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# Ionic liquids based on metal halide complex salts and their applications in extractive desulfurization of liquid fuel: A review

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## Abstract

In this review, different types of sulfur compounds (thiols, sulfides, benzothiophenes, etc.) present in liquid fuel can be conveted by combustion to sulphur dioxide, which is a prevailing source of environmental pollution, so many countries proposed standard S-content to lower than 10 ppm. Although, hydrocracking process produce low-sulfur content, but still needs more desulfurization, researches have done using many technologies, among that were: A: Adsorptive desulfurization (ADS), through adsorptive over such surfaces. B: Oxidative Desulfurization (ODS), using an oxidant agent to convert sulfure into form can be removed. C: Hydrodesulfurization process (HDS), which is most efficient than other methods to remove organo sulfur (aliphatic and aromatic). D: Bio desulfurization (BDS), employed microorganisms to remove sulfur atom from organic S-compounds and can be environmental friendly. E: Extractive desulfurization (EDS), is a prosses using solvent as liquid- liquid extraction. The above technologies faced some disadvenges such as nature of volatile molecular solvent coupled with limitation of loss solvent, difficult of extraction regeneration, environmental pollution and costly, as required industrial unit operation at high temperature and pressure beside the expensive of hydrogen gas and catalysts. Therefore, it has been a challenge research investigation to explore a new deep extractive desulfurization method. Among these treatments was using ionic liquids (ILS) which composed of heterocyclic organic cation (imidazolium, pyridinium, etc.) and different inorganic anions may be applied to decrease temperature, non-toxic, chemical stability, environmental friendly as green solvent, so, (ILS) used for many applications and deep eutectic desulfurization among that. Recently, studies showed that metal contains ionic liquids for extractive sulphur removal have a high influence and ability for sulphur removal than metal free (ILS), which may be a good solvent in separation and removal of aromatic sulphur from fuel. The Fe, Co, Ni, Zn, Cu, etc. metals halides were used with organic cation to form complexes salts. The mechanism was investigated that the metal (ILS) have almost good extraction ability explained by the complexation of metal moiety with sulfur compounds.

## 1- Sulfur in fuels

In general, diesel fuel is a liquid fuel that used in diesel engines which can be produced through the fractional distillation of crude oils, it is a mixture of 75% saturated hydrocarbons and 25% aromatic hydrocarbon containing 8 and 21 carbon atom per molecule. The combustion products of petrodiesel are water, nitrogen and carbon dioxide. However, sulfur is one of the main pollutant in diesel fuel as result from incomplate combustion of fuel; which emission as sulfur dioxide (SOX). Sulfur presents as inorganic and organic forms in fuel, and it is a third abundant element in fossil fuels after carbon and hydrogen. sulfur in crude oil occurs as either:

1. Elemental sulfur as trace.

2. Organic sulfur can be separated into

2-A: Aliphatic s-compounds; mercaptans and thiols (R-SH). sulfide is also present as thioethers (R-S-R) and disulfides (R-S-S-R). The aliphatic s-compounds are very active due to:

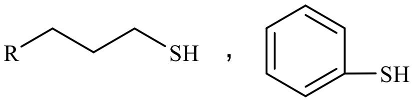
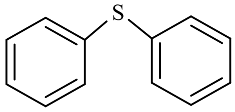
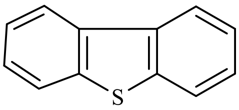
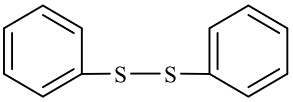
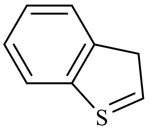
- Sulfur attached at the end of compounds.

- Low molecular weight and boiling point. Table .1

The aliphatic organic s-compounds can be completely removed by hydrodesulfurization (HDS).

2-B: Aromatic s-compounds; thiophenes, benzothiophene (BTS) and alkyled compound i.e. dibentothiophene (DBT) and methyl dibenzothiophene (MDBT) table (1). These derivatives are the most important because, their presence makes the desulfurization process more difficult due to their high melting point [1-7]

**Table 1.** fuels compounds of sulfur compounds

| name | structure |
|---|---|
| Thiols |  |
| Sulfide | R-S-R ,  |
| Benzothiophenes(BTS) |  |
| Bisulfides |  |
| benzothiophene |  |

## 2- Alternative desulfurization technologies

In recent years, production of clean fuel has become an important topic research around world. $SO_x$; which are generated by the burning, of hydrocarbon fuels containing organic sulfides have become one of the important reasons for the pollution of environmental through the formation of haze weather.

To prevent the pollution from transport emissions the decrease of sulfur contain from the sources has been studied and a new methods were suggested to reduce sulfur in fuel, [8-12].

Petroleum of higher viscosities contains higher amount of more sulfur compounds. Thermal process used to remove the sulphide from aliphatic hydrocarbon, while the sulfur in aromatic rings can be removed by hydrodesulfurization [13].

The conventional method used in the industry depends on the type and amount of sulfur contain. A number of alternatives methods have been mentioned in the literature, these include, adsorption, hydrodesulfurization, oxidation, extraction and biodesulfurization.

### Adsorptive Desulfurization (ADS)

In (ADS), the organosulfur compounds in fuel oil are removed through adsorption, one of adsorbent that is typically to be non-reactive and porous. The efficiency of this method depends on the properties and type of the absorbent material, selectivity to organo-sulfur compounds [14-16]. There are two types of adsorption: one can be physical adsorption of sulfur on the surface which is do not involves chemical bonds. The regeneration depends on the strength of the absorption. The type two: chemosorption which involves a chemical interaction between organo-sulfur compound with solid surface. Regeneration of the sorbent can be done by thermal treatment [3,17.18]· sulfur is removed as $H_2S$, Sox, depending on the process or the nature of stock. Different types of sorbent materials were investigated for desulfurization, among them activated carbon, alumina, zeolites, amorphous silica-alumina and metal organic [19-22].

