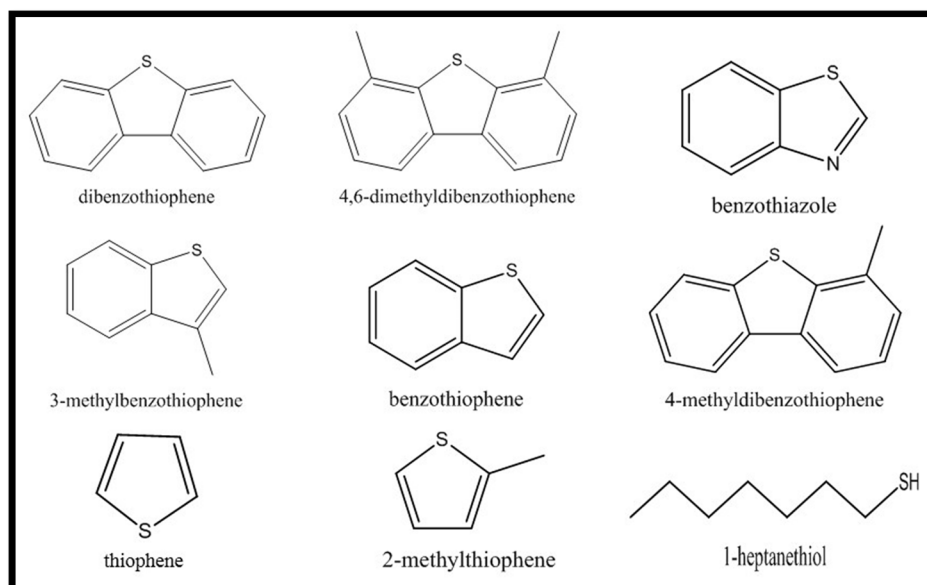
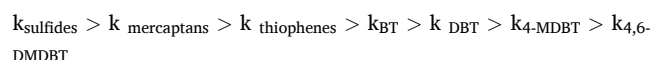


Fig. 1. Possible organosulfur compounds present in the fuel.

4,6-dimethyldibenzothiophenes as sterically hindered compounds react at a slow rate due to alkyl substituent on 4 or/and 6 site protect the surface of catalyst from S-atom and BT core is planar because of aromaticity. Consequently, sterically hindered compounds should be saturated first as a result, 1 or 2 of 6-carbon rings are no longer aromatic, so permitting molecule to twist and the surface of the catalyst to approach S-atom [19]. Thus, sulfur compounds such as sulfides, thiols, and disulfides can be effectively eliminated by HDS. Though S-compounds for instance dibenzothiophene (DBT), benzothiophene (BT), and its alkyl derivatives are tricky to eliminate, therefore they are termed as recalcitrant S-compounds [24]. The cost of HDS is high but, presently, it is considered as an economical desulfurization process. Many problems arise such as consumption of more hydrogen, a decrease of catalyst lifespan, and increased capital and operating costs when HDS is applied for treating the refractory S-compounds [25].

The desulfurization cost would be four times larger for decreasing the S-content from 200 to 50 ppm. Hence new innovative methods are effectively planned to enhance the current HDS by emerging more efficient catalysts and upgrading the reactor designs [26]. Further approaches for the advancement of HDS have been also recommended like the elimination of nitrogenous compounds before HDS, as they can inactivate the catalyst of HDS [27]. Table 1 sums up the benefits and drawbacks of HDS.

2.2. Biodesulfurization

Biodesulfurization (BDS) is another substitute process for the desulfurization of fuels. In this method, microorganisms are used to eliminate sulfur compounds present in the fuel. Microorganisms need sulfur to live. However, the sulfur atom is usually present in a few microorganism enzyme cofactors, proteins, and amino acids. Up to now, BDS has been established by different routes: In 4S route, the first attack is on the sulfur atom; In the Kodama route, the first attack is on the carbon atom [28]. Recently, BDS has fascinated interest as a potentially green process. Numerous genus of bacteria which can desulfurize the fuel has been recognized now comprising *Rhodococcus* spp, *Brevibacterium*, *Pseudomonas*, *Arthrobacter*, and *Gordona*. The possible uses of BDS comprise significantly less discharge of greenhouse gases, lower capital and operating costs, enzyme specificity, and significant byproducts, specifically for DBT and its derivative [29].

Though, BDS has numerous downsides which restrain it from being practically applicable. For instance, the BDS is comparatively time-consuming in contrast to chemical reactions, biomass is mandatory in huge quantities (generally biomass 2.5 g/sulfur g), and susceptible microorganisms must be kept alive in occasionally harsh input circumstances present in refineries [29]. Additionally, the desulfurization rate is significantly reliant on pH, dissolved oxygen concentration, and temperature, and these parameters must be cautiously regulated and examined. The key purpose for not employing BDS currently is that numerous biochemical routes utilized by microorganisms (MO) for sulfur removal are also destructive paths for hydrocarbons (HC), which result in an undesirable reduction in the energy content of fuel [30].

Many reports have been studied that using bacteria, dibenzothiophene, and alkyl sulfides can be converted. Though there are few details of recognizing bacteria to eliminate BT and fewer for thiophene (Th). Overall, BDS is not capable to reduce the sulfur quantity to very less concentration, approximately 10–100 ppm. Perhaps this is the outcome of larger bacterial action at greater concentration. Though there are numerous obstacles regarding the actual feasibility of BDS, searching for the new microbial strain to remove S-compounds in fuel persists as the most significant in biotechnological investigations [14]. Table 1 states the pros and cons of BDS.

2.3. Adsorptive desulfurization

A substitute opportunity to separate the sulfur compounds from fuels

Table 1
Summary of different desulfurization methods.

Different desulfurization methods	Advantages	Disadvantages
HDS	<ul style="list-style-type: none"> ✓Well-known mechanism and conventional technology [10]. ✓In light fractions, hydrogen gas is feasibly applied for desulfurization.✓Removal of sulfides, thiols, and thiophenes successfully [15]. 	<ul style="list-style-type: none"> ✓Needs high pressure and temperature [41]. ✓Employs expensive catalyst.✓Does not eliminate 4,6-DMDBT. ✓Decreases octane grade of gasoline [15].✓Does not eliminate refractory S-compounds efficiently [15].
BDS	<ul style="list-style-type: none"> ✓Modest operating conditions i.e. lower pressure and temperature. ✓Environmentally friendly with fewer greenhouse emissions.✓Produces less acid rain gases [7].✓High specificity of the enzyme [3]. ✓Lower capital and operating costs [29].✓High valuable by-products [3].✓Recalcitrant S-compounds can be removed under mild pressure and temperature [7]. 	<ul style="list-style-type: none"> ✓Does not employed commercially because of sanitation, handling, and storage.✓Reduces fuel value.✓Costly and tricky to incorporate with the current operation.✓Very slow rate [29].✓Deep desulfurization cannot attain (10–100 ppm sulfur) [15].✓Cost of culture media to cultivate the microorganisms [7]. ✓Sensitive microorganisms [3].
ADS	<ul style="list-style-type: none"> ✓Operates at a lower temperature [23].✓No need of H₂ [3].✓No release of H₂S gas [23].✓Capability to eliminate refractory S-compounds. 	<ul style="list-style-type: none"> ✓High amount of sorbent is required for surface reactions.✓Some adsorbents are investigated with higher specificity for the adsorption of recalcitrant S-compounds.✓Poor selectivity of S-compounds [3].✓Numerous adsorbents have less adsorption capability, hence demanding multiple large adsorbent beds [3].
ODS	<ul style="list-style-type: none"> ✓Non-catalytic process.✓Low-cost raw materials.✓For light fractions, the mechanism is well studied.✓The rate of reaction is larger as compared to hydrodesulfurization.✓No use of costly H₂ gas [3]. ✓Minor temperature and pressure [15]. ✓Complementary chemistry to HDS [15].✓Recalcitrant S-compounds easily converted [3] 	<ul style="list-style-type: none"> ✓Robust oxidizing agent e.g. H₂O₂ is costly for larger-scale applications [10].✓No widespread study on heavy fractions e.g. bitumen [10].✓Catalyst is required for deep desulfurization [10]. ✓More reactions on oxidation may result in the production of non-essential products particularly when H₂SO₄ is utilized.✓Tough to convert thiophene [29].
EDS	<ul style="list-style-type: none"> ✓Operating conditions viz. lower pressure and temperature [23].✓Easy to integrate with a refinery method.✓Solvents such as DESs can be recycled✓Does not require hydrogen [23]. ✓No use of catalyst [28]. ✓Does not react with desired fuel oils [28].✓Process simplicity and less energy input.✓Extracted S-compounds can be utilized as raw materials [28]. 	<ul style="list-style-type: none"> ✓Solubility of sulfur in solvents is restraint therefore appropriate choice of solvent is necessary.✓With the oxidation of sulfur, higher efficiency can be achieved. ✓The task to eliminate S-compounds from fuel without extracting preferred sulfur-free hydrocarbons [15].

is the adsorption desulfurization method (ADS). In this (non-reactive adsorption) route, S-compounds are specifically adsorbed by adsorbent without any reaction. While adsorbent is retained on an unreactive, porous substance to enhance the surface area. The adsorption of S-compounds above adsorbents e.g., zeolites, alumina, zinc oxide, activated carbon, and aluminosilicates, etc. has been studied. It is reported that some adsorbents are efficient for specifically recalcitrant S-compounds for instance 4,6-dimethyldibenzothiophene [3]. The possible benefits of ADS are minor operational temperature and less S-level which might be attained if recalcitrant S-compounds are eliminated [23].

