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Feasibility Study Of Phosphonium Ionic Liquids As Efficient Solvent For Sulfur Extraction From Liquid Fuels

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Abstract. Nowadays there are serious regulations to eliminate sulfur from fuels because the SOx created through the combustion of fuel containing sulfur compounds which causes air pollution and have hazardous environmental influence. Amongst numerous extractants, ionic liquids (ILs) are capable enough to extract sulfur due to their desirable green properties. This work demonstrated that trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl) amide (CyphosIL-109) was presented as promising extractant for EDS of dibenzothiophene (DBT), thiophene, benzothiophene, and other alkyl substituted derivatives of sulfur from liquid fuel. The FTIR and TG/DSC spectra have been discussed for the molecular and purity confirmations. Further, physical properties of CyphosIL-109 were carried out. Effects of time, temperature, sulfur compounds, ultra-sonication, and recycling/regeneration on DBT removal from fuel were also examined. In EDS, the DBT removal in n-dodecane was 83.1% with mass ratio (1:1) in 30 min at 30 °C. CyphosIL-109 might be reclaimed six cycles without a substantial S-reduction. Also, S-removal from real fuel and multistage extraction performance was tested. The experimental data and results provided in this article discover the remarkable understandings of phosphonium ionic liquids as promising solvent for EDS.

INTRODUCTION

Sulfur content (S-content) specifications in fuel are becoming increasingly stringent worldwide because sulfur oxide (SOx) emissions from automobile exhaust highly pollute the environment. Many countries have legalized stern environmental regulations to control fuel S-content. Ultraclean fuels (< 10 ppm) have been projected in many countries to meet the growing demand [1,2]. Therefore, the removal of sulfur compounds (S-compounds) from fuel has become a worldwide subject. Hydrodesulphurization (HDS) has mostly recommended industrial desulfurization process, in which organic S-compounds are converted to H_2S and the corresponding hydrocarbons [3,4]. HDS requires high temperatures and pressures, as well as massive amounts of hydrogen (H_2), make HDS a costly and relatively environmentally unfriendly process. Moreover, HDS requires even more expensive operating conditions for S-compounds removal, like dibenzothiophene (DBT) and its derivatives [5, 6]. Therefore, scientists explore innovative environmentally friendly and energy-saving processes.

In recent years, several technologies such as extractive desulfurization (EDS), catalytic oxidation, selective adsorption [7, 8], and bio-desulfurization [9] were applied. Among these, EDS is an eye-catching technology, which may be carried out at ambient temperature, pressure, and without H_2 as a catalyst. A good extractant must have noble S-extractive ability, free of fuel contamination, non-toxicity, environmental benignity, and stability for repetitive use [10]. Solvents commonly used in industry are volatile organic compounds (VOCs) that exhibit high vapor pressure. Furthermore, volatile organic solvents are flammable and are of varying toxicity, depending on their nature, so the main task of many researchers is to find a way of replacing VOCs with environmentally friendly solvents, so-called green solvents [11, 12]. Owing to their negligible vapor pressure, ILs are considered as green

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solvents, but, even if ILs is not responsible for air pollution, their impact on complete ecosystem is still unexplored [11-13].

Ionic liquids (ILs) have attracted much attention due to their peculiar chemical and physical properties [14-17]. In order to develop innovative processes using ILs, two aspects have to be urgently considered. The first is the need to synthesize more task-specific ILs to capture the industrial demands, which is the foundation for studying ILs. ILs are a new kind of solvent with many exciting properties such as negligible vapour pressure, large liquid range, high thermal stability, high ionic conductivity, large electrochemical window and the ability to solvate compounds of widely varying polarity [18-21]. Because of their tempting properties, ILs has prompted extensive research and the rapid growth based on ILs. However, nearly all the attention has been paid to the imidazolium-based ILs [12, 18-19]. Actually, except imidazolium-based ILs, other kinds of ILs have also been proven to have bright and exciting prospects in industrial applications [22]. For example, compared with imidazolium-based ILs, phosphonium-based ILs are proved to be more stable in thermodynamics and less expensive to manufacture [22-24].