The activated carbon is the one which studied because its effective surface area and porosity; different types of activated carbon investigated from different sources raw materials Table 2.

**Table 2.** different absorbents types for desulfurization of dibenzthiophene (DBT) [21]

| Absorbents | Model oil | % S-removal |
|---|---|---|
| Activated carbon | Gas oil | 95 |
| Alumina | Gas oil | 88 |
| Ni Mo Pt/ $Al_2O_3$ | hexane | 63 |
| Ruthenium Complexes | ----- | 55 |

### Oxidative desulfurization (ODS)

Oxidative desulfurization involves chemical oxidation by different oxidants (hydrogen peroxide, air, ozone, organic peroxides) to react with the divalent organic s-compounds in fuels at low temperatures ($<93^0$ C) and low pressure (<6.8 atm) to form the corresponding hexavalent sulfur.

The oxidazing agents have a great effect on the desulfurization process as they have synergistic role with the catalysts [23-27].

The oxidative technology is being considered for deep sulfurization of fuel to remove s-compounds which are interactive to (HDS) process, i.e thiophene, and its alkylated derivatives as advantage of the method. The main disadvantage of (ODS) is a problem of sulfanes recycling which are by products of (ODS) as costs to remove the sulfane by new unit [28].

The review of literature dealing specific with (ODS) indicating the importance industry application in refining process that is employed for conversion of thiols into disulfide (eq.2.1) in basic medium [22,29,30].

$$2R\text{-}SH + 1/2O_2 \longrightarrow R\text{-}S\text{-}S\text{-}R + H_2O\text{---}(2.1)$$

The most recent oxidative desulfurization process of heavy crude oil using potassium permanganate and hydrogen peroxide ($KMnO_4/H_2O_2$) as oxidant agents over formic acid and acetic acid as catalyst to give desulfurization efficiency of 73% and 27% respectively.

**Hydrodesulfurization process (HDS)**

Hydrodesulfurization is the more efficient than other processes in an elimination of aliphatic sulfur compounds, at the same time it is not effective in removal of organic sulfur compounds. Also, Hydrodesulfurization is not economically active as it is performed by co-feeding oil and H2 to fixed bed reactor packed with an expensive and selective type of catalysts like $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, and using hard conditions, i.e. high pressure and temperature; it needs additional removal of by-product $H_2s$ using Clause process to get the sulfur as element [31].

Aliphatic sulfur is very reactive in which, may be eliminated totally by (HDS) process (eqs. 2.2-2.4)

$$\text{Thiols: } R\text{-}SH + H_2 \longrightarrow R\text{-}H + H_2S\text{---}(2.2)$$

$$\text{Sulfide: } R_1\text{-}S\text{-}R_2 + 2H_2 \longrightarrow R_1\text{-}H + R_2\text{-}H + H_2S\text{---}(2.3)$$

$$\text{Disulfide: } R_1\text{-}S\text{-}S\text{-}R_2 + 3H_2 \longrightarrow R_1\text{-}H + R_2\text{-}H + H_2S\text{---}(2.4)$$

The aromatic sulfur contains compounds in fuels such as thiophene rings is more difficult to remove. The lone pair electrons from sulfur participates in the π- electron structure of the conjugated C=C system, this resonance stabilization is enough to make (HDS) energetically demanding.

There are two pathways of desulfurization Figure (1), so, the resonance stabilization of the sulfur in the thiophene ring makes the direct hydrogenolysis difficult and the main (HDS) pathway requires saturation of the aromatic ring before (HDS) can be take place [17].

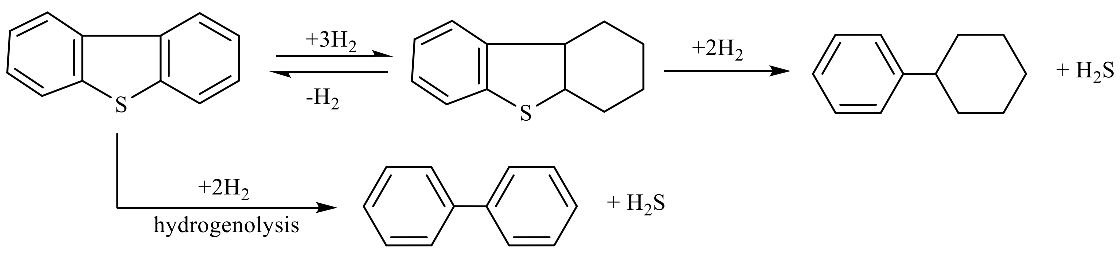


**Fig. 1** Hydrogenation and hydrogenolysis pathway of hydro sulfurization as explained by sulphur removal as benzothiophene.

## Bio desulfurization (BDS)

(BDS) is considered as an ecologically friendly (green process) in which microorganisms (bacteria, microbe), that the bacteria selectivity oxidizes the S-element, and splitting the carbon-sulfur bonds. The biochemical process must be at ambient temperatures and atmospheric pressure, so these will have required less energy and operating condition as it does not need hydrogen compared with hydro desulfurization methods to remove sulfur percent below the required standards [32-35].

The sulphur removal in this process is limited by the kind of bacteria which can be used for desulfurization*: Rhodococus*, *pseudomonas, Gordona, Thiobactillus and Arthrobacter* [36-38]. Dispite the advantages of (BDS) method, the (BDS) technology can be only applied as a complementary process, due to fact that it cannot do as (HDS), in addition to remove s-compounds induce solvation of carbon-carbon double bonds and also improves the creating characteristics of materials.

Based on above disadvantages the bio desulfurization technology has not as yet been shown to be economically voluble on a commercial scale [39].

## Extractive desulfurization (EDS)

(EDS) is a liquid-liquid extraction and is the most widely used alternative, desulfurization technology. It depends on the solubility of organosulfur compounds and on the type of solvent. The products involve of one or more components and the feeding through contact liquid; called solvent to produce an extract which can stripe as liquid phase [39-40].

The soluble organosulfur compounds in mixed tank moved to the solvent (depends on the solubility, and can be separated from solvent and hydrocarbon with lower sulfur content. The solvent recycled to new extraction process.