The perfect adsorbent should have high adsorption capability, adsorb the sulfur compounds quickly, and have the ability to regenerate. Hence, adsorbents must particularly adsorb recalcitrant aromatic S-compounds without adsorbing other aromatic hydrocarbons in liquid fuels that is a big task. However, ADS can be very effective, adsorbent regeneration is substantially a restraining step where adsorbents often need calcination or solvent washing. Few reports showed the low adsorption capacity of adsorbents and to overcome this phenomenon, multiple and large adsorbent beds would be compulsory to keep the process continuous and minimize the replacement. Subsequently, numerous investigations have been explored to enhance the surface area of adsorbent materials along with their low cost [3]. The efficiency of ADS is directly linked to the attributes of the adsorbent nanomaterials: adsorption capability, regenerate-ability, durability, and selectivity to sulfur derivative compounds relative to fuels. Table 1 summarizes the advantages and downsides of ADS.

2.4. Extractive desulfurization

Extractive desulfurization (EDS) employs the consumption of extractant solvents to particularly eliminate the S-compounds from liquid fuels. Because the S-compounds have larger solubility as compared to other hydrocarbon compounds. Various traditional extraction solvents involve in EDS are for instance methanol, acetonitrile (AcN), dimethyl sulfoxide (DMSO), pyrrolidones, dimethylformamide (DMF), and other volatile organic compounds (VOCs) [31]. The consumption of organic solvents associated with the challenges such as flammability, volatility, toxicity, and sulfur elimination efficacy is not significant [15]. The potential benefits of EDS are that it does not require hydrogen or catalyst and can be operated at mild conditions [15].

Additionally, EDS specifically extracts sulfur compounds from liquid fuel without reacting with other preferred hydrocarbons; and removed S-compounds can be utilized as raw material [28]. Due to same polarity of aromatic S-compounds and aromatic sulfur-free hydrocarbons in liquid fuels, the selection of extractants is of huge significance [15]. It is investigated that EDS causes a huge quantity of co-extraction of desired sulfur-free hydrocarbons with little proportion of sulfur removal (less than 50%). By oxidizing the sulfur compounds (ODS) before extraction, the amount of sulfur extraction and selectivity of desired compounds can be increased. It enhances their polarity resulting in extraction procedures becoming simpler because of the improved partition coefficient of S-compounds in the extractant [15]. Nowadays, ionic liquids and deep eutectic solvents are used as extractants in EDS. The investigators have used a diversity of ionic liquids structures to eliminate S-compounds, meanwhile, they are beneficial owing to thermal stability, low volatility, and high solubility for numerous inorganic and organic compounds [32].

Though consumption of ILs has certain limits, for instance, weak efficacies in the EDS, and few of them are toxic and hazardous. Thus, ILs implementation in the industry will exhibit huge tasks as they can produce environmental contamination [33]. To prevent several downsides of employing ILs, DESs attained massive attention in the research community because of several benign attributes, outstanding chemical and physical properties, generally biodegradable, inexpensive, non-toxic, and preparation process can be done at close to room conditions

[34]. Table 1 summarizes the advantages and disadvantages of EDS. The EDS employing DESs will be further discussed after DESs are introduced in Section 3 in detail.

2.5. Oxidative desulfurization

Oxidative desulfurization comprises S-compounds oxidation to their relating sulfones and/or sulfoxides. It causes an increase in polarity and molecular weight, hence assisting their elimination through processes for instance adsorption, distillation, and extraction [3]. ODS method takes place when the oxidant reacts with the liquid fuel till the S-compounds are oxidized. The commonly used oxidants are hydro-peroxides, nitrogen oxides, peroxy salts, and ozone [35]. Earlier nitric oxide or nitric acid oxidants for instance NO/NO₂ or HNO₃ gases used for ODS [36]. But, later it was established that these oxidants give rise to a high quantity of residues [37]. The oxidants hydro-peroxides for example hydrogen peroxide (H₂O₂), *tert*-butyl hydroperoxide effectively yield sulfones from the oxidation of organosulfur compounds without generating a high amount of residual products [15]. Hence, the ODS method includes two phases: (i) oxidation using an oxidant; (ii) followed by separation processes. Both oxidant and extraction solvent are the main important factor in ODS. Few oxidants may cause undesirable reaction with sulfur-free hydrocarbons that reduces the grade of the fuel.

The inappropriate extractants give rise to the undesirable co-extraction of sulfur-free hydrocarbons, for instance, olefins (alkenes) and aromatics from liquid along with sulfones [38]. The potential advantages of ODS are minor operating specifications and similar chemistry as HDS (viz. HDS includes reduction using H₂ gas, while ODS includes oxidation using oxidant) and utilizes traditional refinery apparatus for the reaction and separation [39]. The careful regeneration of adsorbent or extractant utilized is significant along with the waste management of sulfone compounds produced [39]. Amid various oxidants, currently the most popular is H₂O₂ since it is environmentally friendly [40] and the oxidation/extraction phase is immediate with increased sulfur elimination can be achieved. Hydrogen peroxide has several benefits such as high activity, low price, stability, and gives the highest percentage of active oxygen.

Though, the developments must be prepared to build ODS economical involves:

(i) H₂O₂/sulfur proportion must be decreased (ii) Mass transfer between polar stage and fuel must be high (iii) Post-treatment process for produced sulfones should be enhanced. While the ODS method using traditional solvents are VOCs, which are combustible and may cause adverse environmental effects [40]. For this purpose, DESs and ILs were presented as an alternative in ODS. Now, DESs and ILs are appealing attention for employing in ODS due to several desired properties such as less volatility and capability to behave as both catalyst and extractant. But in this review, we will focus only on the DESs. ODS advantages and disadvantages are enlisted in Table 1.

3. Deep eutectic solvents

Deep eutectic solvents (DESs), a substitute to ILs were first proposed by Abbott and are composed of the quaternary halide salts or hydrogen-bond acceptor and hydrogen-bond donor which may be (carboxylic acids, alcohols, polyols, or carbohydrates) [8]. The connections between HBAs and HBDs include mainly hydrogen bonding, occasionally van der Waals, and electrostatic forces [42]. The most significant intramolecular bond in DESs is the hydrogen bond formed between HBD and the halide anion of HBA. The intrinsic properties of DESs, for instance, low volatility, low melting points, high solubility, low vapor pressure, non-flammability, thermal and chemical stability, dipolar nature, ease of storage because of chemical inertness with water, tuneability, high biodegradability is due to the extensive hydrogen bonding [43].

Hydrogen bonding is responsible for the formation of DESs (room temperature liquid phase), while the less lattice energies of HBAs and

HBDs huge asymmetric ions result in less melting temperatures [9]. DESs show several advantages such as accessible raw material, simple synthetic conditions, low price, non-toxicity, environmental friendliness, and can be used for particular purposes. Fig. 2. shows the hydrogen-bonded structure of choline chloride and ethylene glycol forming DESs [44,45]. DESs do not utilize organic solvents thus environmental impact ensuing from noxious organic solvents can be removed. The preparation of DESs is comparatively simple and the interacting constituents are cheap, green, and readily accessible raw materials. DESs can be designated by the following formula: $\text{Cat}^+\text{X}^-z\text{Y}$; where Cat^+ stands for cation which may be ammonium, sulfonium, or phosphonium salts, X^- is a halide anion of salt, Y is Lewis or Brønsted acid, and z is the number of molecules of Y [9]. The advantage of DESs is that these can be used at moderate pressure and temperature during EDS as compared to HDS that needs elevated temperature and pressure.

3.1. Classification of DESs

DESs can be categorized into four different types as presented in Table 2 [9]. The type I of DES did not get much attention as the type-III due to the intrinsic hygroscopic nature of metal salts (e.g., AlCl_3) used to prepare them [47]. However, type I is formed from quaternary ammonium salts (QAS) and the metal halide. The example comprises chloroaluminate/imidazolium salts combined with many non-hydrated metal chlorides for instance FeCl_2 . Further metal chlorides which have been established in type-I involves copper(I) chloride (CuCl), silver chloride, copper(II) chloride, tin(IV) chloride, lithium chloride, tin(II) chloride, cadmium chloride (CdCl_2), yttrium(III) chloride, zinc chloride and lanthanum(III) chloride [48]. Type II is made from hydrated metal halides and QAS. Due to insensitivity to moisture or air and a broader range of hydrated metal salts available for synthesis, type II involves better applications [49].

Type III is formed from HBD and QAS and has been most investigated in the literature. The eutectic formed from HBD and choline chloride can dissolve a wide range of liquids which comprises transitional metals, chlorides along with oxides which make them more attractive. The prepared eutectic is comparatively cheap, highly biodegradable, simple preparation, non-reactive with water, and adaptability to a broad range of HBD [47]. In type-III, HBD affects physical properties whereas combination with ChCl as HBA concludes for which purpose it assists. Type III has been used in numerous applications e.g., heat transfer in fluids, liquid–gas separation, nanoparticle synthesis, catalyst in reactions, and electro-deposition of metals [50]. Examples involve the renowned $[\text{ChCl}]\text{-}[\text{Carboxylic acids/Amide}]$ prepared by Abbott and his colleagues

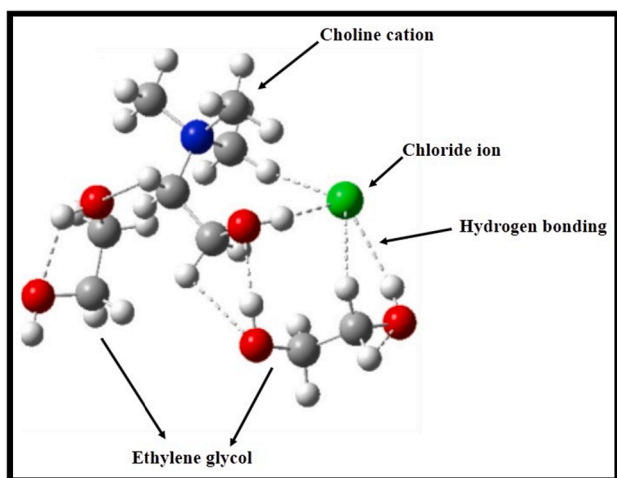


Fig. 2. Hydrogen-bonded structure of choline chloride and ethylene glycol forming DESs [46].