Relatively unexplored group of ILs in EDS are the phosphonium and quaternary ammonium based ILs [20]. These ILs however, possess higher thermal and chemical stability than their imidazolium and pyridinium counterparts in addition to their unique behavior and solvating properties [25]. Phosphonium based ILs were reported to possess, in general, higher thermal stability and electronic polarizabilities than their ammonium based analogues [20, 23]. Phosphonium salts became an important subclass of ILs and especially over the past decade an integral part of these industrially relevant solvents [26]. Although the chemistry of phosphonium cations is well recognized and some phosphonium salts are accessible commercially, they are amazingly under signified in development and use of ILs [26]. But EDS with few ILs has some complications, for example, imidazolium based ILs are the effective solvents for EDS, but they are expensive [27]. Fluoride based ILs can absorb humidity and produces toxic hydrogen fluoride known as undesirable product [28, 29]. Thus, It has been recognized that ILs based on phosphonium cation are less expensive, easily synthesis, and chemically more stable in comparison with the imidazolium, pyridinium, and thiazolium based ILs [27, 30].

In the present work, we have reported that the trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl) amide (CyphosIL-109) was synthesize, characterize, and employed as promising solvent for EDS of liquid fuels to investigate efficiency of sulfur extraction. Also, the physical properties and other parameters that effects on this process like extraction time, temperature, S-compounds, and CyphosIL -109 recycling up to six cycles and regeneration of spent IL are examined.

MATERIALS AND METHODS

The CyphosIL -109 was synthesized using analytical grade chemicals without any further processing and purification. Real fuels (diesel and gasoline) were purchased from petroleum station. The details of the all the chemical used including compound name, molecular structure, abbreviation, make, CAS number, and purity are as given in Table 1.

TABLE 1. Chemical Details

Chemical Used	Abbreviation	Make	CAS No	Purity (%)
Trihexylphosphine	-	Sigma Aldrich	4168-73-4	90
1-chlorotetradecane	-		109-65-9	99
Lithium bis(trifluoromethanesulfonyl)imide	-		90076-65-6	98
Diethyl ether	-		60-29-7	99
Ethyl acetate	-		20108-L25	99.5
Dibenzothiophene	DBT		132-65-0	98
n-dodecane	-		112-40-3	99
Benzothiophene	BT		95-15-8	99
Thiophene	TS		110-02-1	99
4-methyldibenzothiphene	4-MDBT		7372-88-5	96
4,6-dimethyldibenzothiophene	4,6-DMDBT		1207-12-1	97
3-methylthiophene	3-MT		616-44-4	98

Synthesis of Trihexyl(Tetradecyl)Phosphonium Chloride

Trihexyl(tetradecyl)phosphonium chloride [THTDP]Cl was synthesized by adding equimolar amount of trihexylphosphine and 1-chlorotetradecane at 140 ºC under nitrogen atmosphere and vigorous stirring for 12 h. After reaction completion, the mixture was vacuum stripped to remove volatile organic components and excess 1-chlorotetradecane. This yielded a clear, pale yellow liquid. The yield of synthesized [THTDP]Cl obtained was found to be 97% [32].

CyphosIL -109 Synthesis

CyphosIL -109 was synthesized by adding equimolar amount of [THTDP]Cl and lithium bis (trifluoromethanesulfonyl) imide in acetone (50 mL). The reaction mixture was stirred for 16 h at room temperature. After reaction completion, the solvent was removed and added diethyl ether (25 mL). Lastly, unreacted lithium bis(trifluoromethanesulfonyl)imide were removed by filtration. After filtration, solvent got removed completely and product was dried under vacuum at 50°C to get colorless, viscous liquid. Yield of synthesized CyphosIL -109 was found to be 94% [32, 49]. The purity and molecular confirmation of CyphosIL -109 were confirmed with FTIR, and TG/DSC analysis.

Fuel Configuration

A model fuel was prepared in n-dodecane with S-concentration of 500 ppm; DBT used here as sulfur source. Likewise, other fuels were prepared by adding thiophene (TS), benzothiophene (BT), 4-methyldibenzothiophene (4-MDBT), 4,6-dimethyldibenzothiophene (4, 6-DMDBT), and 3-methylthiophene (3-MT) in n-dodecane respectively. Total S-content in gasoline and diesel used in experiment were 75 and 180 ppm respectively.