Extractive desulfurization considered as industrial application, can be performed at mild conditions (low temperature and pressure) without catalyst and hydrogen [17]. However, there are some problems:

A- The volatile, flammability and toxicity of organic solvents, and these can effect on its efficiency and recyclability.

B- The low selectivity of organic solvents means that some kind of sulfur contain this leads to decrease a quality of fuel.

C- The two phases, oil and solvent must be immiscible.

D- The sulfur contains, compounds in oil have a different boiling point.
E- Traces of sulfur remains in solvent after distillation.

## 3- Ionic liquids

### Definition

Ionic liquids are salts are often defined as those which liquid in a range below 100°C even at room temperature can be justified by the definit improvement in the range of applications for liquid salts below this temperature [41]. The volatile organic compound (VOCs) are the media for industrial process such as extraction catalytic applications and organic chemicals synthesizing process which require solvents. However, these solvents are one the major air pollutions giving rise to health and environment concerns. Due to these restrictions; regulations have been put to eliminate the emission of these compounds. In the past few years the significant research has been available in the area of preparation characterization and application of (ILS) in different fields to replacement for (VOCs) due to their suitable properties.

ILS have been classified as new green solvent which have been extensively employed solvents because of their low melting point, wide liquid range, etc, these physical and chemical properties can be changed by using different cations and anions to meet the requirement of specific applications [42,43]

### Structures and properties of ionic liquids

Ionic liquids (ILS) are usually compose with a large asymmetric organic cation. The asymmetry of cation lowering the melting point. The anion may be $F^-$ , $Cl^-$ Br – etc. inorganic (i.e: $[BF_4]^-$,$[PF_6]^-$,$[Sb\text{-}F_6]$,$[AlCl_4]^-$,$[FeCl_4]^-$, or organic $[ACO]^-$,$[CF_3COO]^-$,$[CF_3SO_3]^-$,$[PhCOO]^-$ ,$[RSO_4]$.The characterization of ionic liqides depends on the cation and anion ,some typical formulas for cations and anions are shown in Figure (2) [44-46] .

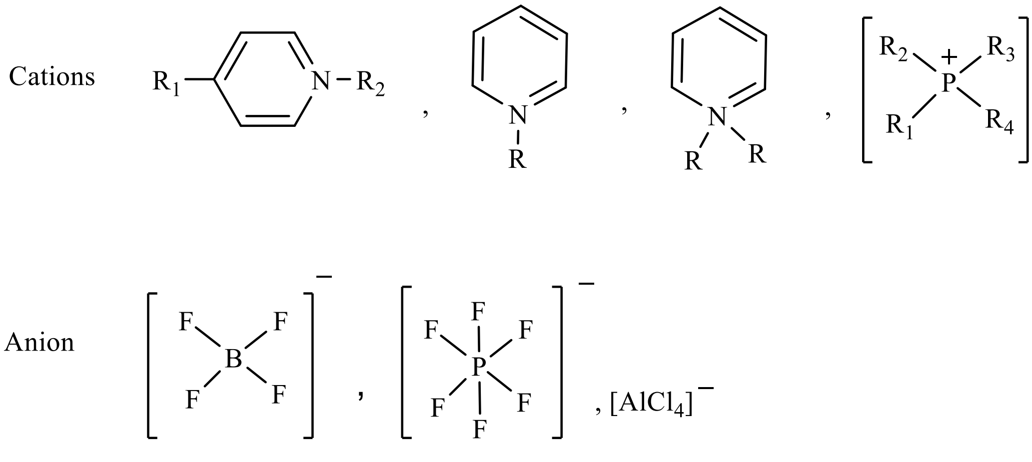


**Fig. 2** Typical structures for cations and anions of (ILS)

The physiochemical properties of (ILS) can be improved by alteration the nature, size and structure of both their cation and anion constituents. The most important properties of (ILS) that are changed them in very active solvents as desirable properties [46-49] such as:

- Melting point, ionic liquids are known as insignnificant vapor pressure undr their decomposition.

- Thermal stability, thermal stability has been reported for several ionic liquids and it depends on the power of their hetro atom carbon and H- bond. The thermal analysis show the pyrolysis generally take place between 350-450 °C.

- Stability, many ionic liquids have the capability to dissolve the organic, inorganic compounds and polymers, and these properties can be altered to immiscible with or ordinary solvents. The effect of contains on the stability have been studied ionic liquids are good solvents in many chemical reactions.

- Electrochemical stability, its often got wide range electrochemical potential and as a good for electrical conductivity transformation.

- Non-flammability, its safe for store because of their nonvolatile and non-flammable at ambient and higher temperature.

- Relativity moderate, surface tensions.

- Nontoxic and environmentally friendly.

## 4- Applications of metal containing ionic liquids

Room temperature ionic liquids have emerged as versatile alternative organic solvents for a wide variety of organic reactions, and considered a new have unlike applications in wide areas like solvent for synthesis catalysis or purifications, in batteries, as lubricant supplement, in polymerization, in pharmaceutics medicine, in synthises of nanoparticles, in wood related industries, in analytical chemistry, liquid-liquid extractions for inorganic and materials syntheses, desulfurization of model gasoline, etc. [50- 57] .

In addition, to these applications of ionic liquids, it can be found that these noble solvent are very useful in many other fields, from these points that (ILS) could be a convenient solvents for a lot of interest in academic scientist and in an industrial Figure 3.

