زانکۆی سەلاحەدین - هەولێر
Salahaddin University- Erbil

Desulfurization of Gasoline fuel by Deep Eutectic Solvents (DESs)

Research Project

Submitted to the department of Chemistry in partial fulfillment of the requirements for the degree of BSc.

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CERTIFICATE

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Date / / 2024

Dedication

The Salahaddin University, my second magnificent home.

My great parents, who never stop giving of themselves in countless ways.

My beloved brothers and sisters.

To all my family and my friends who encourage and support me.

All the people in my live who support me in academic life.

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Abstract

The abstract for a study on the desulfurization of gasoline fuel using deep eutectic solvents (DESs) might read as follows:

"Desulfurization of gasoline is a crucial process to meet stringent environmental regulations and improve fuel quality. Deep eutectic solvents (DESs) have emerged as promising alternatives to conventional solvents due to their low cost, low toxicity, and tunable properties. This study investigates the efficiency of DESs in removing sulfur compounds from gasoline. The study reviews various DES formulations been evaluated for their desulfurization performance using different process parameters such as temperature, pressure, and solvent-to-feed ratio. The results demonstrate the ability of DESs to effectively remove sulfur compounds, including thiophenes and benzothiophenes, from gasoline. Furthermore, the mechanistic aspects of the desulfurization process are explained, shedding light on the interactions between DESs and sulfur-containing compounds. Overall, this research highlights the potential of DESs as promising solvents for the desulfurization of gasoline, offering insights into the optimization of process conditions for enhanced sulfur removal efficiency."

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1. Introduction

1.1 Fuels

Lexical meaning of the word “fuel” is a material that can be made to react with other substances in order to release chemical or nuclear energy as heat or to be used for work. Down the ages, energy has been one of the most important part of the human life. From past to present, heating and cooking are used intensively and during the history, fuel has been used both for cooking and heating. This paper introduces an integrated multiple criteria decision-making approach for fuel provider selection in food industry. Seven conflicting evaluation criteria namely lead time, reliability, sustainability, cost, service quality, location and warranties, are determined in this work. In order to illustrate the application, a numerical example is given by conducting a case study in Turkish food sector. (Goker and dursun, 2019)

1.2 Types of Fuels

- Natural or primary fuels, which are found in nature, such as coal, wood, crude oil, natural gas, etc.
- Artificial or secondary fuels, which are derived from natural fuels, such as kerosene, charcoal, petrol, water gas, etc.
- Solid fuels, which are in solid state, such as wood, coal, cow dung cakes, etc.
- Liquid fuels, which are in liquid state, such as kerosene, LPG, petrol, diesel, etc.
- Gaseous fuels, which are in gaseous state, such as propane, natural gas, hydrogen.

1.4 Desulfurization of fuels

Deep desulfurization of transportation fuels is receiving increasing attention in the research community worldwide due to increasingly stringent regulations and fuel specifications in many countries for environmental protection purpose 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 SO_2 could result in lung diseases for instance chronic bronchitis, emphysema, and asthma, and can cause neurological ailments as well(Ma et al., 2002, Chandran et al., 2019).

Sulfur oxide (SO_x) exhausted from the combustion of fossil fuels such as coal, gasoline, and diesel, which causes irreversible damage to human health and environmental systems has brought about intense concern all around the world. Prolonged exposure to SO_X poses a great threat to lungs, skin, eyes, and even the respiratory system of the human body.Moreover, SO_x is one of the main sources of environmental pollution, such as acid rain and haze.5,6 The combustion of fuel oil containing organic sulfide in automotive engine was the largest contributor except for SO_x emission from the process of electricity generation using coal as an energy provider.7 Sulfur in fuel oil (mainly gasoline and diesel) generally exists in the form of organic species, such as mercaptan, thioether, disapplied, thiophene, and benzothiophene derivatives, as shown in Fig. 1.