Extraction

Extraction tests were carried out in 20 mL chromacol vials with mixing of model fuel and CyphosIL -109 using (fuel/IL ratio as 1:1, 3:1, and 5:1) under energetic stirring for a given time (5-35 min). All experimentations were conducted under atmospheric pressure in a thermomixer. After extraction, the top phase was separated and reaction mixture settling was done and further, top stage was examined for S-concentration. Sulfur removal efficiency is presented in equation 1, which was used to determine the percentage of S-removal.

$$\%\mathrm{SR} = \frac{C_O - C_t}{C_O} \times 100 \qquad \mathrm{s} \tag{1}$$

Where % SR is % S-removal, C_0 is initial S-concentration (ppm) and C_t is S-concentration after (t) min of experiment.

Instrumentation

CyphosIL-109 was characterized for purity and molecular confirmation using Fourier transform infrared spectrophotometer (FTIR) (Bruker Vertex-70). Thermogravimetric (TG) and differential scanning (DSC) analysis were performed using STA-449C (Jupiter, NETZSCH corp.) under nitrogen (N_2) atmosphere. Moisture content was analyzed by Karl Fischer coulometric titration (Metrohm, 831 KF coulometer system). CyphosIL-109 solubility measurements with various solvents were determined by High Performance Liquid Chromatography (HPLC). The lower phase was measured using gravimetric method to investigate the solubility of fuel in ILs. Ultra-sonication experimentation for EDS was conducted using ultrasonic cleaner (BRANSON-2510), with bath power rating is 320 W on the scale of 0-100%. S-content analysis in model and real fuels before and after sulfur extraction was performed using HPLC (Agilent Technologies, 1200 series), equipped with quaternary pump, variable wavelength detector, column (C-18), 4.6 mm x 150 mm, 5 μm, mobile phase, 20% water, 80% acetonitrile at flow rate, 1.0 mL/min; injection volume 1 μL; column temperature, 25 ˚C; detection wavelength, 237 nm).

RESULTS AND DISCUSSION

ILs Characterization

FTIR and TG/DSC analysis were carried out for CyphosIL-109 characterization.

FTIR Analysis

The broad peaks of wave number in the range of 2925 cm^{-1}and 2856 cm^{-1} are due to salt formation with amide anion. The aliphatic asymmetric and symmetric (C-H) stretching vibrations and in-plane bending vibrations observed at 1465 cm^{-1} due to methyl groups. At wavenumber 1029 cm^{-1} are due to C=C stretching's. The peaks at wave number 1465 and 536 cm^{-1} is due to P-C stretching vibration and deformations. The peak at wave number 516 cm^{-1} is contributed to P-C rocking. Based on FTIR analysis, it was confirmed that a synthesized compound was CyphosIL -109 are shown in Fig. 1. No effect of time and temperature before and after the S-removal was seen on FTIR spectra, it's indicated that the ILs efficiency was stable before and after the S-extraction.

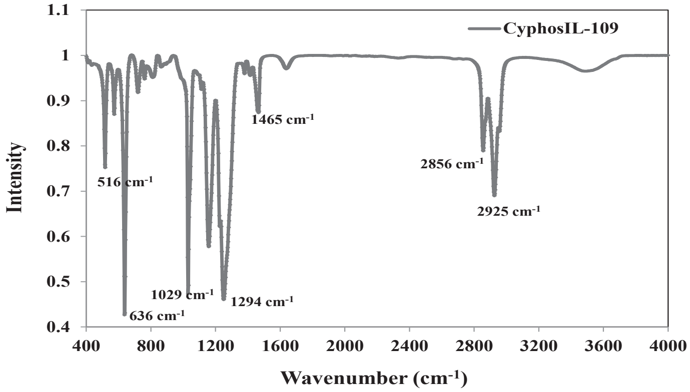


FIGURE 1. FTIR spectra of CyphosIL-109.