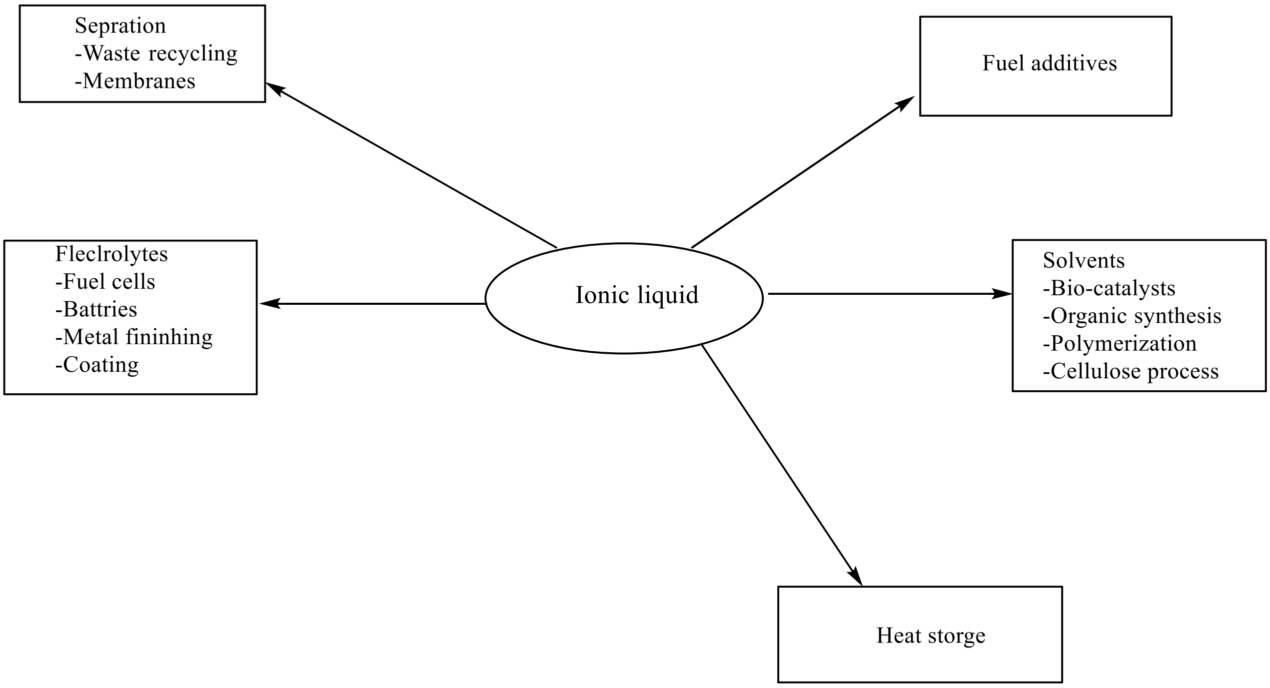


**Fig. 3** The application of ILS in different fields of chemistry

Ionic liquids containing various transition metal ions have been prepared, notable examples include halides of V, Fe, Co, Ni, Cu, Pt, etc, In 1993 Hitchcock et.a prepared $[Emim]_2(MCl_4)$, Emim: 1 - ethyl-3-methyl imidazolium cation, M= Co, Ni, the complex salts have been characterized by magnetic properties I.R.,U.V-vis. Spectroscopy and single-crystal X-ray diffraction [58].

Many researches were appeared in this area,for example [Bmim]Cl in combination with $FeCl_3$ is successfully used for oxidative desulfurization of fuels and as lewis acid solvents [59].

In 2007 (Tourneut eta) [60] prepared palladate salts from chiral prydiniun ionic liquid and the single crystal X-ray structure was studied Figure 4.

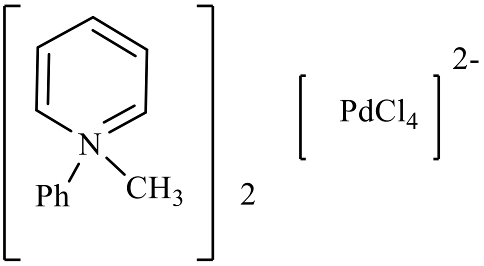


**Fig. 4** Prydiniun ionic liquid

Amonir and Co-workers prepared the Bis (2-6-dimethyl prydinium) hexa chloridoplatinate (IV) $[C_7H_{10}N]_3[[PtCl_6]$ and the single crystal shows the asymmetric unit cell, the pt atom has an octahedral geometry and the hydrogen bond N-H---Cl; C-H----Cl with π-π interaction between the prydinium rings [61].

As copper halids Figure 5 have huge drug applications or anticancer, antifungal, etc. due to optoelectronic and magnetic properties [62,63], for these reason Mokadden and Boughzala prepared and determined single X-ray diffraction of tetra chloroido cuprate (II) anion with imidazo [1,2-α] pryridin-1-ium organic cations [64].

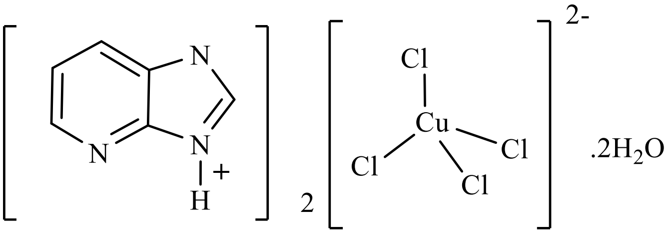


**Fig. 5** Tetra chloroido cuprate (II) imidazo [1,2-α] pryridin-1-ium organic

Alyass and Mohammed preperated some new complex salts of divalent and trivalent ions with tetrapropyl ammonium iodide, characterized by elemental analysis molar conductance, U.V-visible spectra and magnetic measurements.

Recently efforts and huge investment have been made in the field of ionic liquid in drugs, among that in the preparation and characterized of ionic liquids and their salts of anionic penicillin G and amoxicillin hydrolyte derivatives and their in vitro antibacterial activity against sensitive and resistant E *Scherichia* [56].

## 5- Ionic liquids for desulfurization.

## Deep eutectic solvents (DESs)

Deep eutectic solvents are a new sort of solvents, cognate to (ILS) that have a enormous attractive attention as their attractive physical properties such as low melting point far below its constituents, which can be easily changed for specific use [65-68].

(DESs) exist of two or more component having H- bond donors (HBD) and H-bond acceptors (HBA) that forms a eutectic mixture, prepration of (DESs) is almost easy and does not require organic solvents, the interacting components are green easily usable and cheap raw materials [69].