Table 2
Main types of DESs [9]

Type	General formula	Terms
Type-I	$\text{Cat}^+ \text{X}^- z\text{MCl}_x^-$	M: Sn, Al, Fe, In, Ga, Zn
Type-II	$\text{Cat}^+ \text{X}^- z\text{MCl}_x \cdot y\text{H}_2\text{O}$	M: Cu, Co, Fe, Cr, Ni
Type-III	$\text{Cat}^+ \text{X}^- z\text{RZ}$	Z: COOH, CONH ₂ , OH
Type-IV	$\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1} \cdot \text{RZ} + \text{MCl}_{x+1}$	M: Zn, Al and Z: CONH ₂ , OH

[51]. Type IV is formed from HBD and metal halides. Inorganic cations acquire large charge density and are incapable to make eutectics. Though, the combination of urea with halides makes eutectics. A novel class of DESs is introduced which is obtained by utilizing combinations of HBDs from bio-renewable materials. Hence are termed as natural deep eutectic solvents (NADES).

3.2. Preparation of DESs

In two ways, DES can be prepared by merely mixing HBA and the HBD at an appropriate temperature. In first approach, low melting point constituent is melted initially, and later high melting point constituent is added to liquid, and then mixtures are mutually melted. Conversely, it is problematic to prepare DESs in this way when both constituents have higher melting points. In the second approach, both constituents are combined and melted mutually [52]. In 2003, choline chloride and urea (U) were melted at 80 °C and agitated till a uniform liquid was obtained. DESs were identified through NMR, FTIR, and Mass Spectrometry [8]. The choline chloride and glycerol in a specific mole ratio (1:2) kept on stirring below 80 °C until a homogenous and transparent liquid was formed [53]. In another study, choline chloride and malic acid in a mole ratio (1:2) kept on heating below 80 °C until a colorless and transparent mixture was obtained [54]. Fig. 3 displays the generally used HBA and HBD for the desulfurization of fuels.

3.3. Physicochemical properties of DESs

With the invention of DESs, the properties of DESs have fascinated significant consideration to the researchers. The designable ability of the compositions is normally attributed to the physicochemical properties of DESs. Hence, physicochemical properties for instance melting point, viscosity, freezing point, density, and conductivity can be fabricated depending on the structure of DESs [52]. Generally, the melting points of the DESs are meaningfully lower than the melting points of their distinct constituents [9]. The ratio of HBD of the DES is expected to decide their melting points as increased hydrogen-bond connections with anionic groups cause reduced connections with cationic groups. This weak connection (low lattice energy) between the cationic and the anionic groups leads to the decline of melting point [52]. Fig. 4. illustrated the attractive properties of DESs.

The type of salt, type of HBD, and molar ratios are the aspects that affect the viscosity, density, and surface tension of DESs [55]. In general, DESs have larger viscosities and lesser conductivities than other molecular solvents and ionic liquids [9]. The DESs viscosities have been described to be very high, and mostly have viscosities larger than 100 cP [52]. The higher viscosity of DESs is considered due to the occurrence of widespread hydrogen bonding among the compounds which confines mobility of free species inside the DESs. Other connections, for instance, van der Waals and electrostatic interactions, can also influence to larger viscosity of DESs, which obstructs their application in industry. The addition of water and modification of DESs components have been utilized to overcome this drawback [47]. Though, it must be mentioned that excessive water addition may result in the weakening of hydrogen-bonding connections between the components of DESs [56]. Most DESs are considered as, readily biodegradable because most constituents of forming DESs come from natural materials and can be metabolized by diverse types of organisms in nature. Due to the high tunability of DES,

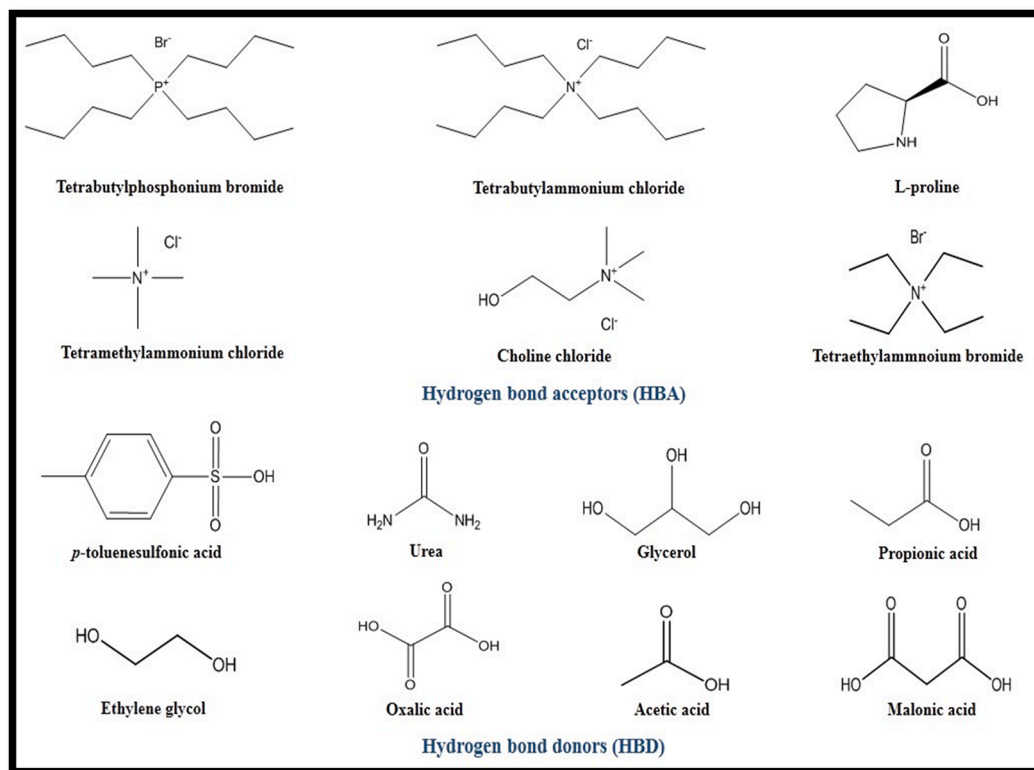


Fig. 3. Generally employed HBAs and HBDs for desulfurization of fuels.

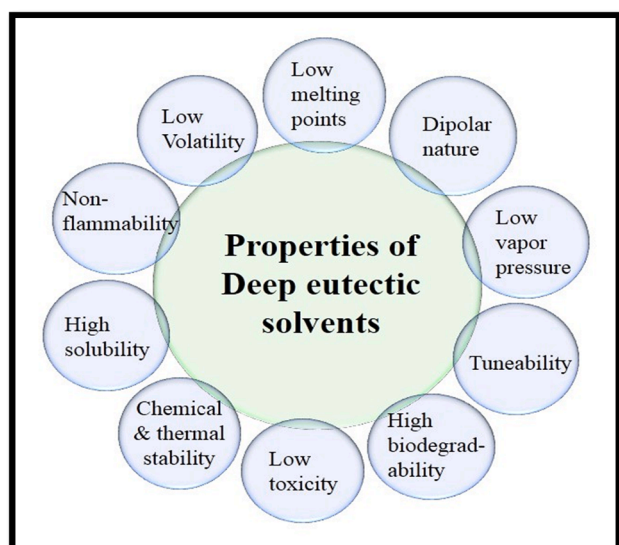


Fig. 4. The attractive properties of DESs.

they are termed as, “designer solvents” [57].

3.4. Applications of DESs

DESs have fascinated more interest as an emerging research area, especially in the chemistry field. DESs have been investigated as possible sorbents for carbon dioxide storage and capture [58]. Though DESs have been used in wide-ranging processes, in the domain of substitute energies, for instance, hierarchical carbon electrodes for capacitors and fuel cells [59], electrolytes for energy storage devices [60], and solar cells [61]. The effort has now been directed on the conversion of

lignocellulosic biomass into useful energy products. Owing to economic and environmental effects, DESs have been generally observed in the biomass processing range, more specifically in biodiesel production and in the pretreatment of lignocellulose and transformation of sugars. Concerning the pretreatment phase, due to the renowned capability of DESs to dissolve phenolic compounds, DESs have been utilized as delignification agents [62].

In the production of biofuels, DESs have been essentially considered for biodiesel synthesis. Though firstly DESs were employed for the elimination of glycerol as residue [63], now have been also studied as the solvent and/or catalyst in the esterification reaction [64]. In the field of biotechnology, DESs have also huge potential as substitute reaction media for biotransformations for instance whole-cell, plant-based, and enzyme bio-catalysis, increasing activity, regioselectivity, and stability. DESs have been effectively employed for the extraction of bioactive compounds, e.g., essential oils [65], catechins, alkaloids, and flavonoids [65], and xanthenes, that have been extracted from plant leaves.