TG/DSC Analysis

Thermogravimetric and differential scanning (TG/DSC) analysis of CyphosIL -109 under N_2 in Fig. 2, showed that this IL was thermally very stable and there was not obvious mass loss before 447.2 °C. The significant weight loss took place in the region of 447.2 °C to 462.4 °C, being attributed to the loss of main trihexyl(tetradecyl)phosphonium and bis-(trifluoromethylsulfonyl)amide. The exothermic peak of DSC curve demonstrated the corresponding liquid transition of CyphosIL-109. The similar kind of observation was found in the literature [31, 32].

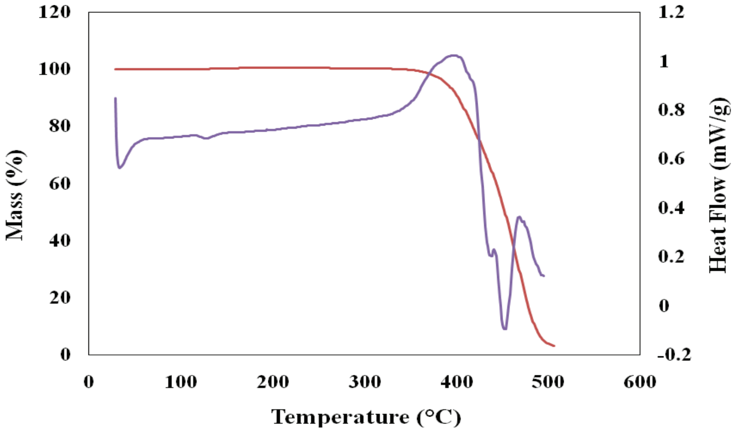


FIGURE 2. TG/DSC curve of CyphosIL-109.

Observed 37% weight loss suggested that the residue may be of amide anion. The melting point determined with DSC obtained only one transition, indicating that the product was pure.

Physico-Chemical Properties

Physical parameter such as solubility, moisture content, and mutual solubility of CyphosIL-109 were presented.

Moisture Content Analysis

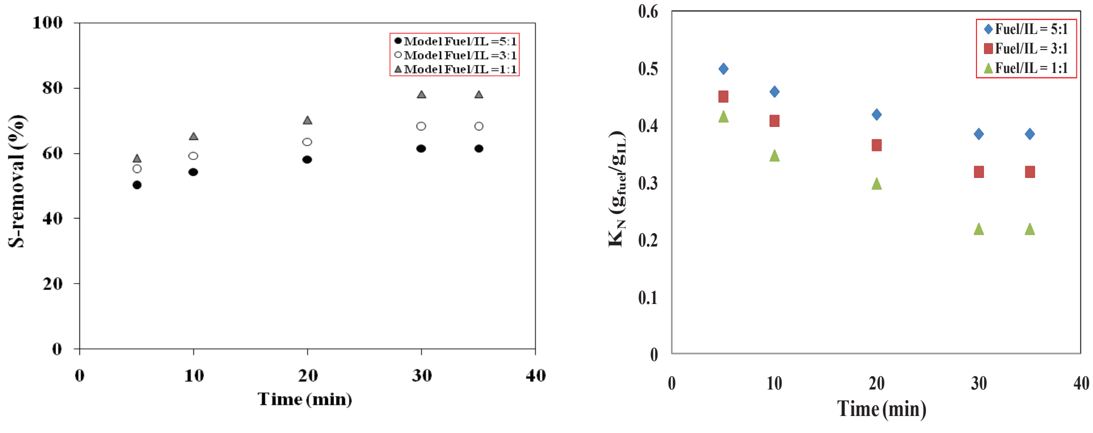
The presence of moisture content in the IL reduces viscosity of heavy fuel. A definite amount of moisture was found more or less in all dense oil reservoirs. Less than 10% of moisture content is better to promote and decrease the fuel viscosity using phosphonium ILs [35, 36]. In CyphosIL-109 the moisture content found to be 1.9%.