The deep eutectic solvents consist of different kinds of metal halides and hydrate metal halides with imidazolium or other heterocyclic salts. In general, the eutectic solvent can be classified into four types.

Type one formed from cation salt and metal halide, such imidazolium chloroaluminate halides such as $FeCl_2$, AgCl, $CuCl_2$, LiCl, $CdCl_2$, $SnCl_2$, Tin(II), $ZnCl_2$, $LaCl_3$.

Type two: formed from cation with hydra metal ions as are not moisture stable and cheaper. The type three consists of cation salts (COOH, $CONH_2$) with compounds having H-bond donors (HBD), the properties of this type inactive with water, biodegrable easy preparation and can be applied in many industries process. The type four formed hydrogen-bond, (HBD) and metal halides [70-72].

Therefore, (DESs) are investigated to be an another choice to volatile organic solvent has been widely concerned in many chemistry technology process [73,74].

## Ionic liquids of imidazolium cation as extractive and deep eutectic solvent for desulfurization of liquid fuels.

Although first (IL) was prepared before 1914, but until 1990 That (ILS) had raised consideration as a new sort of solvents for different application [73-75].

In 2001 the use of room temperature molten salts in fuel desulfurization was first reported by wassercheid and Co-workers, they used 1-butyl-3-methylimidazolium halides with aluminum halides [BMIM] $AlX_4$ to remove up to 50% of sulfur contain. The further research into ionic liquids as a solvents in separation desulfurization using imidazolium-based ionic liquids with different anion such as $[BF_4]^-$,$[PF_6]^-$,$[MeSO_4]^-$, $[OCSO_4]^-$ etc, the anion $[OCSO_4]^-$ showed the most results in the desulfurization diesel; the efficiency was tested for multistage desulfurization experimental using diesel oil at 15 minute and 5/1 mass ratio oil fuel (ILs at $60^0$C).Table 3 [71,74-81] .

**Table 3.** percentage sulfur removed by multistage desulfurization of diesel oil with (ILS) [80,81]

| Extraction stage | [BmIm]/$AlCl_4$ | [BmIm]/octylsulfat |
|---|---|---|
| 1 | 41.3 | 14.7 |
| 2 | 57.3 | 25.3 |
| 3 | 65.3 | 30.6 |
| 4 | 80.0 | 37.3 |

Several other workers studied anion such as $Cl^-$, $(PFO)^-$ etc. with imindazolium base, these anions showed high efficiency for organic-S-compounds removal, unfortunately ionic liquids with hydrogen-based anion cannot be applied in an industry process due to their hydrolysis and toxicity [41]. There are many factors effecting the efficiency of imidazolium-based ionic liquids for fuel; desulfurization, among the factors are, the size and structure of both cations and anions. Two types of ionic liquids of 1-alkyl-3-methyl imidazolium [Amim] $BF_4^-$ and hexafluorophosphat and trimethyl amine hydrochloride were tested to remove sulfur from fuels the heavier anions showed high selectivity toward aromatic sulfur [82].

The absorption of aromatic-sulphur compounds were studied, organic compound with greater electron density were favorably absorbed. The bulky alkyl chain on aromatic ring reduce the absorbance due to a hindrance effect of ions and size of the ionic liquid are importing parameters for absorption ability [83].

Ionic liquids can be referred as a new noval green solvent to know clean fuel in the future due to their physiochemical properties to be a good extractive of s-compound from fuels [84]. In the latest decades (EDS) using (ILS) have been studied extensively. Extraction of sulfur compounds from petroleum and hydrocarbon industries by using [BMIM]Cl/$AlCl_3$,[EMIM]$ClAlCl_3$ at room temperature, the comparing showed the efficiency of extraction which depends on Bronsted acid [85,86].

A new kind of efficient solvent know as an ionic liquid becomes the aim of many researchers. Alkyl imidazolium based as cation with different anions were used in chemical process as a green solvent [87].

Researches on imidazolium fascinated much interest by many authors through the synthesis of imidazolium based such as [Bmim]Br, [Bmim]Cl, [Bmim]$BF_4$, [Bmim]$PF_6$ [88-89]. These ionic liquids characterized by physicochemical properties such as conductivity and solubility, the efficiency as solvent for extractive desulfurization of fuels were employed as bellow.

Imidazolium based 1-butyl-3-methyl imidazolium tetrafluoroborate, [Bmim]$BF_4$ and 1-butyl-3-methyl imidazolium hexafluorophosphate [Bmim]$PF_6$ [84-94] have tested for s-compounds as effective agents in desulfurization of model liquid fuel (DBT in octane). The time effect on extractive were carried out at 5, 10, 20 and 30 min. at $30^0$C with mole ratio 5:1 (Fuel:IL). The results show that thet time of 30 min between the model liquid fuel and IL to achieve the equilibrium.

The extraction by imidazole ionic liquids was due to Polarizable π- electron and π-π interaction between imidazolium and the thiophenic of DBT [ 92,93]·

The interaction mechanism in extractive desulfurization between imidazolium and aromatic ring of sulfur compounds becomes an interest subject by Quantum chemical calculation and NMR studies [94].

The influence of interaction mechanism between the salute and solvent was reviewed by Adulla and Co-worker [95]. For model and real fuel, the mechanism involves various interactions such as acidic-basic and electron transfer. There are different proposed theories of extractive desulfurization.

The mechanism involves π-π interaction and CH-π interaction aromatic ring imidazolium cation and sulfur compounds as below [83].

- Electrostatic field effect (such as columbic) between anion and cation of ionic liquids.
- The hydrogen bond between ILS with sulfur atoms.
- Anion effect
- Dilution effect of ILS by s-compound insertion is not the dominant factor.

The regeneration or recyclability of ILS is become an important as ILS is quite expensive and taking in mind the environment effects. The behave makes ILS as feasible for regeneration to reduce the cost of process [96].