Moreover, DESs are also used to extract phenolic acids, polyphenols, saponins, anthraquinones, rosiglitazones, and tanshinones bioactive compounds from numerous kinds of natural resources [66]. Fig. 5. displays the potential applications of DESs. Whereas DESs have been useful in several zones, for instance, enzymatic reactions [67], organic reactions [68], and electrochemistry, due to the green properties and different varieties of DES. The separation and extraction methods using DESs have been applied effectively in numerous arrays, for example, metals, biodiesel, aromatic hydrocarbons, and bioactive components. DESs and NADES, have currently been employed as washing agents for the elimination of lead from the polluted soil [69].

4. Desulfurization of fuels using DESs

As previously discussed, the effective achievement of fuels with less sulfur concentration is an important and demanding objective to attain the reduction of raw oil resources with less sulfur content. Several non-

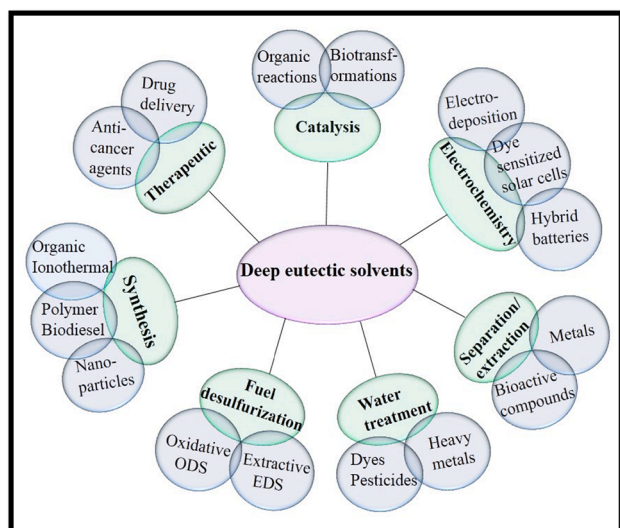


Fig. 5. The potential applications of DESs.

HDS methods have been established, for instance, oxidative desulfurization (ODS), adsorptive desulfurization (ADS), and extractive desulfurization (EDS). Amid them, EDS is deemed as the utmost desirable means to achieve diesel fuels with less sulfur concentration [69]. In the review, DESs utilization in EDS, ODS, and ECODS are discussed in detail.

4.1. Extractive desulfurization using DESs

In EDS, a solvent is employed to extract S-compounds from fuel through liquid–liquid extraction (LLE). Although, EDS is an appropriate substitute due to the less utilization of energy. It can be operated at minor operational conditions without the consumption of hydrogen.

Besides, it has several advantages as it does not alter the chemical form of compounds present in fuels. Previously, various organic solvents, for instance, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and other VOCs have been utilized as solvent extraction agents in EDS [31]. Although, consumption of organic solvents owing to their toxicity, flammability, and volatility, and sulfur elimination efficacy is not meaningful.

Deep eutectic solvents have a huge ability to reach this goal. DESs have several advantages as a substitute to traditional organic solvents, for example, they have low volatility, and are chemically and thermally stable. DESs achieved intensive attention in the research area as a green alternative to ILs due to several benign features, such as outstanding chemical and physical properties, non-toxic, inexpensive, much cheaper, generally biodegradable and preparation process can be done at room conditions. The process of EDS is displayed in Fig. 6. It was verified that hydrogen bonding is the key driving force in EDS method which was also confirmed by ^1H NMR. In EDS process using DESs, when BT was in contact with DESs, active-hydrogen in DES interacts with the sulfur atom of BT to form a hydrogen bond. Conversely, hydrogen-bond of itself DES become damaged and S-compounds went into the DESs phase and hence separated [70].

4.2. EDS mechanism of DESs

It is significant to understand the extractive mechanism of EDS for improving superior molecule design. Investigators suggested that hydrogen-bonding, π - π , and CH- π are the major interactions in EDS [69]. ^1H NMR and FTIR are used for mechanistic investigation. As described above hydrogen bonding is responsible for the formation of DESs. With addition of DBT, hydrogen bond of DES that is formed between the Cl^- and active hydrogen H^+ has been damaged. This might be due to connection of H^+ of DESs and S-atom of DBT. It can be reasoned that connection of Cl^- with DBT gets stronger and consequently hydrogen bond of DES itself is damaged. From the above study, hydrogen bond

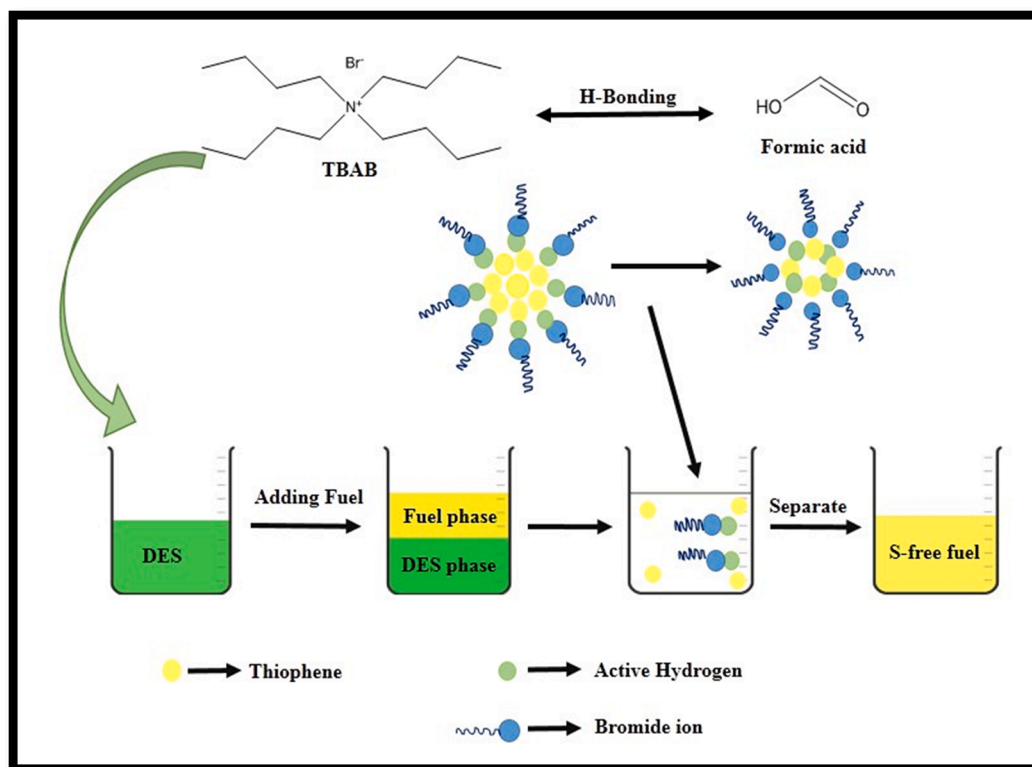


Fig. 6. Process of extractive desulfurization using DESs [70].

formed between active hydrogen of DES and S-atom of DBT results in desulfurization [10]. Fig. 7. shows the proposed mechanism of EDS using DESs.

The ability of different kinds of synthesized DESs in the elimination of sulfur compounds which involved numerous organosulfur compounds e.g. dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene, 4-methyldibenzothiophene, thiophene, 2-Methylthiophene, 3-methylthiophene, and benzothiophene (BT) in prepared model fuel for instance n-heptane and n-octane have been reported in Table 3. Numerous factors which influence the extraction efficacy of DESs in EDS like extraction temperature, the molar ratio of DES, initial sulfur concentration, selection of DESs, model oil ratio, extraction time, regeneration, and multistage extractions and some of them are reported in detail.

4.2.1. Effect of different kinds of DESs

Combining different HBA with different HBD in a proper amount, formed the DESs. DESs formed from diverse kinds of HBAs and HBDs acquire different physicochemical characteristics like viscosity, density, and freezing point, which have an influencing effect on extractive performance of DESs. Shu and Sun [71] reported the TBAC-based DESs and TBAC/EG possess 64% extraction efficiency for model gasoline at 30 °C in 10 min. Extraction efficacies of different DESs obeyed the sequence such as TBAC/EG > TBAC/GI > TBAC/malonic acid. It was indicated that alcohol-based HBD is more effective than acid-based HBD. Alternatively, the yield of DES depends on HBA/HBD molar ratio. Also, DESs from dissimilar HBA to HBD molar ratios have distinct physicochemical characteristics and have a significant impact on extraction performance of DESs. TBAC/EG in 1:2 M ratio attained higher extraction efficacy of 65% which is greater than that of most conventional ILS.

Li et al. [72] synthesized ammonium-based DESs and TBAC/PEG displayed desulfurization efficacy of 82.83% for one cycle and after five cycles reached up to 99.48% under ideal circumstances. Authors proposed that HBA has a larger impact on desulfurization method. Extraction sequence for HBAs are listed as: TBAC > TMAC > ChCl, while for HBDs: PEG > Pr > EG > TEG > GI > MA. So, TBAC-based salts are more chosen as HBA than ChCl-based for this particular method. Although for HBD, alcohol-based HBD like PEG is more effective than others.

Jiang et al. [73] reported choline-based DESs and among them, [C₁₂DMEA]Cl/FeCl₃ exhibits an effective performance of 52.9%. Many DESs such as, [BzMDEA]Cl/FeCl₃, [BzDMEA]Cl/FeCl₃, [C₁₂DMEA]Cl/

FeCl₃, [C₈DMEA]Cl/FeCl₃, and [C₄DMEA]Cl/FeCl₃, were synthesized for DBT extraction. C₁₂DMEA/Cl/FeCl₃ displayed a higher extraction capability of 52.9% at 30 °C, which is a little higher than that of C₈DMEA/Cl/FeCl₃. While, [BzMDEA]Cl/FeCl₃, and [BzDMEA]Cl/FeCl₃ possess only 37.6 and 39.2%. Extraction experiment with [C₄DMEA]Cl/FeCl₃ was not operated at 30 and 40 °C owing to its melting point of approx. 42 °C. The difference might be ascribed to a dissimilar connection between DES and DBT. From this, it was established that aliphatic-DESs with long chains of carbon exhibit improved performance than aromatic ones. Since, interaction between DESs and S-compounds contains mostly π - π interaction, CH- π interaction, and hydrogen bonding. Authors suggested that CH- π interaction and coordination effect dominates in the extraction ability of DESs in their work. Hence, the DESs selection and molar ratios of HBA/HBD greatly affect S-elimination efficiency.