Mutual Solubility of CyphosIL-109 and Fuel

Quality of fuel gets reduced when the fuel and ILs have mutual solubility. Thus, an experiment was conducted in order to evaluate the mutual solubility of CyphosIL-109 and model fuel. CyphosIL-109 solubility in a saturated n-dodecane sample was determined using HPLC. No CyphosIL-109 peak was observed, which could be the sign that CyphosIL-109 has negligible solubility in model fuel. The CyphosIL-109 solubility in n-dodecane is 0.30 ppm at 25 ºC which is very negligible in comparison with those in other ILs [37-38, 22].

Effect of Extraction Time

Effects of different extraction time on S-removal using CyphosIL-109 were investigated for EDS. The experiments have schemed under 5 to 35 min at 30 °C with mass ratios of 1:1, 3:1, and 3:1 as shown in Fig. 3 (a). In EDS, with increased in extraction time S-concentration in fuel decreased and was reduced from 500 to 209.5 ppm (58.1%), 182.5 ppm (63.5%), and 149 ppm (70.2%) with mass ratios of 5:1, 3:1, and 1:1 respectively in 20 min. Later, with increased in extraction time up to 30 min S-concentration decreased continuously and diminish from 500 to 192.5 ppm (61.5%), 159.5 ppm (68.1%), and 109.5 ppm (78.1%) by EDS with ratios of 5:1, 3:1, and 1:1 respectively. S-removal efficiency is seen to increase as the extraction time increases from 5 to 30 min. Initial stage of the reaction, S-content in fuel was very high and therefore extraction rate becomes high with highest S-removal efficiency. As the reaction remains further the rate of extraction becomes low with slight S-removal.



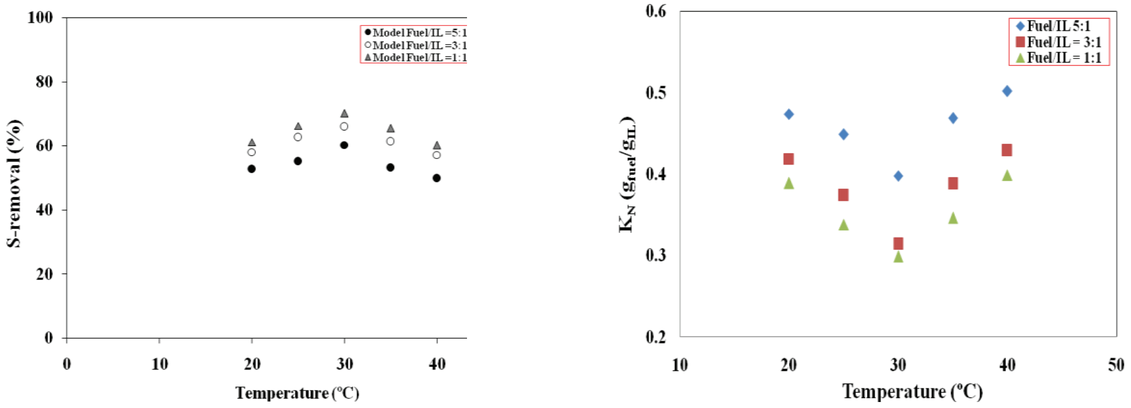
(a) **(b)**

FIGURE 3 (a):-S-removal from model fuel using CyphosIL-109 at different extraction time. b) K_N of S-removal from model fuel using CyphosIL-109 at different extraction time
(Temperature = 30 °C, extraction time = 5-35 min, Initial S-concentration = 500 ppm)

Fig. 3(a), shows that 30 min contact between the fuel and IL is enough to achieve the equilibrium owing to the low ILs viscosity that helps in increasing the mass transfer rate. This observation further supports that prolonged extraction time has minimal effect on the S-removal efficiency of CyphosIL-109. The utmost S-removal rate was found to be within 25-30 min as observed in Fig. 3 (a). Consequently, most favorable contact time for this set of study was selected as 30 min. Nernst partition coefficient (K_N) is used to appraise the performance of EDS. K_N is the ratio of S-concentration in IL to fuel. K_N values of CyphosIL-109 with DBT removal are shown in Fig. 3(b). K_N value of DBT was also not significantly altered by the increase in extraction time for example K_N value of DBT remained at 0.38, 0.31, 0.21 in EDS from 30 to 35 min with mass ratios 5:1, 3:1, and 1:1 respectively. The researcher has reported similar kind of observation in the literature [39, 40].