Also, [$C_4$mimCl] $CoCl_2$ ionic liquid was synthesized by mixing cobalt chloride $CoCl_2$ with 1-butyl-3-methyl imidazolium chloride [bmim]Cl and used with Ox one ($KHSO_5$) as selected oxidized agent for desulfurization of fuels. The results indicated that the removal of s-compounds efficiency can be reached 97% under the optimal experimental conditions [97].

The binary mixture of nonvolatile organic solvent Dimethyl formide DMF with [Hnmp] $H_2PO_4$ and [Hnmp] $HSO_4$ ILS were studied for extractive desulfurization and the operating conditions such as time, temperature multiple steps are the ratio were examined [98].

Ml-based ionic liquids are divided into three kinds: metal chloride (ILS), metal oxide (ILS) and metal complex, the properties of (ILS) such as a good thermal and chemical stability etc. therefor (MILS) used extensively for fuel desulfurization [99].

### Metal containing ionic liquid of different types of quanternry ammonium holides as eutectic solvent for desulfurization of liquid fuels

Extractive desulfurization with ionic liquid has been attracted significant attention by using different types other than imidazolium as cation like, tetrabutyl ammonium halides (TBAX), morpholine, pyridine, etc. from growing number of scients due to current environmental restrictions of fuel.

Abott and Co-workers prepared an excellent solvent by mixing choline chloride $C_5H_{14}ClNO$ (CHCl) and urea $(NH_2)_2CO$ or lactic acid and used for (DES) studies [100].

Tetrabutylammonium bromide (TBABr) based with ethylene glycol was prepared and characterized by their physical properties such as density, viscosity and ionic conductivity [101]. The desulfurization conditions as solvent was studied including the effect of temperatures, density and viscosity. The difference intensity indicates that DESs are highly sensitive towards temperature, as heating may weaken the attractive forces between molecules [102]. The effect of temperature on ionic conductivity shows, the increasing of conductivity with temperature; this may be due to collision between molecules and the weaks of the bond forces [103].

The extractive desulfurization of liquid fuel, by ionic liquid, ILS instead of organic solvents provides an alternative clean fuel, the literatures reviewed imidazolium, prydinium, quinolinium based ionic liquids with anions such as alkylsulfates, alkylphosphates, or hydrogen containing anions. Inspite that ionic liquid, have high distribution coefficient for model fuels containing sulphur with the heavy fuels the situation become worse. The efficiency process with (ILS) increase by oxidazing organo sulfur with oxidizing agents [104,105].

In 2019, Fonseca and (CO-Workers) [106] prepared morpholine based ionic liquids $[NmorPh]^+[HCOO]^-$ via reaction between absorbent acid formic and morphine or N.methylmorpholine Figure (6)

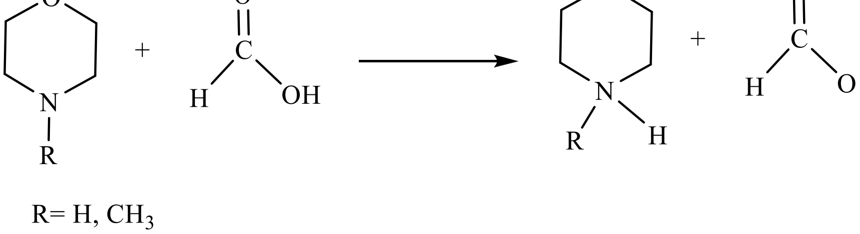


**Fig. 6** synthesis of $[NMorPh]^+[MorPh]^+$ ionic liquids

These ILS were used as solvents in extractive desulfurization of model oil and commercial diesel fuel, the parameters of conditions such as, mole ratio, time of extraction and cycles were studied to get an optimize operating factors.

As industrial process required large volume of ILS for desulfurization [107]. The efficiency of desulfurization for multi stage shows that it can be used active for three time cycles.

Warrag and Co-workers [108] synthesized a series of ionic liquids methyltriphenyl phosonium bromide, gly and tetraethylammonium chloride; the effect of chain length of alkyl group was studied for extra five desulfurization of n-hexane and thiophene. The solute distribution coefficients and selectivity were calculated and compared with literature.

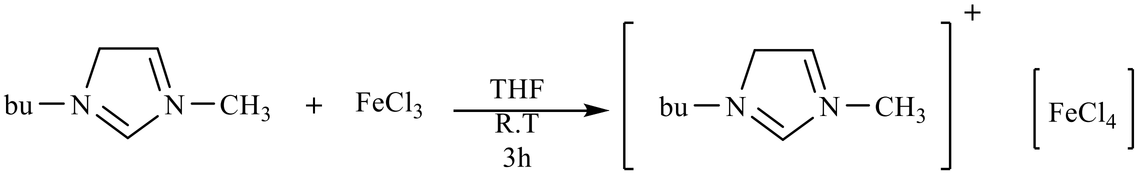
In 2020 Wang and Co-workers [109] prepared a series of tri alkyl amine based as ionic liquids (PILS) and characterized then the extraction desulfurization for thiophene (TH), benzothiophene (BT) and dibenzothiophene (DBT) in model oil, the effective of alkyled groups of (IL), on time and temperature were investigated.

The ILS can be mixed with certain organic solvents to overcome the difficulties and to get new favorite properties and many advantage for s-removal [110]. Kiran and Coworkers [99] prepared[Hnmp]$HSO_4$ and [Hnmp]$H_2PO$ ionic liquids for methylpyrrolidne (nmp)$H_2SO_4$ and $H_3PO_4$ and mixed with non-volatiles organic solvents such (DMF) dimethyl formamide as a binary solvent with low viscosity and reduced the cost of solvent. The efficiency of these solvents for desulfurization were examined at operating conductions such as temperature and time. It was noticed that s-removal efficiency increased from 20°C-50$^0$C for all time periods. The effect of multiple extraction steps optimal conditions were evaluated; as it indicates that desulfurization by multiple step extraction is an effective way to significant reduce s-contenting fuel for five steps as reported in previous studies [111,112].