4.2.2. Effect of temperature

For any extraction process, reaction temperature is always important. Shu and Sun [71] reported the TBAC-based DESs and TBAC/EG possess 64% extraction efficiency for model gasoline at 30 °C in 10 min. For any DESs, extraction efficacy rises in the beginning and is reduced subsequently with the increase of temperature. From the 20–40 °C temperature range, maximum value of extraction efficacy was attained. The reason may be that the viscosity (η) of DESs alters considerably with the temperature i.e., an increase in temperature results in a decline in the viscosity. The decline of viscosity is in favor of mass transfer in process, thus increasing the extraction efficacy. Conversely, excessively high temperatures will damage integration of DESs and organosulfur compounds present in fuel, which will reduce extraction capability.

Almashjary et al. [10] reported ChCl-based DESs and ChCl/Pr (1:3) exhibited higher efficiency of 64.9% for DBT at 37 °C in 10 min. The DES was performed from 25 °C to 70 °C to examine the temperature effect. When temperature was varied from 25 °C to 47 °C, there is an increase in DBT removal from 64% to 65.8%. Though, there was a decrease in DBT removal efficiency with a further increase in temperature. The decline in efficacy was possibly owing to the evaporation of n-octane at elevated temperature and hence not favorable for EDS. This response can be attributed further due to exothermic character of acid-base complexation and consequently, huge temperature reduced the extraction efficacy [74].

Shirazinia et al. [75] reported metal-complex-based DESs (MCDESs)

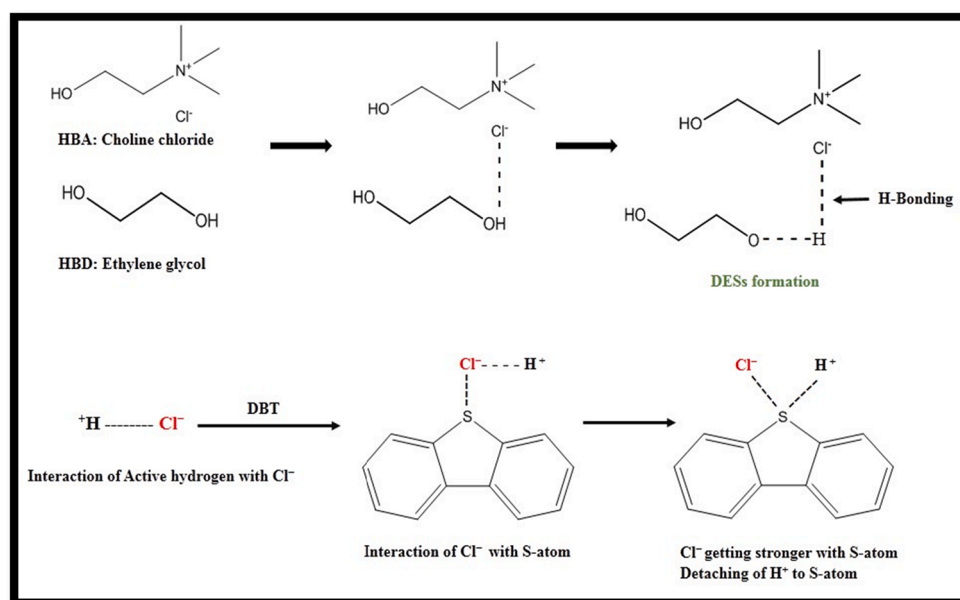


Fig. 7. Proposed mechanism of EDS using DESs.

Table 3
Reported studies on EDS using DESs.

Sulfur compounds	Model fuel	DESs (HBA/HBD)	Desulfurization efficiency	Ref.
Th, DBT	Iso-octane, n-Decane	TBAB/PEG	82.40%	[81]
BT, Th, DBT	n-octane	THA/BA [BDMA]/BA TEA/[OHBA] TEA/[OMOBA] TEA/[OMBA] TEA/[OFBA] TEA/[OCBA] TEA/[OBBA] TEA/[ONBA]	[TEA]/[OHBA] reduced BT amount 500 ppm to 10 ppm	[82]
DBT, Th	n-decane, iso-octane	FeCl ₃ [CH ₃ (CH ₂) ₃] ₄ PBr	64% DBT and 44% Th.	[83]
4,6-DMDBT, DBT, 3-MBT, 4-MDBT, BT	n-octane	[C ₁₂ DMEA]Cl/FeCl ₃	52.9%	[73]
BT, 4,6-DMDBT, DBT	n-octane	MIM/PA DEA/PA	MIM/PA 54.7%	[84]
Th, DBT, BT	n-octane	TBAB/For TBAB/Ac	TBAB/For BT 98.32%, DBT 98.24% and Th 97.6%	[70]
DBT	n-octane	ChCl/Pr	64.9%	[10]
Th	n-hexane	TEACl/EG TEACl/Gly MTPPBr/EG MTPPBr/Gly	–	[85]
DBT, Th	Iso-octane, n-decane	SnCl ₂ ·2H ₂ O: [CH ₃ (CH ₂) ₃] ₄ PBr	DBT 69.57% and 47.28% Th	[86]
DBT, BT, 4,6-DMDBT	n-octane	[TEtA]/[Fo] [TEtA]/[Ac] [TEtA]/[Pr] [TEtA]/[Bu] [TEtA]/[Pe]	[TEtA]/[Pr] 52.3%	[79]
Th, DBT	n-decane, iso-octane	TBAB/imidazole	70% DBT and 47% Th from simulated fuel. 47% from commercial diesel	[87]
DBT, Th	n-heptane	ChCl/Gly ChCl/EG ChCl/PEG TBAC/EG TBAC/PEG-200 TBAC/PEG-300 TBAC/PEG-400	TBAC/PEG-400 85% and 68% for DBT and Th.	[80]
DBT, Th, BT	n-octane	TBAC/PEG/FeCl ₃	–	[88]
DBT	n-octane	TBPB/DMF	82.1%	[89]
BT, Th	n-heptane	THAB/EG THAB/GI	–	[90]
Th, BT, DBT	n-octane	[TBA][Br]-FA	–	[91]
BT, DBT, 3-MT	n-heptane	Toluene/AlCl ₃ /chlorinated paraffins-52	In real oil 84.5%	[92]
Th	n-heptane	TBAB/EG TBAB/Sul TBAB/TrEG	TBAB/Sul 98%	[93]
Th	n-hexane, n-octane	THAB/EG THAB/Gly	–	[94]
BT, 2-MT	n-octane	TBAC/EG TBAC/GI TBAC/MA	TBAC/EG 99.5%	[71]
BT	n-octane	ChCl/GI ChCl/EG TMAC/EG TBAC/EG TBAC/PEG	TBAC/PEG 99.48%	[72]
DBT	n-octane	TBAC/PEG/FeCl ₃	89.53%	[69]
BT, DBT	n-octane	–	–	[95]

Table 3 (continued)

Sulfur compounds	Model fuel	DESs (HBA/HBD)	Desulfurization efficiency	Ref.
Th	n-octane, n-hexane	ChCl/EG ChCl/U TEACl/EG TEACl/Gly ChCl/Gly	–	[96]
DBT, 4,6-DMDBT	dodecane	–	97.06%	[97]
2-MT, 3-MT	n-heptane	THAB/EG THAB/GI	–	[98]
DBT	n-octane	MTPPBr/TetEG	85%	[77]
Th, BT, DBT	n-octane	[BPY]Br/MA	94.14%	[99]
DBT, Th, 2-MT	n-heptane	TBAB/DG	DBT 92%, 2-MT 86%, Th 71%	[100]
Th, BT, DBT	n-heptane	ChCl/phenol	91.5% Th, 95.4% BT, 99.2% DBT	[78]
BT, DBT, Th	n-heptane	TEAB/EG TEAB/1,4-BD TEAB/1,3-PD TEAB/1,5-PD	TEAB/1,4-BD reduced S-content less than 10 ppm	[101]
Th, DBT, 3-MT	n-octane	DPC-ChCl-SnCl ₂ DPC-ChCl-FeCl ₂ DPC-ChCl-CuCl ₂ DPC-ChCl-FeCl ₃ DPC-ChCl-ZnCl ₂ DG-ChCl-SnCl ₂ DG-ChCl-ZnCl ₂ DG-ChCl-FeCl ₂ DG-ChCl-CuCl ₂ DG-ChCl-FeCl ₃	DPC-ChCl-SnCl ₂ possess 95.2 % for DBT, 3-MT 94.5%, and 92.1% Th.	[75]
Th	n-octane	ChCl/U ChCl/EG ChCl/GI	Molybdate nanofluid-based ChCl/EG 98.01%	[102]

and among MCDESs, Sn(II)-DPC-ChCl possess higher efficiency of 95.2, 94.5, and 92.1% for DBT, 3-methylthiophene, and Th in 10 min at 35 °C. It was revealed that desulfurization efficacy increased from 25 °C to 35 °C and then reducing manner was noticed. It verifies the exothermic nature of connections between MCDESs and desired sulfur compounds [76]. At elevated temperatures owing to fractional evaporation of fuel, desulfurization efficacies would decline. Sudhir et al. [77] reported MTPPBr based DESs and MTPPBr/TetEG (1:4) exhibited 45% DBT elimination at 20 °C in single-stage extraction. Initially, extraction efficacy is enhanced with rising temperature and approximately remains constant after 20 °C on further rising temperature. Between 20 and 30 °C, maximum extraction efficiency was attained.