Therefore, many national governments have put forward more and more stringent regulations to decrease sulfur contents in fuel oil. Nowadays, environmental concerns about the sulfur content of liquid fuel have been raised worldwide. Sulfur compounds in fossil fuels have caused several issues such as major effects on public health, air pollution, corrosion in pieces of equipment, and poisoning of the catalysts. The developed countries have legislated strict laws for the sulfur content of diesel and gasoline fuels. The sulfur removal processes are classified into two main categories, including hydrodesulfurization (HDS) processes and non-HDS processes. Although HDS is an efficient method to reduce the sulfur components of light middle distillate fuels. However, the operating cost of this process is considerable for high boiling cuts due to the presence of the HDS refractory sulfur compounds such as thiophilic compounds and its derivatives.

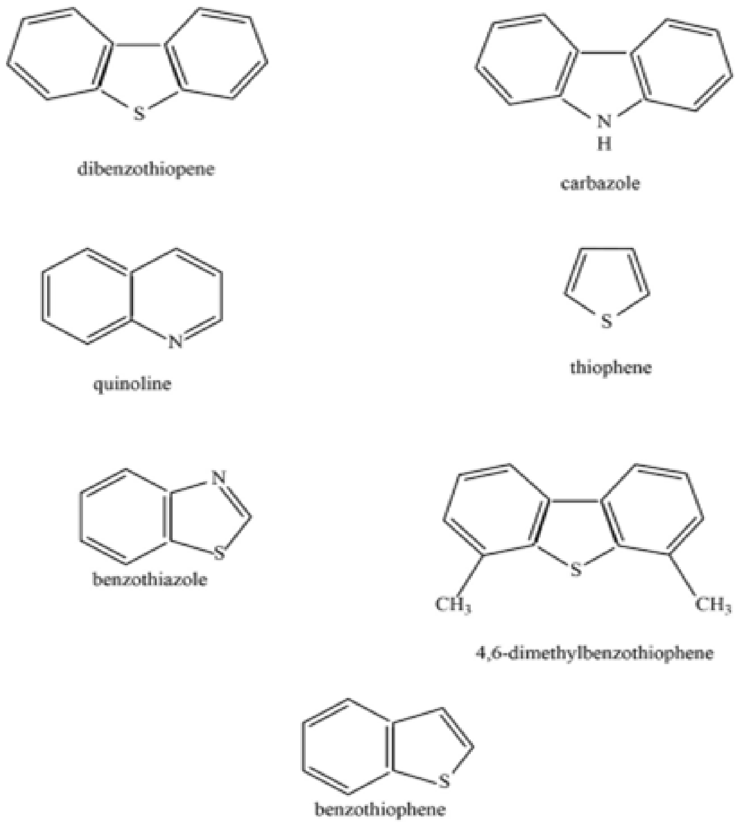


Figure 1: Organo-sulfur compounds present in fuels.

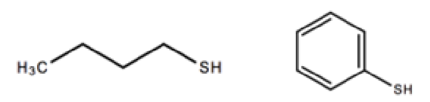
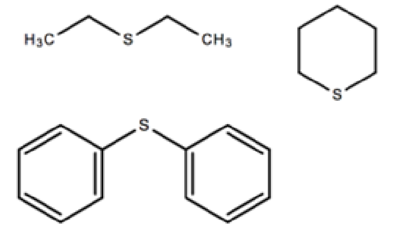
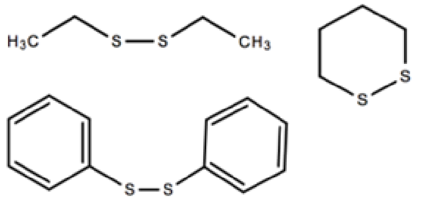
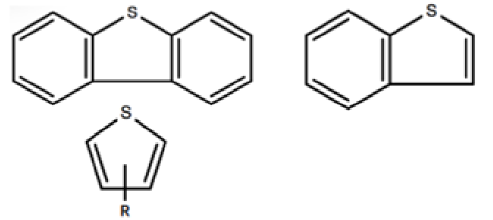
Non-HDS processes includes adsorptive desulfurization (ADS), oxidative desulfurization (ODS), biological desulfurization (BDS), and extractive desulfurization (EDS) can be applied as the complementary desulfurization processes. The EDS is an attractive desulfurization process due to its simplicity and mild operating conditions. The selection of a suitable solvent is a key step in developing the EDS process. Sulfur removal efficiency, volatility, price, safety issues, and environmental impacts of the solvent should be considered in the solvent selection.