## Extractive desulfurization by metals-containing of imidazolium ILS

Over the past decade ILS containing metal have been incorporated for applications and regarded much interest, which can be air and moisture stable, to applied for green and chemical process. Many of the metal anion used have the formula [$MCl_4$], were M: is metal such as Zn, Sn, Fe, Cu, Ni, etc [113-115].

Iron (II)-containing imidazolium salt [bmim][$FeCl_4$], bmim=1-butyl-3-metal imidazolium cations was prepared as non-hygroscopic and air-stable complex by reaction[bmim]Cl and $FeCl_3$ [116-118]·



It was observed that metal containing ionic liquids show more effect desulfurization efficiency than metal free (ILS), So, Metal-ILS can be a special sort of chemical to remove aromatic sulphur from fuel. Among, that [bmim][$MCl_4$]M=Zn (II), Fe(II), Cu(II), etc. The Cu metal ionic liquids have identical excellent desulfurization extraction ability [119-121].

[Bmim][$FeCl_4$] has an excellent performance for desulfurization of natural gasoline, due to $Fe_2Cl_7^-$ anion and Fe-Cl-Cl bonds are longer and less strength than those in M-Cl of $MCl_4$ anion. The desulfurization could be due to donation-backdonation [122].

In 2013, S.A.Dharaska and Co-workers [123] prepared acid ionic liquid [Bmim]Cl/$FeCl_3$, [Bmim:1-butyl3-methyl imidazolium-chloride, [Omin]Cl/$FeCl_3$ (Omin=1-octyl1-3-methyl imidazolium chlorides, [Bmim] Cl/$ZnCl_2$, [Bmim] Cl/ $SnCl_2$, [Bmim] Cl/$MnCl_2$, [Bmim] Cl/$CoCl_2$ and [Bmim] Cl/$AlCl_2$

And used for extractive desulfurization of the model liquid fuel. The results are shown in Table 4.

**Table 4.** EDS of model liquid fuel for dibenzothiophenene (DBT) using metal – based ionic liquid of imidazolium.

| Metal -ILS | Sulfur removal% |
|---|---|
| [Bmim] Cl/$FeCl_3$ | 75.6 |
| [Omim] Cl/$FeCl_3$ | 70.2 |
| [Bmim] Cl/$AlCl_3$ | 68.7 |
| [Bmim] Cl/$ZnCl_2$ | 42.1 |
| [Bmim] Cl/$SnCl_2$ | 50.4 |
| [Bmim] Cl/$MnCl_2$ | 40.1 |
| [Bmim$Cl_2$] $COCl_2$ | 33.0 |

The ionic liquids based on $FeCl_3$ showed on excellent efficiency compared with others for desulfurization, the amount of sulfur removal was increased by increasing the mole ratio of $FeCl_3$ [BMIM]/Cl. The use of $FeCl_3$ without Fe(II)-ionic liquid show a much lower ability extraction [124].

Another, interesting of [Bmim]Cl/$FeCl_3$ was reused, but some what a less efficiency compared with a starting [Bmim]Cl/$FeCl_3$, Table 5.

**Table 5.** recycle use of [Bmim]Cl/$FeCl_3$ for sulfur removal in model liquid fuel

| Fe(II)-ils | No. cycle | S% removal |
|---|---|---|
| [Bmim]Cl/$FeCl_3$ | 1 | 75.6 |
| | 2 | 63.2 |
| | 3 | 47.2 |

$FeCl_3$ based ILS are immiscible with the model ion and formed a binary system, $H_2O_2$ is used as strong oxidant agents with $FeCl_3$-ILS as a good extract [124].

The future of the desulfurization process will be proposed using oxidizing agents with ionic liquids [125,126] regarding these ideas, Dharaskar and co-workers [127] developed a noval solvents by a combination of [$C_4$min]Cl/$FeCl_3$ with $H_2O_2$ as oxidante for extractive Co-oxidation desulfurization removal of dibenzothiophene thiophene, 3-methyl-thiophene and 4, 6-dimethyl dibenzothiophene in designed fuel. The optimization conditions, such as molar ratios of $FeCl_3$/[Cumim]Cl and temperature were studied as its more efficiency compared with EDS extraction [128] Table 6.

**Table 6.** Desulfurization of fuel with [$C_4$mim]Cl/$FeCl_3$

| Diesl /IL | S-removal | |
|---|---|---|
| Mass ratio | EDS | EODS |
| 5:1 | 43.4 | 60 |
| 3:1 | 55 | 70 |

T=30°C, time=40 min

The mechanism of extraction for the EODS process was performed on model fuel, the sulfur compounds were extracted into [$C_4$mim]Cl/$FeCl_3$

Phase after that selectivity oxidized to $DBTO_2$ by $H_2O_2$Figure (7). The process of $FeCl_3$ - ionic liquid can be successfully runs for multistage extraction with a slight decrease in activity [129].

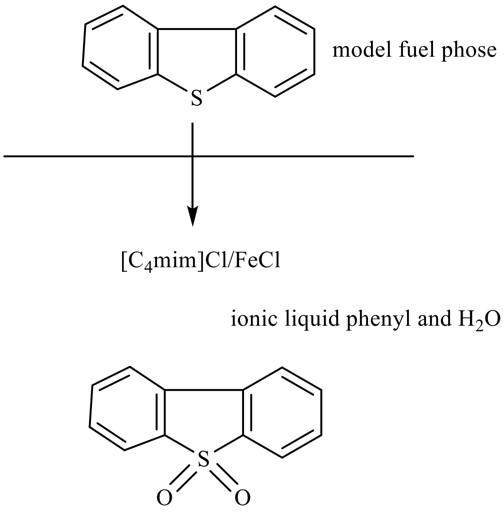


**Fig. 7** EODS mechanism of DBT in model fuel to [$C_4$mim]Cl/$FeCl_3$ with $H_2O$.

In 2012 Chen and Co-worker [130] prepared a series of Lewis acidic ionic liquids based on 1-butyl-3-methylimidazolium metal – Cl i.e [$C_4$mim]Cl/ $MCl_2$ (M=Zn, Fe, Cu, Mg, Co) and used for the oxidative removal of s-compounds for diesel fuels with 3% of hydrogen peroxide solution as oxidant. The highly efficient [C4min]Cl/ZnCl2 is selected to investigate the effect of $ZnCl_2$ contact of desulfurization up to 99.9%.