Effect of Temperature

Temperature plays an energetic role in EDS, thus, extraction temperature on S-removal using CyphosIL-109 has been studied. As shown in Fig. 4 (a), S-removal efficiency increases originally with increasing temperature from 20 ˚C to 40 ˚C, and then declined. High temperatures are not much suitable for S-extraction since they negatively affect the catalytic and extraction processes**.** However, high temperatures help to diminish the IL viscosity which is suitable for achieving a good mixing between the fuel and IL. At 30 ˚C, the viscosity of CyphosIL-109 is very high, thereby significantly hindered the mixing process between fuel and IL [39]. Consequently, CyphosIL-109 was best suitable to extract DBT at 30 ˚C which was considered as the best possible temperature for S-extraction.



(a) **(b)**

FIGURE 4 (a):- S-removal from model fuel using CyphosIL-109 at different temperatures(˚C); **(b):-** K_N of S-removal from model fuel using CyphosIL-109 at different temperature(˚C).
.(Temperature = 20 - 40 °C, extraction time = 30 min, initial S-concentration = 500 ppm)

In EDS, S-content from model fuel reduced at 30 ˚C from 500 to 237 ppm (52.6%), 209.5 ppm (58.1%), and 194.5 ppm (61.1%) was achieved after EDS with mass ratios 5:1, 3:1, and 1:1 respectively at 30 ˚C as shown in Fig. 4(a). S-removal significantly decreased was observed when temperature reached 40 ˚C, and the S-removal was only 49.8%, 57.1%, and 60.1% in EDS with ratios of 5:1, 3:1, and 1:1 respectively. The negative impact of increasing temperature might be due to the extraction equilibrium reached the optimum point (30 ˚C). Thus, an increase in extraction temperature above 30 ˚C did not contribute any improvement in EDS because the ILs stability is worse with increasing temperature [38]. The K_N values of CyphosIL-109 decreases as extraction temperature increased are shown in Fig.4(b). This clearly indicated that the concentration of DBT in ILs phase decreased as the extraction temperature increased. Similar results were reported in the literature [22, 30].

Effect of Sulfur Compound on S-Removal

Generally, the results for thiols, sulfides, and related additional complexes are not much notable. Nevertheless, the results for DBT, BT, TS, 4-MDBT, 4,6-DMDBT, and 3-MT are outstanding.

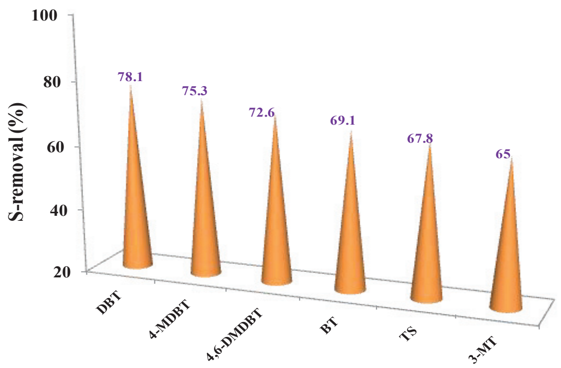


FIGURE 5. Effect of S-compounds on extraction using CyphosIL-109.
(Temperature = 30 °C, Fuel/IL= 1:1, Extraction time = 30 min, Initial S-concentration = 500 ppm)

In diesel, lots of varieties of alkyl substituted DBTs are present like BT, TS, 4-MDBT, 4,6-DMDBT, and 3-MT. The DBT removal reached 78.1% by EDS in 30 min with IL/Fuel as 1:1. However, the removal of 4-MDBT, 4,6-DMDBT, BT, TS, and 3-MT were only 75.3%, 72.6%, 69.1%, 67.8% and 65% by EDS in 30 min with IL/Fuel as 1:1 respectively as shown in Fig 5. However, reactivity sequencing was in the order of DBT > 4-MDBT > 4,6-DMDBT > BT > TS > 3-MT. This order for equilibrium behavior can be explained based on the aromatic π-electron density and steric hindrance on sulfur atoms [30, 41].