1.5 Organic sulfur compounds

Sulfur presents inorganic and organic forms in diesel, and analyzing the amount of organic sulfurs is considered the key to evaluating the process of desulfurization. Organic sulfur compounds are separated into four groups: thiols (R-SH), sulfides

(R-S-R), disulfides (RS-S-R), and thiophenes. Table 1.1 shows the chemical structures of the major organic sulfur groups in petroleum.

Table 1: Major organic sulfur in petroleum.

Sulfur compound	General structure	Structural examples
Thiols	R-SH	
Sulfides	R-S-R	
Disulfides	R-S-S-R	
Simple and condensed thiophenes		

Among them, thiophene groups such as benzothiophene, dibenzothiophene, and their derivatives are the most important because their presence makes the desulfurization process more difficult.

1.6 Types of desulfurization

The main desulfurization techniques are:

1. Oxidative Desulfurization (ODS)
2. Microbe desulfurization (MDS)
3. Adsorptive Desulfurization (ADS)
4. Supercritical water Desulfurization (SCW)

5. Hydro-desulfurization (HDS)
6. Desulfurization by ultrasound oxidation
7. Desulfurization by extraction
8. Aerobic microbe desulfurization
9. Desulfurization by alkylation
10. Anaerobic microbe desulfurization

1.6.1 Oxidative Desulfurization (ODS)

oxidative desulfurization is a method in which chemical reaction ion on proceed between an oxidant and sulfur containing compounds ODS looks like a single process method but chemic ally involves two phases. In the first phase oxidation of sulfur takes place then in second phase sulfur removed from the star ting material.

1.6.2 Adsorptive Desulfurization (ADS)

Removal of sulfur by adsorption method is very prominent industrial method. In this method sulfur compounds from hydrocarbon adsorb on the solid adsorbent surface

1.6.3 Desulfurization by Photo oxidation

Removal of sulfur content from hydrocarbon through photo oxidation is very coherence process. This method is favorable in very lenient reaction condition.

1.6.4 Hydro-desulfurization (HDS)

In petroleum sector the most common method used for the removal of sulfur content in crude oil is hydrodesulfurization. HDS is execute when oil feed stock is with hydrogen in the presence of standard HDS catalyst. The standard catalyst used for this method are $NiMo/Al_2O_3$ and $Como/Al_2O_3$ .In this method the sulfur containing compound in crude oil is transformed in to hydrogen sulfide.

1.6.5 Microbe desulfurization (MDS)

Desulfurization followed by specific microorganism and reaction proceed at mild condition i-e at low temperature and pressure is commonly known as MDS. In this method the sulfur compounds in feed stock are metabolized by specific microbes

1.6.6 Supercritical water Desulfurization (SCW)

Supercritical water method is a useful method for the removal of sulfur compounds from the hydrocarbon. In this method experimentally found that at a temperature of 400 degree centigrade and at pressure of 25 MPa. the bonds between carbon and sulfur becomes disintegrate.

1.6.7 Desulfurization by ultrasound oxidation

Removal of sulfur compound from hydrocarbons by a method of oxidation followed by ultrasound is a useful method. This method required an energy which acquired from ultrasound. In this method the feed stock and oxidant are mixed in the presence of surfactants and water in the reactor.

1.6.8 Aerobic microbe desulfurization Aerobic MDS

is another method and it is an alternate to HDS method of crude oil. It was noted that 91% of sulfur content removed from the crude oil by the help of combining two methods i-e oxidative desulfurization and microbe.