There a number of reports on deep catalytic oxidative desulfurization of fuel using 1-n butyl-3-methylimidazolium chloride with CoCl2 and oxone (KHSo4) as selected and deep oxidizing agent the results indicate that the efficiency of sulfur-removal was99.7% [97].

The tungsten trioxide $WO_3$ was also reviewed as catalytic material with ionic liquids to decrease of s-removal [131].

The extractive desulfurization of gasoline using CuCl as [HMIM]Cl/CuCl by methylimidazolium chloride and investigated as extracting for sulfur removal of gasoline at room temperature the used ionic liquids can be regenerated and be reused several times [132].

In 2019 Zhao and Co-workers [133]prepared many of complex ionic salts of N,N-Dimethyl hydrochloric acid [HDME]Cl/$XMCl_n$, M=Zn, or Fe n=2or 3 characterized by IR spectroscopy , (NMR etc., and tested for sulfur removal of metal oil. The investigated includes the effect of $H_2O_2$ (oxidant agent temperature and the ratios, to get the optimal desulfurization conditions. The recycling desulfurization was reconverted at optimal conditions, the desulfurization activity was decreased for 48 to 96 after seven cycles.

Moreover, the use of other cations rather than imidazolium, such as n-butyl pyridinium tetrachloro ferrate [Bpy][$FeCl_4$] and phosphomolybdate as anion were tested for deep oxidative sulphur removal process of designed and real fuels [61,133-136].

Transition metals (Fe(II), Co(II), Ni(II) and Cu(II)) complex salts are prepared as Lewis acid and identified by U.V-spectroscopy, mass spectroscopy, elemental analysis, molar conductivity and magnetic properties, these complex salts were tested in extractive desulfurization of bentenothiophene DBT.

The optimization of sulfur removal conditions was studied as show that can be used several times without regeneration [137].

The mechanism of extractive desulfurization was studied by comparative of Cu(II) and Zn(II) based ILS[$C_4$mim][$MCl_4$], the type π-π and C-H----π interaction plays an important roles in extractive sulfur removal for both Cu(II) , Zn(II) based ILS [138].

The poor extraction efficiency and the high cost of complex salt preparation were a further limited application in an industrial scale, so a series of metal based ionic liquid of triakylamine were reviewed by many researchers for desulfurization thiphnene (TH) benzo thiophene (BT) and dibenzothiophene (DBT), the selectivity, conditions, regeneration and recycling were discussed [100,109,139,140].

## Conclusion

The content of sulfur compounds in the fuel is the main pollution results from incomplete combustion of fuel which emission as sulfur dioxide (SOx). Many desulfurization processes were applied such as, hydro desulfurization (HDS), adsorptive desulfurization (ADS), oxidative desulfurization (ODS), bio desulfurization (BDS) etc. Recently different ionic liquids (ILS) and ionic liquids containing metals used as deep eutectic solvents (DESS) for extractive desulfurization of liquid fuel. The ILS and ILS-metal have enormous advantage (efficient and selective) for sulfur removal and can regenerated and recyclable

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# السوائل الأيونية المعتمدة على أملاح الهاليدات المعدنية المعقدة وتطبيقاتها في إزالة الكبريت الاستخلاصي للوقود السائل: مراجعة

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**معلومات المؤلف**

الايميل:

**الخلاصة:**

في هذه المقالة تم التطرق الى الانواع المختلفة من مركبات الكبريت المتواجدة في الوقود السائل مثل (الثايول والبنزوثايوزول والكبريتيدات ----- الخ) وعند احتراقها في الوقود السائل تتحول الى اكسيد الكبريب المحتملة SOX والتي تلوث البيئة. ان الحد المسموح به لهذه الاكاسيد اقل من 10 جزء من المليون لذا حاول الباحثون ايجاد طرق وتقنات عديدة لازالة الكبريت من الوقود السائل ومن هذه الطرائق: أ – ازالة الكبريت بطريقة الامتزاز (ADS) من سطح مادة مازة. ب – الازالة بطريقة الاكسدة (ODS) من خلال اكسدة الكبريت الى شكل ممكن ازالته بطريقة سهلة. ج – الازالة بالهدرجة (HDS) وتعتبر أكثر كفاءة في ازالة الكبريت وخاصة الكبريت العضوي (الاليفاتي او الاروماتي). د – ازالة الكبريت بالطريقة الحيوية (BDS) باستخدام كائنات مجهرية وتعتبر هذه الطريقة صديقة للبيئة وغير مكلفة. ه – الازالة بالاستخلاص المذيب (EDS). واجهت الطرق المذكورة العديد من الصعوبات منها السمية العالية للمذيبات والحاجة الى استخدام عوامل مساعدة وصعوبة التطبيق على المستوى الصناعي لانها تحتاج حرارة وضغط عاليين لذا تسابق الباحثون لأجراء التجارب والبحوث لأيجاد طرق بديلة ومن بين هذه الطرق الاستخلاص بالسوائل الايونية (ILS) والتي تتكون من مجاميع ايونات موجبة للحلقات العضوية مع ايونات لفلزات لاعضوية مختلفة ويمكن ان يستخدم لازالة الكبريت من الوقود السائل بدرجات حرارة واطئة وبكفاءة عالية ويمكن استرجاعها بسهولة وغير مؤثرة على البيئة (مذيبات خضراء). وفي الاونة الاخيرة تم استخدام سوائل ايونية حاوية على فلزات ( M-ILS ) كمعقدات للسوائل الايونية واستخدم بكفاءة عالية لازالة الكبريت من الوقود السائل.