

Novel phenolic deep eutectic solvents for desulfurisation of petrodiesel

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Novel phenolic deep eutectic solvents for desulfurisation of petrodiesel

Abstract

In this work, a novel production of “deep eutectic solvents (DESs)” has been utilised for the elimination of sulfur composition, particularly from crude oil by liquid-liquid extraction. Herein, we present the first demonstration of the use of novel DESs formed by phenol, catechol, resorcinol and o-cresol as “hydrogen bond donors (HBDs)” with trimethyl hydroxyammonium chloride (ChCl) as the hydrogen bond acceptor to affect the efficient separation of organosulfur compounds from diesel. These DES electrolytes have been applied for the sulfur extraction from Iraqi real diesel fuel as determined using X-ray fluorescence sulfur measurements. The optimisation condition factors in this research have been studied, containing reaction time, the temperature of extraction process, the ratio of mass of diesel to DES and regeneration of DESs. The results indicated that phenol-based DESs extracted more than 38% of S-compounds from true diesel fuel when the mass ratio DES:fuel was 1:2 at 55 °C. Anhydrous ferric chloride (FeCl₃) was also utilised as a catalyst in this work, where it was demonstrated that charge-dipole interaction between the DES and sulfide compounds was the key driving force behind the desulfurization process. We have shown that the extraction efficiency could be summarised as o-cresol + ChCl < catechol + ChCl < resorcinol + ChCl < phenol + ChCl. More than 44% of sulfur species could be removed when a 1:1:1 molar ratio of ChCl: phenol: acetic acid was utilised with H₂O₂ as an oxidant.

Keywords

“deep eutectic solvents”, desulfurization of diesel fuel; solvent extraction, air pollution

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1. Introduction

With the current state of development of the modern world, petroleum refineries need to produce environmentally acceptable fuels due to the existence of undesirable and hazardous emissions associated with their combustion [1], the emissions from which contain toxic sulfur-based gases like SO_x , which are produced from the sulfur species combustion. The combustion products can mix with water vapour in the air and give rise to acid rain [2,3]. The presence of sulfur species can result in major problems with regard to public health, and owing to the fact that adsorption of sulfur species on the active positions of catalysts during refinery chemical processes can lead to deactivation [4].

For the reasons mentioned above, the elimination of sulfur materials has become a particularly important issue for researchers [5]. Therefore, the purpose of the research is to reduce sulfur compounds from petroleum fractions to a minimum ppm level. Amongst the most main catalytic processes that the petroleum industry uses for the extraction of sulfur-containing materials are hydrodesulfurization (HDS), which has been utilised for around 80 years. In recent years, many additional developments or modifications through several novel ideas about hydrodesulfurization catalysts have been introduced in commercial areas to improve the performances of these processes [6]. However, owing to the lack of reactivity of certain refractory organo-sulfur compounds (thiophenic compounds), the HDS process has historically been unable to remove them completely [7]. Thus, researchers have been constantly searching for alternative methods to HDS including extractive [4,8], oxidation [9,10], adsorption [11,12], and biodesulfurisation [13,14], of which extractive desulfurisation appears to be the best [15] owing to the advantageous process characteristics such as low pressure, low temperature, elevated extraction rate, appropriate recycling of extractants, no hydrogen consumption and the possibility to reuse extracted compounds as raw materials. Over the last three decades, different ionic liquids (ILs) based on extractants have been utilised for extraction of sulfur compounds in fuels and as a complementary part of HDS such as imidazolium [16], pyrrolidinium [17], pyridinium [18],

and phosphonium [19]. However, these liquids have many drawbacks to their experimental application, regeneration and recycling after utilisation, as well as being expensive to prepare [20–22].

Recently, DESs have been successfully utilized to extract sulfur and nitrogen compounds from petroleum derivatives [23]. It is well-known that the constituents of DESs are biodegradable, cheap and environmentally friendly. Thus, these solvents are significantly used in different aspects. Ionic liquids and DESs are similar in terms of their physical and chemical properties, therefore, applications of these new solvents have been increasing considerably, especially in desulfurization progression as they are biodegradable and readily available [24,25].