1.6.9Anaerobic microbe desulfurization

Anaerobic microbe desulfurization is more convenient method than aerobic MDS.Anaerobic MDS method edge on the aerobic MDS method in that way upon hydrocarbon oxidation anaerobic MDS produced negligible amount of colored and sticky material as compare to aerobic MDS.

1.6.10 Aerobic ODS systems

Oxidative desulfurization concept was discovered in the early 1950s (Liotta and Han, 2003). Nevertheless, the ODS technology was not given a considerable focus on research and development before the introduction of stringent environmental regulations. Recently, various studies have been reported on the development of advanced and improved ODS systems. These studies can be categorized into eight broader classifications based on the oxidant used: gaseous oxidant systems; liquid oxidant systems; solid oxidant systems; emulsion generation systems; ultrasonic-assisted systems; plasma-assisted systems; photocatalytic oxidation systems and in-situ oxidant generation systems. Among these oxidation systems, aerobic oxidative systems are the most promising systems for deep desulfurization performance due to environmental friendliness, abundant availability, nontoxicity, and low cost. During the last decade, several types of catalytic systems with diverse characteristics have been reported. Herein, we present and deliberate nearly all types of aerobic oxidative desulfurization catalysts underneath distinct organization by scrutinizing their characteristics and catalytic activities. The catalytic systems have been classified into metal oxides, polyoxometalates, organometallic frameworks, carbon-based catalysts, nanoparticles, etc

1.6.11 Bio desulfurization (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.

2.1 Definition of Deep Eutectic Solvents (DESs)

Deep eutectic solvents are frequently defined as binary or ternary mixtures of compounds that are able to associate mainly via hydrogen bonds. Combining these compounds at a certain molar ratio result in a eutectic mixture (Zhang et al. 2012). The word “eutectic” comes from the Ancient Greek εὔτηκτος or eutectic which means easily melted, also called deep eutectic ionic liquids (DEILs) or low melting mixtures (LMMs) or low transition temperature mixtures (LTTMs) in the literature, 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).

2.2 Types of deep eutectic solvents

Types of DESs are shown Figure 2.

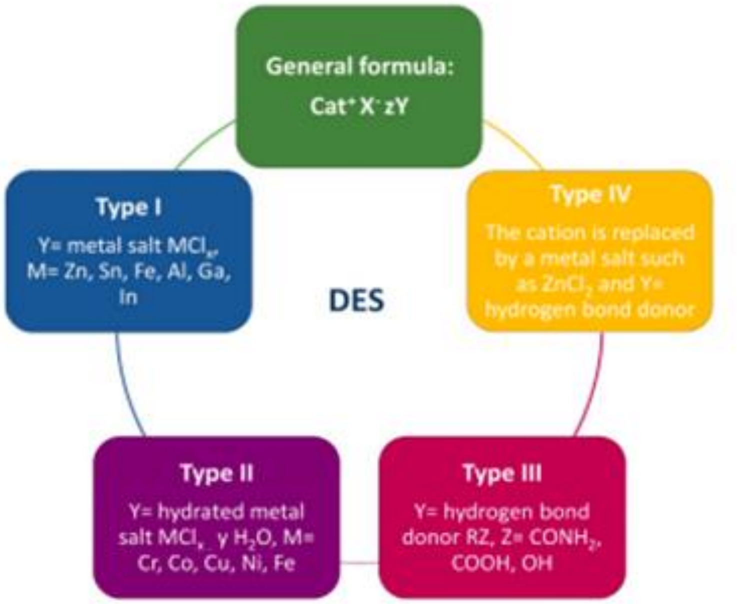


Figure 2: Four types of deep eutectic solvents (DES) based on the general formula Cat+ X− ZY, where Cat+ (cation) is generally an ammonium, phosphonium, or sulfonium, while X is a Lewis base, usually a halide anion. Y represents a Lewis or Brønsted acid and z is the number of Y molecules.