From the above discussion, it is observed that an appropriate temperature (usually 20–30 °C) is more favorable for EDS. High temperature causes the reduction in viscosity which then favors mass transfer phenomena in LLE process leading to an increase in extraction efficiency. But higher temperature damages the integration of DESs and organo-sulfur compounds of fuel. Also, the elevated temperature is responsible for the evaporation of model fuel i.e., n-octane desulfurization efficacies decreases.

4.2.3. Effect of time

Extraction time is another factor that influences the desulfurization method. Sudhir et al. [77] reported MTPPBr based DESs and MTPPBr/TetEG (1:4) exhibited 45% DBT elimination at 20 °C in single-stage extraction. Initially, extractive efficacy increases quickly up to 15 min. But, on further increasing reaction time, rate of desulfurization remains constant. Hence, 30 min was chosen as an appropriate time to reach equilibrium. Li et al. [72] synthesized ammonium-based DESs and TBAC/PEG displayed desulfurization efficacy of 82.83% for one cycle at 25 °C and after five cycles reached up to 99.48%. During less than 10 min, S-content was reduced remarkably with increasing reaction time. It was concluded that equilibrium can be attained in 10 min with greater extraction efficacy about 71% for TBAC/PEG and TBAC/Pr. This might be due to lesser viscosity and higher extractive ability of DESs which

account for shorter equilibrium time. So, 30 min was chosen for extraction method.

Reaction time plays a significant role on desulfurization efficiency. Shorter equilibrium time can be associated with less viscosity and higher extraction capability of DESs.

4.2.4. Effect of regeneration

The reuse and recycling of DESs after the desulfurization process are highly desirable, not only from an environmental aspect but from an economic aspect as well. Fortunately, DESs can be effectively recovered with conventional solvents. Makos and Boczkaj [78] synthesized $\text{ChCl}/\text{phenol}$ (1:4) which showed 99.2% DBT removal at 40 °C in 40 min. After reaction process, DES was recovered via washing through diethyl ether (DES 1:diethyl ether 1), owing to its ease of regeneration and purification. Saturated DES was agitated for 60 min and diethyl ether was eliminated. The DES can be reused 15 times without an obvious decline in extraction efficacy. After regeneration, DES contained 10.3, 27.9, and 47.5 mg/L of DBT, BT, and Th.

Li et al. [72] reported ammonium-based DESs and TBAC/PEG displayed desulfurization efficacy of 82.83% for one cycle and after five cycles reached up to 99.48% under ideal circumstances. To observe if DESs have become saturated, the repeated consumption of used-DESs for EDS was performed. It was noticed that increasing the consumption of repeated times will result in decline of extraction ability of DESs. DESs become saturated and its extraction ability was dropped after reusing six times. The consumed DESs can be merely reused by washing with diethyl ether. The extraction efficacies were stable after four times of recycling. The recycled DESs were characterized by ^1H NMR to investigate their stability and revealed that the structures of DESs did not change. During whole extraction process, DESs were stable not only from extraction ability aspect but also confirmed from ^1H NMR.

Jiang et al. [73] reported $[\text{C}_{12}\text{DMEA}]\text{Cl}/\text{FeCl}_3$ DESs and exhibits an effective performance of 52.9%. The prepared DESs can be easily regenerated with deionized water since they can dissolve in water but cannot dissolve DBT. After reaction process, an upper layer of fuel is separated by decantation. Then deionized water was added into DESs phase and DESs could be regenerated after filtration and drying. Regenerated DESs was characterized through Raman spectroscopy and a characteristic peak at 332 cm^{-1} remained which is responsible for anion FeCl_4^- . S-elimination decreased slightly from 52.9% to 52.5% due to little loss of DESs in regeneration stage.

Wang et al. [79] reported $[\text{TEtA}][\text{Pr}]$ DESs which reduced sulfur content from 500 ppm to 10 ppm after four times of extraction. Due to distillable reactants, DESs were regenerated by distillation. Under reduced pressure, consumed DESs were treated at 100 °C to get the distillate. The distillate was regenerated DESs as the boiling point of DBT was greater than 332 °C. The structure of regenerated DESs was confirmed by ^1H NMR. Active hydrogen signal shifted upfield, which revealed that less triethylamine escaped in the regenerated procedure. After recycling five times, the sulfur partition coefficient (K_N) value was reduced from 2.14 to 1.96. This decline might have resulted from the loss of triethylamine in the regenerated method.

The DESs can be regenerated through various ways and retaining a similar structure, confirmed by ^1H NMR and FTIR. In some cases, the extraction capability increases but not in all. It is due to two main reasons, (i) the presence of S-compounds in recovered DESs (ii) a minimal loss of DESs during the regeneration process.

4.2.5. Multistage extractions

Lima et al. [80] reported PEG-based DESs and TBAC/PEG-400 showed the best results, 85% and 68% of extraction efficiency for DBT and Th in a single extraction step. After being reused six times, TBAC/PEG-400 kept extraction efficiency of 53% and 17% for DBT and Th, respectively. In single-stage extraction, using TBAC/PEG-400 deep desulfurization was not achieved. Hence, for the extraction of DBT and Th multiple cycles were investigated. After two succeeding extractions,

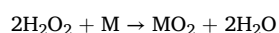
sulfur content regarding DBT was reduced to 10 ppm. For extraction of Th, three extraction cycles are required to obtain the same result. Wang et al. [79] reported $[\text{TEtA}][\text{Pr}]$ which reduced sulfur content from 500 ppm to 10 ppm after four times of extraction. Multistage extraction was performed using 1.75 g of $[\text{TEtA}][\text{Pr}]$ at 30 °C with 5 mL of model oil. After first extraction stage, an upper layer of oil was collected for next EDS with fresh DESs. After four times of extraction, S-content was reduced from 500 ppm to 10 ppm.

In general, it can be concluded that single-stage extraction does not decrease the adequate amount of sulfur in model fuel, thus, multistage extractions are studied. Hence using multistage extraction, deep desulfurization i.e., less than 10 ppm can be achieved but this depends on two factors (i) type of S-compounds to be extracted (ii) extraction capability of DESs

4.3. Oxidative desulfurization using DESs

Oxidative desulfurization includes the oxidation of S-compounds to respective sulfones using an oxidant and elimination of sulfones from diesel/fuel by extraction using a solvent. Many polar organic solvents, for instance, N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), methanol, furfural, and acetonitrile are typically employed in ODS [103]. These solvents are usually combustible and VOCs, which will cause further environmental and security issues and also make solvent recovery more difficult. ODS has been achieved widespread attention because of its benefits like higher efficacy and average reaction circumstances [104]. Regarding ODS, the diversity of oxidants are available with various oxidizing potentials and active oxygen. Consequently, it's essential to choose an appropriate oxidizing agent established on these features, i.e., eco-friendly, cost, and readily available.

Generally, oxidants utilized in ODS comprise superoxide anion (O_2^-), organic hydroperoxide, hydrogen peroxide (H_2O_2), and organic peracid [23]. Hydrogen peroxide is an extensively employed oxidant due to its high activity, low price, stability, and also environmental friendly since it yields water as a byproduct. Moreover, H_2O_2 gives the highest percentage of active oxygen. The reaction exhibits the oxidation employing H_2O_2 in Eq. (1) [105]



Superoxide anion is a free radical having one electron that is unpaired [86]. These O_2^- carriers may occur in gaseous or solid form for instance quaternary ammonium salts (QAS) and alkali metals. Numerous research has been kept ODS employing H_2O_2 to boost sulfur elimination. Numerous factors which influence the extraction efficacy of ODS like extraction temperature, oxidant, the molar ratio of DES, selection of DESs, extraction time, regeneration, and multistage extraction, and some of them are reported in detail.

4.4. ODS mechanism of DESs

In an acidic medium, hydrogen peroxide is a strong oxidant. The DBT was first extracted into DESs phase and then oxidized to DBTO_2 under the action of H_2O_2 and DESs. During ODS process, DESs performed not only as extractant but catalyst as well, thus continuous reduction of DBT concentration in fuel was examined until H_2O_2 was entirely decomposed. The DBTO_2 can be easily removed from reaction system by polar solvents like DMSO, DMF, and NMP, etc. Fig. 8. shows the suggested mechanism of ODS using DESs.