“Deep eutectic solvents (DESs)”, as a modern kind of green extraction solvent, might represent an alternative solvent to ILs for the sulfur removal from fuels [26–28]. DESs are low melting point solvents due to complex formation between mixtures of Brønsted and Lewis bases and acids [29,30]. They are considered alternatives to the more traditional volatile organic solvents and ionic liquids [31,32] as extractants in the extraction processes due to their properties being well suited to such processes. DESs are known as green solvents because they have low-cost production, are easy to prepare, are chemically and thermally stable, non-toxic, biocompatible, and biodegradable, and have high conductivities [33]. These solvents show excellent performance in many industrial applications such as metal extraction as they are capable of dissolving metal salts, and can be used in the extraction of non-hydrocarbon species from petroleum products [27,29,34]. Furthermore, DESs are extensively employed in a wide range of fields in particular, metals electrodeposition [35–38], polymer synthesis [39–42], electropolishing [43], and metal recycling [44]. A specific extraction process like desulfurisation is one of the areas where DESs have seen extensive use [45].

The purpose of the current investigation was to reduce the amount of sulfur-containing materials from real diesel fuel in Erbil (a city in Iraq) by liquid–liquid extractions utilising novel phenolic-based deep eutectic solvents for the first time. Initially, sulfur species are extracted from local diesel fuel using four deep eutectic solvents. Here, the DESs which served as extractants were phenol, catechol, resorcinol, and o-cresol, which acted as hydrogen bond donors to choline chloride. These DESs provide the greatest ability to

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extract sulfur compounds. In the second part, the extractions were carried out using ferric chloride (FeCl_3) and hydrogen peroxide (H_2O_2) as the catalyst and oxidising reagent, respectively. Therefore, various factors such as functional group position of HBDS, catalysts, oxidizing agents, temperature, and DES:-diesel fuel molar ratios were utilised to optimize desulfurisation processes.

2. Material and methods

2.1. Material

All chemical materials used in this study are shown in Table 1 and were used as received.

The fuel used in this research was a hydrotreated diesel produced by Kar Company (Kar Refinery, Iraq) with a total sulfur content of 0.0573%. Table 2 illustrates the physicochemical features of the diesel.

2.2. Methods

DESs were synthesised in a similar manner to that reported previously [46]. A mixture of ammonium salts

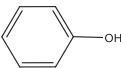
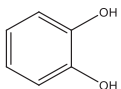
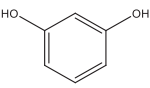
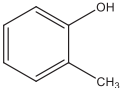
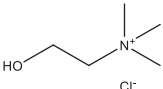
Table 2

Some basic characteristics of the diesel fuel employed in this research.

| Characteristic | Value | Test methods |
|-------------------------------------------------|--------|--------------|
| Colour | 1.0 | ASTM6045 |
| Specific gravity @ 15.5 °C / g ml ⁻¹ | 0.839 | ASTM4052 |
| Total sulfur content / % | 0.0573 | ASTM D4294 |
| Flash point / °C | 61 | ASTM D6450 |
| Kinematic viscosity @ 40 °C / mm/sec | 2.91 | ASTM D7042 |
| Cetane number | 52.4 | ASTM D4737 |
| Cetane index | 53.2 | ASTM D976 |
| Pour point / °C | -15 | ASTM D97 |
| Initial boiling point (IBP) / °C | 169 | ASTM D7345 |
| Final boiling point (FBP) / °C | 362 | ASTM D7345 |
| Aromatic containing compounds / % | 25.6 | ASTM D1319 |
| Recovered / Vol% | 98 | ASTM D7345 |
| Residue / Vol% | 2 | ASTM D7345 |

and the hydrogen bond donors are prepared regarding to the specified salt:HBD molar ratio to form a homogeneous liquid. Choline chloride (ChCl): catechol was synthesised by combining ChCl with catechol in an equal molar ratio. The mixture was placed on a hot plate, heated, and stirred by a magnetic constant stirrer (500 rpm) at ca. 80 °C until a clear uniform electrolyte was performed. The same strategy described above was