Four types of deep eutectic solvents (DES) based on the general formula Cat+ X− zY, where Cat+ (cation) is generally an ammonium, phosphonium, or sulfonium, while X is a Lewis base, usually a halide anion. Y represents a Lewis or Brønsted acid and z is the number of Y molecules Environmental Chemistry Letters 1 3 bromide, menthol, thymol, and fatty acids as hydrogen bond acceptors together with long alkyl chain alcohols and carboxylic acids as hydrogen bond donors (Florindo et al. 2019; Osch et al. 2015)

2.3 Methods of preparation

Researchers generally use one of the two main methods to prepare deep eutectic solvents: the heating method and the grinding method. The heating method consists of mixing and heating the compounds, under constant stirring, until a homogeneous liquid is formed (Abbott, Boothby, et al. 2004a, b). The heating temperature usually ranges between 50 and 100 °C. However, a high temperature may potentially lead to a degradation of the deep eutectic solvent due to an esterification reaction regardless of the preparation method, as demonstrated by Rodriguez et al. for solvents based on choline chloride and carboxylic acids (Rodriguez Roderiguez et al. 2019). The grinding method is based on mixing the compounds at room temperature and crushing them in a mortar with a pestle until a clear liquid is formed (Florindo et al. 2014). Another method based on the freeze-drying of the aqueous solutions of the components of deep eutectic solvents was also revealed by Gutierrez et al. (Gutiérrez et al. 2009). An evaporation method was also reported by Dai et al. consisting of dissolving the components of deep eutectic solvents in water, followed by evaporation at 50 °C. The resulting liquid is then placed in a desiccator in presence of silica gel (Dai et al. 2013). Considering the optimization of time and energy consumption, a greener microwave-assisted approach was proposed for the preparation of natural deep eutectic solvents within seconds (Gomez et al. 2018). Lastly, an ultrasound-assisted synthesis of natural deep eutectic solvents was recently introduced (Santana et al. 2019).

2.4 Physicochemical properties

The physicochemical properties of deep eutectic solvents are one of the main reasons behind the rising researchers' interest in these solvents. Besides having low volatility, nonflammability, low vapor pressure, and chemical and thermal stability, deep eutectic solvents are chemically tunable meaning they can be designed for specific applications given the wide variety of the possible deep eutectic solvents' forming compounds. Herein, the main physicochemical properties of deep eutectic solvents, are shown.

- Freezing point
- Density
- Viscosity
- Ionic Conductivity
- Acidity
- Hydrophilicity/hydrophobicity
- Polarity
- Surface tension
- Diffusion

3. Advantages and Disadvantages of different desulfurization methods

Table 2: Summary of different desulfurization methods.

Desulfurization methods	Advantages	Disadvantages
HDS	✓Well-known mechanism and conventional technology ✓In light fractions, hydrogen gas is feasibly applied for desulfurization. ✓Removal of sulfides, thiols, and thiophenes successfully	✓Needs high pressure and temperature. ✓Employs expensive catalyst. ✓Does not eliminate 4,6-DMDBT. ✓Decreases octane grade of gasoline. ✓Does not eliminate refractory compounds efficiently

BDS	✓Modest operating conditions i.e. lower pressure and temperature. ✓Environmentally friendly with fewer greenhouse emissions. ✓Produces less acid rain gases. ✓High specificity of the enzyme. ✓Lower capital and operating costs. ✓High valuable by products ✓Recalcitrant compounds can be removed under mild pressure and temperature .	✓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. ✓Deep desulfurization cannot attain (10–100 ppm sulfur). ✓Cost of culture media to cultivate the microorganisms. ✓Sensitive
ADS	✓Operates at a lower temperature ✓No need of H_2 ✓No release of H_2S ✓Capability to eliminate refractory S-compounds.	microorganisms. ✓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. ✓Numerous adsorbents have less adsorption capability, hence demanding multiple large adsorbent beds.
ODS	✓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 H_2 gas.	✓Robust oxidizing agent e. g·H_2O_2 is costly for larger-scale applications. ✓No widespread study on heavy fractions e. g. bitumen ✓Catalyst is required for deep desulfurization. ✓More reactions on oxidation