4.4.1. Effect of different kinds of DESs

Yin et al. [106] utilized acidic based-DESs in oxidation/extraction desulfurization to attain higher desulfurization efficacy. Though, controlling the acidity of DESs is comparatively simple, which can be achieved through appropriate selection of HBD. p-TsOH, SSA, and PAS were

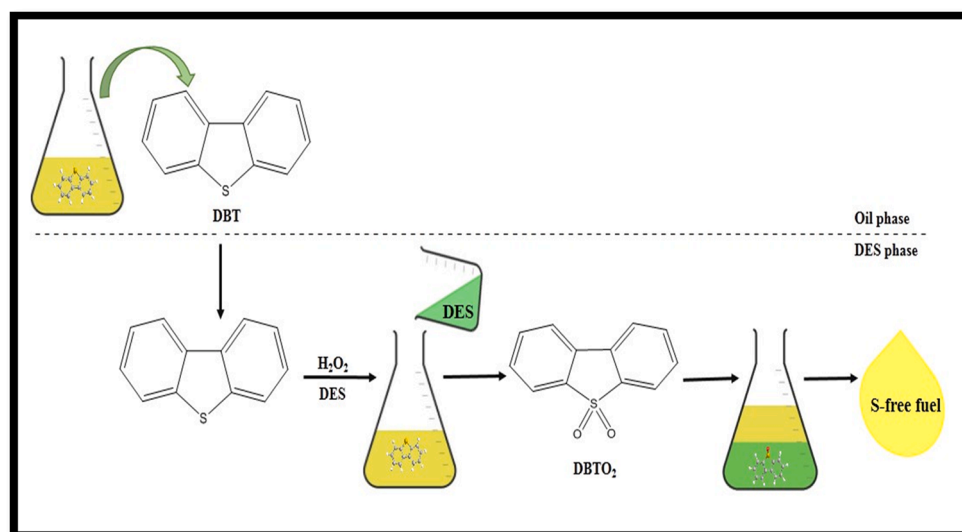


Fig. 8. The suggested mechanism of ODS using DESs.

selected as HBDS and ChCl, TBAC, TBAB, TEAC, and TEAB as HBA. Results revealed that both HBD and HBA greatly affect oxidation/extraction method. But, HBD has more impact on desulfurization method than HBA. Acidity of DESs is another major factor that influences oxidation/extraction method. Hence, stronger the acidity of DESs, higher will be desulfurization efficacies. Molar ratios of HBA/HBD greatly influence desulfurization process. With (1:2) molar ratio, sequence of efficiency are listed as p-TsOH > SSA > PAS. The efficiency of desulfurization by (choline chloride/p-TsOH) and (TBAC/p-TsOH) with (molar ratio 1:2) achieved up to 99.99%.

Jiang et al. [107] synthesized boric acid-based ternary DESs and ChCl/BA/PEG (1:1.5:1) showed higher desulfurization efficiency of 99.2% in 2 h at 60 °C with (O/S) molar ratio 6. It was noticed that composition of DESs significantly affects the desulfurization process. Without H₂O₂, when ChCl/BA was employed as an extractant in EDS, efficiency was only 3.2%, but this increased to 36.4% with PEG owing to its good extraction capability and hydrogen bonding connections [108]. When TBAC as HBA was employed, EDS efficacy further improved to 41.8%, possibly due to adsorption of longer chains of carbon. With the addition of H₂O₂, S-removal was 8.9% for BA and 31% with PEG as catalysts. With binary ChCl/BA DES, S-elimination enhanced from 3.2% (EDS) to 34.0% (ODS). S-elimination enhanced a little from 23.2% (EDS) to 27.4% (ODS) with ChCl/PEG. These outcomes specify that catalytic action might be derived from BA however not from PEG. With ternary ChCl/PEG/BA as extractant and catalyst was employed, an apparent rise in ODS efficacy was seen. Authors realized that S-removal improved as BA amount increased however reduced since PEG amount increased. ChCl/PEG/BA with molar ratio (1:1:1.5), attained higher efficiency of 96.4%. Moreover, DES with long carbon chain HBA displayed insufficient catalytic action, although possessed higher EDS efficacy. In the ODS method, there exhibits a positive relationship between the acidity of DESs and the extraction efficacy of S-compounds. The stronger the acidity of DESs, higher will be desulfurization efficacies.

4.4.2. Effect of temperature

In chemical reactions, temperature is one of the most significant factor. Jiang et al. [109] reported [PSTEtA]Cl/OA DES, which exhibits 97.7% sulfur removal efficiency at 50 °C. The viscosity of DESs, rate of oxidation, and decomposition of H₂O₂ have been influenced by reaction temperature. In the starting 50 min, the reaction rate at 60 °C was faster than that at 40 or 50 °C. Though, sulfur elimination was merely 65.6% in 3 h owing to non-productive breakdown of H₂O₂. Due to higher viscosity of DESs at low temperature, lesser sulfur elimination was achieved at

40 °C, which retarded the mass transfer rate. So, 50 °C is the suitable reaction temperature with sulfur elimination as high as 97.7%. Mao et al. [110] utilized trifluoromethanesulfonic acid-based DESs in the ODS method. ChCl/1.5CF₃SO₃H displayed higher desulfurization activity 98.65% for DBT at 40 °C in 60 min. When the temperature increased from 30 to 40 °C, rate of desulfurization was increased and DBT removal rate also increases from 98.27% to 98.65%. Though, above 40 °C, the desulfurization rate was no longer increased. This can be due to higher temperature accelerate the breakdown of H₂O₂, which decline the oxidative ability in the ODS.

Lu et al. [111] reported TBAC/oxalic acid DESs along with H₂O₂, and 91% DBT removal was attained in 3 h at 50 °C. At the temperature of 40, 50, and 60 °C, the elimination of DBT attained up to 67%, 91%, and 98% in 180 min, respectively. The results show that TBAC/oxalic acid (1:2) DESs is very effective in oxidation of DBT into sulfones at minor circumstances. Though, DBT removal was reduced to 92% at 70 °C. The concentration of H₂O₂ reduces with increasing temperature, which is due to non-productive decomposition.

Mao et al. [112] employed phenylpropanoic acid-based DESs as extractants and catalysts in ODS. C₉H₁₀O₂/0.5ZnCl₂ DESs exhibit high desulfurization efficacy of 99.23% for DBT at 50 °C in 1 h. The rate of sulfur elimination was enhanced from 94% at 30 °C to 98% at 50 °C over 3 h. Though, sulfur elimination reduced sharply from 98% to 90% in 3 h, when temperature was increased from 50 to 60 °C. Hence, it is observed that temperature above a specific threshold is unfavorable for elimination of S-compounds.

To sum up, ODS is more dependent on reaction temperature than EDS. Higher temperatures accelerate the breakdown of H₂O₂ into H₂O and oxygen which decline the desulfurization efficiency of the ODS.

4.4.3. Effect of oxidant

Several diverse kinds of oxidizing agents are employed in ODS method-H₂O₂ is frequently preferred as it is environmentally friendly and strong oxidation ability. Lu et al. [111] used oxalate-based DES for the sulfur elimination in ODS method. ChCl, TBAC, and TMAC were selected as representative HBA and oxalic acid was selected as HBD. Authors investigated that when oxalate-based DES only were utilized, less desulfurization was noticed with barely any removal of dibenzothiophene. Though, with the addition of H₂O₂, 91% sulfur extraction was attained with TBAC/oxalic acid (1:2) for 3 h at 50 °C. Moreover, for a longer period, extraction efficacy could achieve up to 98% respectively. Investigators proposed that this is due to the production of sulphone compounds owing to higher solubility and polarity in DESs.

Yin et al. [106] utilized acidic based-DESs in oxidation/extraction desulfurization to attain higher desulfurization efficacy. The efficiency of desulfurization by (choline chloride/*p*-TsOH) and (TBAC/*p*-TsOH) achieved up to 99.99%. Investigators described that the stronger acidity of DESs, the higher will be the desulfurization efficacy. Maximum desulfurization efficacy attained utilizing ChCl/*p*-TsOH and TBAC/*p*-TsOH without adding H₂O₂ were 25.2% and 37.8%, although with the addition of H₂O₂ up to 99.9% desulfurization efficacy could be attained [106]. Mao et al. [112] employed phenylpropanoic acid-based DESs in ODS and C₉H₁₀O₂/0.5ZnCl₂ exhibit high desulfurization efficacy of 99.23% for DBT at 50 °C in 1 h. In ODS, using the accurate amount of H₂O₂ to acquire an appropriate O/S ratio is crucial. If O/S ratio is less, ability of the system to oxidize DBT in model fuel is compromised. Though, an excessive amount of H₂O₂ yields H₂O which dilutes the DESs, affecting its extraction capability. Hence, an appropriate H₂O₂ amount is significant. When O/S ratio increases from 0 to 6, rate of desulfurization improved from 18.08% to 98.46%. However, rate of desulfurization was slightly reduced, when the O/S ratio further increased from 6 to 8. It was observed that an excessive H₂O₂ dosage leads to the production of H₂O, which dilutes the extraction agent and obstructs the catalyst activity. Therefore optimum O/S ratio for desulfurization method is found to be 6.

Hao et al. [113] synthesized caprolactam-based acidic DESs and CPL/OXA (3:1) showed higher desulfurization efficiency 98.4% for DBT at 60 °C in 3 h with (H₂O₂)/(DBT) molar ratio 5. To investigate the effect of oxidant amount on the reaction, elimination of DBT with CPL/OXA (3:1) DESs at various O/S molar ratios (3, 4, 5, and 6) was carried out at 60 °C. The removal of DBT attained 98% in 3 h when the O/S molar ratios were 5 and 6. Hence, 5O/S ratio was chosen as the ideal oxidant amount, from an economic and efficiency point of view.

In general, oxidant plays a significant role in achieving deep desulfurization and remarkably increases the desulfurization efficacy. This is due to the production of sulphone compounds owing to higher solubility and polarity in DESs.

4.4.4. Regeneration/recovery of DESs

Since DESs are regarded as “green solvent” and can be reused, which will lessen the cost and prevent wasting resources. Hydrophilic DESs can be regenerated via water washing, reported in the literature [114]. Jiang et al. [109] reported dual Bronsted acidic DESs and [PSTetA]Cl/OA exhibit sulfur removal efficiency of 97.7% at 50 °C. After reaction, upper phase of fuel was collected by decantation. Deionized water was added to the system. A clear solution was achieved after eliminating white solid on the bottom. Under reduced pressure, the DESs were regenerated after water evaporation. Under similar conditions, sulfur elimination efficacy attained 93.4% in fifth-time recycling.