Ultra-Sonication Effect on S-Removal

In ultra-sonication experiments, the DBT extraction was performed by adding specific amount of CyphosIL-109. It is well known that the use of ultrasound can significantly improve the reaction efficiency under phase transfer conditions [42]. Ultra-sonication promotes the extraction efficiency since ultrasound effect is associated to enhancement of reaction rates in view of the formation of radicals, cleavage of bonds and mass transfer, which could provide useful chemical effects [43]**.** The lower frequency of ultrasound has a strong physical effect that enhances the rate of extraction by improving surface reactions between the IL and fuel phase [43, 44].

TABLE 2. Effect of time using ultra-sonication on S-removal.

Run	Time (min)	S-content (ppm)	S-removal (%)
1	5	182.5	63.5
2	10	154.5	69.1
3	20	127.5	74.5
4	30	84.5	83.1
5	35	84.5	83.1

Model fuel/CyphosIL-109 = 1/1, ultrasonic power = 320 W, extraction time = 5-35 min., sonication temperature = 30 °C, initial S-concentration = 500 ppm.

TABLE 3. Effect of temperature using ultra-sonication on S-removal.

Run	Temperature (°C)	S-content (ppm)	S-removal (%)
1	20	163.5	67.3
2	25	147	70.6
3	30	119.5	76.1
4	35	153.5	69.3
5	40	177	64.6

Model fuel/CyphosIL-109 = 1/1, ultrasonic power = 320 W, extraction time = 30 min., sonication temperature = 20 - 40 °C, initial S-concentration = 500 ppm.

The optimum ultrasonic time (U_t) for ultra-sonication, and S-removal efficiency are systematically studied. Table 2 and 3, shows that maximum S-removal was 83.1% when (U_t) was 30 min. Hence, optimum (U_t) required to achieve highest S-removal was 30 min. However, S-removal was 76.1%, when ultra-sonication temperature reached at 30 °C as shown in Table 3. Hence, it was also noted that the optimum ultra-sonication temperature was 30 °C to achieve highest S-removal [43, 45]**.** The studies have shown that using ultra-sonication in EDS process under mild reaction conditions leads to a considerable increase in the rate of reaction and reduction of reaction time [46].

CyphosIL-109 Recycling and Regeneration

For the practical processes and economical benefit, recycling and regeneration of spent ILs are much necessary to considered for DBT extraction. So, S-extraction performance of CyphosIL-109 without regeneration was effectively recycled up to six cycles with an unremarkable decrease in activity and the results are shown in Fig. 6. It was realized that spent IL was efficiently remove DBT from fuel even, at an inferior efficiency of 49.6% from 61.5%, 53.2% from 68.1%, and 59.1% from 78.1% using EDS with Fuel/IL ratio as 5:1, 3:1, and 1:1 respectively. The results concluded that the S-extraction rate drops slightly after IL was effectively recycled six cycles [19, 39]. Consequently, after six cycles it's become nearly saturated and loss S-extraction ability and must be regenerated. In present work, spent CyphosIL-109 was regenerated by dilution with water, and S-removal performance of phosphonium IL was studied in presence of water. From Fig. 6, it is clear that regenerated CyphosIL-109 can effectively extracts DBT with extraction efficiency as 60%, 64%, and 69.5% with mass ratio fuel/IL as 5:1, 3:1, and 1:1 respectively.

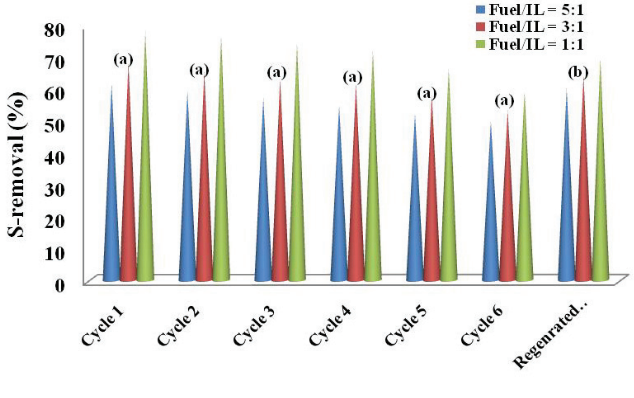


FIGURE 6. CyphosIL-109 recycling and regeneration.
(Temperature = 30 °C, extraction time = 30 min, initial S-concentration = 500 ppm).