	✓Minor temperature and pressure. ✓Complementary chemistry to HDS. ✓Recalcitrant compounds easily converted	may result in the production of non-essential products particularly when H2SO4 is utilized. ✓Tough to convert thiophene.
EDS	✓Operating conditions viz. lower pressure and temperature. ✓Easy to integrate with a refinery method. ✓Solvents such as DESs can be recycled. ✓Does not require hydrogen. ✓No use of catalyst [28]. ✓Does not react with desired fuel oils. ✓Process simplicity and less energy input. ✓Extracted compounds can be utilized as raw materials.	✓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 compounds from fuel without extracting preferred sulfur-free hydrocarbons.

4. Literature Review

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. Extractive desulfurization is another very common and useful method for the removal of sulfur content from the feed stock. The solubility of the sulfur content depends on the particular solvents which are used in this process.

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), pyrrolidone's, dimethylformamide (DMF), and other volatile organic compounds (VOCs). The consumption of organic solvents associated with the challenges such as flammability, volatility, toxicity, and sulfur elimination efficacy is not significant. The potential benefits of EDS are that it does not require hydrogen or catalyst and can be operated at mild conditions. 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. Due to same polarity of aromatic S-compounds and aromatic sulfur-free hydrocarbons in liquid fuels, the selection of extractants is of huge significance. 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. 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. 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. 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, nontoxic, and preparation process can be done at close to room condition. Table 3 summarizes EDS of fuels using DESs.

Table 3: Reported studies on EDS using DESs					
Sulfur compounds	Model fuel	DESs (HBA/HBD)	Desulfurization efficiency	Mole ratio	Ref
Th, DBT	Iso-octane, n-Decan	TBAB/PEG	82.40%	1:2	81(Rahma et al., 2017)
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(Zhao et al., 2018)
DBT, Th	n-decane, iso-octane	FeCl3: [CH3(CH2)3]4P Br	64% DBT and 44% Th	1:3	83(Gano et al., 2015b)

4,6-DMDBT, DBT, 3- MBT 4-MDBT, BT	n-octane	[C12DMEA]Cl/ FeCl3	52.9%	1:6	73(Jiang et al., 2017a)
BT, 4,6- DMDBT, DBT	n-octane	MIM/PA DEA/PA	MIM/PA 54.7%	1:2	84(Jiang et al., 2016)
Th, DBT, BT	n-octane	TBAB/For TBAB/Ac	TBAB/For BT 98.32%, DBT 98.24% and Th 97.6%	1:2	70(Li et al., 2016)
DBT	n-octane	ChCl/Pr	64.9%	1:3	10(Almashjary et al., 2018)
Th	n-hexane	TEACl/EG TEACl/Gly MTPPBr/EG MTPPBr/Gly	-		85(Warrag et al., 2018a)
DBT, Th	So-octane, n-decane	SnCl2·2H2O: [CH3(CH2)3]4P Br	DBT 69.57% and 47.28% Th		86(Gano et al., 2015a)

DBT, BT, 4,6-DMDBT	n-octane	[TEtA]/[Fo] [TEtA]/[Ac] [TEtA]/[Pr] [TEtA]/[Bu] [TEtA]/[Pe]	[TEtA][Pr] 52.3%	1:2	79(Wang et al., 2016)
Th, DBT	n-decane, iso-octane	TBAB/imidazole	70% DBT and 47% Th from simulated fuel. 47% from	1:2	87(Gano et al., 2017)
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	1:2	80(Lima et al., 2018)
DBT, Th, BT	n-octane	TBAC/PEG/FeCl3	-	1:5	88(Shah et al., 2019)