Mao et al. [110] utilized trifluoromethanesulfonic acid-based DESs and ChCl/1.5CF₃SO₃H displayed higher desulfurization activity 98.65% for DBT. After the reaction, upper fuel phase was separated. Using rotary evaporation, water in the DESs was removed. Consuming an equal volume of CCl₄ DESs were extracted three times. Recovered DESs and fresh H₂O₂ were added to model fuel under optimum conditions. After using five recycles, removal rate of DBT reduced from 98.65% to 97.16%. It has been seen that two reasons cause the reduction in the desulfurization rate. Firstly, a minimal loss in DESs during the recovery process; secondly, little amount of remaining oxidation products of sulfide in the recovered DESs.

Jiang et al. [107] synthesized boric acid-based ternary DESs and ChCl/BA/PEG (1:1.5:1) showed higher desulfurization efficiency of 99.2% in 2 h at 60 °C with (O/S) molar ratio 6. After completion of reaction, DESs ChCl/BA/PEG was separated easily from oil phase owing to their immiscibility. The FTIR results of regenerated DESs revealed similar absorption peaks as the fresh one, including bending vibration of O–H (1062 cm⁻¹) and stretching vibration of C–H (2800 cm⁻¹), B–O (1398 cm⁻¹). It was verified that structure of DESs was stable during the reaction process. Though, S-elimination was reduced to 80.8% in the

presence of used-DESs without regeneration. It may be due to the accumulation of oxidative products in DESs phase, which retard extractive capability of DESs. After washing with water, the regenerated DESs gained sulfur removal capability to 96.3%, which also shown the stability of DESs. The previously reported studies on ODS utilizing DESs are presented in Table 4.

4.5. ECODS using DESs

To attain deep desulfurization, several investigations have been reported employing catalytic or/and oxidation to aid extractive desulfurization. DESs were not only utilized as extractants or reaction media for desulfurization, however, also as a catalyst for extraction and catalytic oxidative desulfurization (ECODS). ECODS system based on DESs with phosphotungstic acid (HPW) as a catalyst along with H₂O₂ was evaluated. Amongst all the neutral, basic, and acidic DES, (ChCl/2PEG) exhibited the best performance and 99.1% of DBT could be removed from model oil within 3 h at 50 °C. The authors also studied the factors affecting the desulfurization efficacy, for example, reaction temperature and time, different DES, the dosage of H₂O₂ [119].

Acetamide-based DESs were utilized in ECODS for desulfurization of model and real diesel. The C₂H₅NO/3*p*-TsOH displayed an extraordinary catalytic activity for the elimination of DBT can reach 100% for model fuel and for actual diesel 98%, respectively. C₂H₅NO/3*p*-TsOH could be reused six times and the desulfurization activity was slightly reduced. The authors observed the effect of temperature, oxidant dosage, amount of DES, and recycling of C₂H₅NO/3*p*-TsOH on desulfurization efficacy [120]. The desulfurization of DBT was observed at various temperature ranges. Authors noticed that desulfurization efficacy of C₂H₅NO/3*p*-TsOH increases with higher temperatures. 100% elimination of DBT in 2 h at 50 °C could be attained and can be reduced at temperatures of 70 and 80 °C in 1 h. Though, higher temperature is also promising for self-decomposition reaction of H₂O₂ [121]. The previously reported studies on ECODS utilizing DESs are presented in Table 5.

5. Challenges using DESs in desulfurization process

The DESs possess higher desulfurization efficiencies in EDS, ODS, and ECODS. But applying on the larger scale, there are still many concerns such as DESs synthesis, viscosity, stability (sometimes), and recovery. Although, DESs precursors are usually cheap and can be prepared simply by mixing both constituents but here temperature and energy consumption issues are also present, which should be addressed. DESs can be regenerated using water and conventional solvents and retaining similar structure, physicochemical characteristics, and desulfurization capability in most cases but not in all cases. DESs capability decreases after single-stage extraction and requires recycling which cannot be feasible on a larger scale.

6. Conclusions and perspectives

Currently, immense pressure is constantly applied to the desulfurization method to generate fuels (gasoline and diesel) with less sulfur content. Severe health and environmental effects have motivated in discovering substitute desulfurization technologies. Deep eutectic solvents are acquiring prompt attention in extraction methods due to excellent properties such as low toxicity, biodegradability, and high tunability. In the present review, research on the different desulfurization processes such as ODS, EDS, and ECODS employing DESs has been analyzed. Approximately, 100% sulfur elimination in model fuel can be attained in ODS, EDS, and ECODS employing DESs. Since model fuel is composed of aliphatic hydrocarbons such as *n*-octane, *n*-heptane, etc. in a model sulfur compound like Th, DBT, and BT and hence are easy to desulfurize. However applying for real fuel, desulfurization efficiency decreased owing to the presence of several different organosulfur

Table 4
Reported studies on ODS using DESs.

Sulfur compounds	Model fuel	DESs(HBA/HBD)	Oxidant/catalyst	Desulfurization efficiency	Ref.
DBT, 4,6-DMDBT, 4-MDBT	n-dodecane	[(PSTEtA)Cl]/OA [(PSTEtA)Cl]/AA TBAC/OA	H ₂ O ₂	97.7%	[109]
BT, 4,6-DMDBT, DBT	n-octane	L-Pyro/TFA L-Pyro/For L-Pro/TFA L-Pro/For	H ₂ O ₂	L-Pyro/TFA possess 99.7% DBT, 99.6% 4,6-DMDBT, and 99.2% BT	[115]
BT, 4,6-DMDBT, DBT	n-octane	C ₉ H ₁₀ O ₂ .ZnCl ₂	H ₂ O ₂	99.23% for DBT, BT 96.12%, and 98.4% 4,6-DMDBT	[112]
BT, 4,6-DMDBT, DBT	n-octane	CPL/OXA	H ₂ O ₂	98%	[113]
DBT	n-octane	ChCl/p-TsOH ChCl/MA ChCl/U	H ₂ O ₂	99.1 wt% ChCl/p-TsOH for DBT	[114]
4,6-DMDBT, BT, 4-MDBT, 3-MBT, DBT	n-octane	ChCl/Ac ChCl/PEG ChCl/EG ChCl/GI ChCl/Fo ChCl/Pr ChCl/U	H ₂ O ₂ and [PSTEtA] ₃ PW ₁₂ O ₄₀	ChCl/Ac 100%	[116]
DBT, BT, Th, 4,6-DMDBT	n-octane	ChCl/CF ₃ SO ₃ H	H ₂ O ₂	98.65% for DBT and 4,6-DMDBT 96.8%	[110]
BT, 4,6-DMDBT, 4-MDBT, DBT	dodecane	ChCl/PEG/BA	H ₂ O ₂	99.2%	[107]
DBT	n-octane	ChCl/OXA TMAC/OXA TBAC/OXA	H ₂ O ₂	TBAC/OXA 91% for DBT	[111]
BT, 4,6-DMDBT, DBT	n-octane	L-Pro/OA L-Pro/PA L-Pro/GA L-Pro/p-TsOH	H ₂ O ₂	L-Pro/p-TsOH DBT 99%	[117]
BT	n-octane	ChCl/p-TsOH TBAC/p-TsOH	H ₂ O ₂	For model fuel 99.99%. For real fuels, ChCl/p-TsOH 97.25% and TBAC/p-TsOH 95.90%	[106]
4-MDBT, 4,6-DMDBT, DBT, BT, 3-MBT	n-octane	ChCl/AcChCl/ FoTBAC/Ac	H ₂ O ₂ and [(C ₆ H ₁₃) ₃ P (C ₁₄ H ₂₉) ₃ PMO ₁₂ O ₄₀	BT completely removed by ChCl/Ac.	[118]

Table 5
Reported studies on ECODS using DESs.

Sulfur compounds	Model fuel	DESs(HBA/HBD)	Oxidant	Catalyst	Desulfurization efficiency	Ref.
4,6-DMDBT, DBT	n-octane	TBACl/PEG ChCl/PEG	H ₂ O ₂	complex (1) [MoO ₂ Cl ₂ (DMB) ₂] and (2) [MoO ₂ Cl ₂ (DEO)]	Complex 1 with ChCl/PEG displayed 99.6%.	[122]
4,6-DMDBT, BT, DBT	n-octane	ChCl/PEG ChCl/EG ChCl/GI ChCl/U	H ₂ O ₂	HPW	ChCl/2PEG 99.1% DBT removal	[119]
DBT, 4,6-DMDBT, BT	n-octane	CoCl ₂ -ChCl/PEG CoCl ₂ -ChCl/EG CoCl ₂ -ChCl/GL CoCl ₂ -ChCl/Pr	PMS		CoCl ₂ -ChCl/2PEG showed 100% DBT removal	[123]
BT, 4,6-DMDBT, DBT	n-octane	Acetamide/p-TsOH	H ₂ O ₂		100% model fuel and 98% actual diesel	[120]
DBT, 4,6-DMDBT, BT	n-octane	ChCl/Ac	Air	Isobutylaldehyde (IBA)	96.4%	[124]

compounds. Numerous aspects for instance ratios of HBA/HBD, temperature, DES selection, time, model fuel ratios to DES, oxidant, and multistage extractions influence desulfurization yield. However, the choice of the DES affects both sulfur elimination efficacy and the constituent of organosulfur compounds being extracted. DESs, as potential solvents for the desulfurization process, are assumed to fascinate further research work in upcoming years but some issues must be addressed for applying at a larger scale.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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