S-Removal from Real Fuels

Gasoline and diesel extraction (real fuels) is much more difficult due to its typical content of various S-compounds and other impurities. The results of EDS for real fuels with CyphosIL-109 are favorable. Phosphonium ILs display high S-removal ability from gasoline and diesel within single stage extraction as shown in Fig 7(a). Phosphonium ILs display high capability of S-removal from real fuels in single EDS in 30 min at 30 °C as shown in Fig 7 (a). CyphosIL-109 exhibits the best extraction ability for S-removal in gasoline which was reduced from initial sulfur of 75 ppm to 37.1 ppm (50.5%), 31.3 ppm (58.2%), and 23.6 ppm (68.5%) by EDS with mass ratios of 5:1, 3:1, and 1:1 respectively. However, in diesel, it was reduced from initial sulfur of 180 ppm to 97 ppm (46.1%), 81.9 ppm (54.5%), and 69.7 ppm (61.3%) by EDS with Fuel/IL ratios as 5:1, 3:1, and 1:1 respectively.

Considering the experimental results, it is difficult to reduce S-content of fuel from high values to the statutory limits in single stage extraction. Consequently, multiple extractions can be used to reach clean fuel with low S-content [22, 30]. S-removal using multiple extraction of DBT by fresh CyphosIL-109 is obtained and the results are shown in Fig. 7 (b). The S-content in diesel drops significantly from 180 to 55 ppm (69.44%) after 5 cycles and the S-content in gasoline reduced from 75 to 16 ppm (78.67%) with mass ratio of 1:1 at 30 °C. Accordingly, multistage extractions are effective for S-content reduction from fuel to a considerably minor amount which can meet as per the required standard of sulfur limit [29, 38].

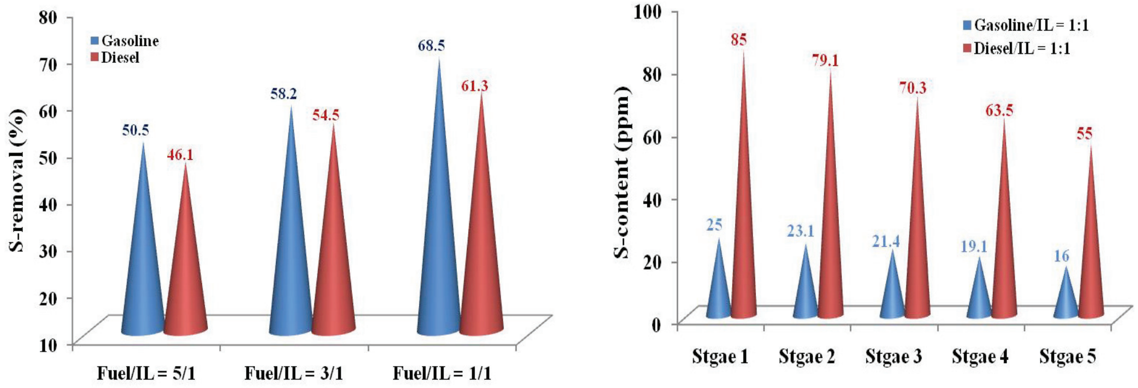


FIGURE 7 (a). S-removal from real fuels using CyphosIL-109. **(b).** Multistage performance of CyphosIL-109 for gasoline and diesel.
(Temperature = 30 °C, Extraction time = 30 min, Initial S-concentration of gasoline and diesel = 75 and 180 ppm)

CONCLUSION

Phosphonium based IL can be used as most promising solvent for EDS of liquid fuels, mainly with regards to those S-compounds that are very tricky to remove by common HDS process. Phosphonium IL is the most competent in extraction of DBT containing liquid fuels and it can reach 83.1% with single stage extraction. Moreover, CyphosIL-109 could be recycled up to six cycles without a significant decrease in activity. The structures of cations and anions in ILs, the extraction time, temperature and recycling of ILs are all important parameters affecting the extracting ability of IL.

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