DBT	n-octane	TBPB/DMF	82.1%	1:2	89(Cheng et al., 2018)
BT, Th	n-heptane	THAB/EG THAB/Gl	-	1:2	90(Alli and Kroon, 2018)
Th, BT, DBT	n-octane	[TBA][Br]-FA	-	1:2	91(Gutierrez et al., 2018)
BT,DBT, 3- MT	n-heptane	Toluene/AlCl3/ chlorinated paraffins-52	In real oil 84.5%	1:3	92(Tang et al., 2015)
Th	n-heptane	TBAB/EG TBAB/Sul TBAB/TrEG	TBAB/Sul 98%	1:2	93(Hadj-Kali et al., 2016)
Th	n-hexane n-octane	THAB/EG THAB/Gly	-	1:2	94(Warrag et al., 2017)
BT, 2-MT	n-octane	TBAC/EG TBAC/Gl TBAC/MA	TBAC/EG 99.5%		71(Shu and Sun, 2016)
BT	n-octane	ChCl/Gl ChCl/EG	TBAC/PEG 99.48%		72(Li et al., 2013)

		TMAC/EG TBAC/EG TBAC/PEG			
DBT	n-ocatne	TBAC/PEG/FeCl 3	89.53%	1:3	69(Mukhopadhyay et al., 2016)
BT, DBT	n-octane	ChCl/EG ChCl/U	-	1:2	95(Wagle et al., 2018)
Th	n-octane, n-hexane	TEACl/EG TEACl/Gly	-	1:2	96(Warrag et al., 2018b)
DBT, 4,6- DMDBT	Dodecane	ChCl/Gly	97.06%		97(Zaid et al., 2017)
2-MT, 3-MT	n-heptane	THAB/EG THAB/Gl	-		98(Alli et al., 2018)
DBT	n-octane	MTPPBr/TetEG	85%	1:2	77(Sudhir et al., 2020)
Th, BT, DBT	n-octane	[BPY]Br/MA	94.14%	1:2	99(Li et al., 2017)
DBT, Th, 2- MT	n-heptane	TBAB/DG	DBT 92%, 2-MT 86%, Th 71%	1:5	100(Jha et al., 2020)
Th, BT, DBT	n-heptane	ChCl/phenol	91.5% Th,	1:2	78(Makoś and

			95.4% BT, 99.2% DBT		Boczkaj, 2019)
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(Lee et al., 2020)
Th, DBT, 3- MT	n-octane	DPC-ChCl-SnCl2 DPC-ChCl-FeCl2 DPC-ChCl-CuCl2 DPC-ChCl-FeCl3 DPC-ChCl-ZnCl2 DG-ChCl-SnCl2 DG-ChCl-ZnCl2 DG-ChCl-FeCl2 DG-ChCl-CuCl2 DG-	DPC-ChCl-SnCl2 possess 95.2 % for DBT, 3-MT 94.5%, and 92.1% Th.		75(Shirazinia et al., 2020)

		ChCl-FeCl3			
Th	n-octane	ChCl/U ChCl/EG ChCl/Gl	Molybdate nanofluid-based ChCl/EG 98.01%	1:2	102(El-Hoshoudy et al., 2020)

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. 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. Earlier nitric oxide or nitric acid oxidants for instance NO/NO_2 or HNO_3 gases used for ODS. But, later it was established that these oxidants give rise to a high quantity of residues. 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. 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 coextraction of sulfur-free hydrocarbons, for instance, olefins (alkenes) and aromatics from liquid along with sulfones . The potential advantages of ODS are minor operating specifications and similar chemistry as HDS (viz. HDS includes reduction using H_2 gas, while ODS includes oxidation using oxidant) and utilizes traditional refinery apparatus for the reaction and separation. The careful regeneration of adsorbent or extractant utilized is significant along with the waste management of sulfone compounds produced . Amid various oxidants, currently the most popular is H2O2 since it is environmentally friendly 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 . For this purpose, DESs and ILs were presented as an alternative in ODS. Now, DESs and ILs are appealing attention for using in ODS due to several desired properties such as less volatility and capability to behave as both catalyst and extractant. ODS using DESs are enlisted in Table 4.

Table 4: Reported studies on ODS using DESs.					
Sulfur compound	Model fuel	DESs(HBA/HBD)	Desulfurization efficiency	Mole Ratio	Ref
DBT, 4,6-DMDBT, 4-MDBT	n-dodecane	[PSTEtA]Cl)/OA ([PSTEtA]Cl)/AA TBAC/OA	97.7%		109(Jiang et al., 2020)
BT, 4,6-DMDBT, DBT	n-octane	L-Pyro/TFA L-Pyro/For L-Pro/TFA L-Pro/For	L-Pyro/TFA possess 99.7% DBT, 99.6% 4,6-DMDBT, and 99.2% BT	1:2	115(Liu et al., 2020)
BT, 4,6-DMDBT, DBT	n-octane	C9H10O2.ZnCl	99.23% for DBT, BT 96.12%, and 98.4% 4,6-DMDBT	1:3	112(Mao et al., 2017a)
BT, 4,6-DMDBT, DBT	n-octane	CPL/OXA	98%	1:2	113(Hao et al., 2018)

DBT	n-octane	ChCl/p-TsOH ChCl/MA ChCl/U	99.1 wt% ChCl/p-TsOH for DBT	1:4	114(Li et al., 2018)
4,6-DMDBT, BT, 4-MDBT, 3- MBT, DBT	n-octane	ChCl/Ac ChCl/PEG ChCl/EG ChCl/Gl ChCl/Fo ChCl/Pr ChCl/U	ChCl/Ac 100%		116(Jiang et al., 2017b)

DBT, BT, Th, 4,6-DMDBT	n-octane	ChCl/CF3SO3H	98.65% for DBT and 4,6-DMDBT 96.8%	1:2	110(Mao et al., 2017b)
BT, 4,6-DMDBT, 4-MDBT, DBT	Dodecane	ChCl/PEG/BA	99.2%	1:5	107(Jiang et al., 2019)
DBT	n-octane	ChCl/OXA TMAC/OXA TBAC/OXA	TBAC/OXA 91% for DBT	1:3	111(Lü et al., 2015)
BT, 4,6-DMDBT, DBT	n-octane	L-Pro/OA L-Pro/PA L-Pro/GA L-Pro/p-TsOH	L-Pro/p-TsOH DBT 99%	1:2	117(Hao et al., 2017)
BT	n-octane	ChCl/p-TsOH TBAC/p-TsOH	For model fuel 99.99%. For real fuels, ChCl/p-TsOH 97.25% And,TBAC/p-TsOH 95.90%	1:2	106(Yin et al., 2015)

4-MDBT, 4,6-DMDBT, DBT, BT, 3-MBT	n-octane	ChCl/AcChCl/ FoTBAC/Ac	BT completely removed by ChCl/Ac	1:2	118(Jiang et al., 2018)

Conclusions

In conclusion, the desulfurization of fuels using deep eutectic solvents (DES) presents a promising avenue for producing cleaner fuels with reduced sulfur content. DES offer several advantages over traditional desulfurization methods, including low cost, high selectivity, and environmental friendliness. Through complexation or other mechanisms, DES can selectively extract sulfur compounds from fuels, resulting in improved fuel quality and reduced environmental impact. Further research and development in this area could lead to widespread adoption of DES-based desulfurization processes in the fuel industry, contributing to cleaner air and enhanced sustainability, additionally, the use of deep eutectic solvents (DES) for fuel desulfurization holds potential for addressing stringent regulatory requirements regarding sulfur emissions in automotive fuels. DES-based processes offer the advantage of being more environmentally benign compared to conventional methods, which often involve harsh chemicals and generate hazardous waste. Furthermore, DES can be tailored to specific sulfur compounds, enhancing their selectivity and efficiency in removing sulfur from gasoline. As research continues to advance in this field, optimization of DES formulations and process parameters could lead to commercial-scale implementation, driving the transition towards cleaner and more sustainable energy sources in the transportation sector.

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