Table 1
Structure, purities and sources of materials used in this research.

| Chemicals | Structure | Source | Purity % | CAS registry number |
|-------------------|-------------------------------------------------------------------------------------|---------------|----------|---------------------|
| Phenol |  | Thomas Baker | 99 | 108-95-2 |
| Catechol |  | Sigma–Aldrich | ≥99 | 120-80-9 |
| Resorcinol |  | Sigma–Aldrich | 99 | 108-46-3 |
| O-cresol |  | Sigma–Aldrich | ≥99 | 95-48-7 |
| Hydrogen peroxide | H_2O_2 | Scharlau | 50 | 7722-84-1 |
| Ferric chloride | FeCl_3 | Sigma–Aldrich | 97 | 7705-08-0 |
| Choline chloride |  | Sigma–Aldrich | ≥98 | 67-48-1 |
| Acetic acid | CH_3COOH | Scharlau | 96 | 64-19-7 |

used for ChCl:phenol, ChCl:resorcinol and ChCl:o-cresol, except for the molar ratios of ChCl:HBD which were 1:2, 1:1, and 2:1, respectively.

In the extraction experiments conducted in this study, DESs with real diesel fuel (wt/wt %) were combined in a 1:2 ratio and stirred for different reaction times at 30 ± 2 °C. In addition, the amount (X) of sulfur compounds extracted at 1 atm pressure was measured as follows:

$$X = \frac{C_i - C_r}{C_i} * 100\%$$

where C_i is the original sulfur concentration in diesel fuel, and C_r is the remaining sulfur concentration in the diesel phase after the reaction had continued for a certain amount of time. The similar strategy was conducted after adding FeCl_3 and H_2O_2 materials into the DES phase. The content of sulfur in the treated diesel fuel phase before and after extraction was measured utilising X-ray fluorescence spectroscopy (Tanaka Scientific Sulfur Meter model RX-360SH) and the ASTM D4294 method. The true diesel fuel was received from the Ministry of Natural Source/Iraqi Kurdistan Region. The applicable sulfur concentration of this method is at least 10 ppm. The error bars for all the data are also given. Aromatic-containing compounds in diesel were measured by FTIR analysis (MiniScan VP Xpert ASTM E1655 correlation to ASTM D1319 from Grabner Company).

3. Results and discussion

3.1. Effect of functional group position

Functional groups and intermolecular forces primarily control the extraction. In this experiment, four extracting agents, which are closely correlated DESs, were used. These DESs include phenol, catechol, resorcinol, and o-cresol as the HBDs mixed with ChCl separately. It may be noted that the eutectic point for each mixture is different. For instance, phenol and o-cresol form eutectic mixtures with ChCl at a molar ratio of 2HBD:1ChCl, because each molecule of phenol and o-cresol contains one OH group, therefore, two molecules of these compounds are required to produce a eutectic mixture with ChCl separately via the chloride ion (Cl^-), while it is apparent that the eutectic mixtures for the diols (catechol and resorcinol) occur in a 1:1 ratio with ChCl. This is due to the fact that these diols, as the HBDs, contain two hydroxyl groups. Therefore, one molecule of the latter can form two hydrogen bonds to produce a eutectic system that

can complex each chloride ion. This result is exactly same as the eutectic systems formed from carboxylic acids and choline chloride described in the literature [47].

In the current study, the effect of various phenolic hydroxyl groups on the removal of sulfur species into DESs was performed at 30 °C. The diesel fuel and DESs phases were mixed in a mass ratio of 2:1, respectively, for 1 h with a continual stirring rate of 500 rpm. The highest extraction efficiency for sulfur was achieved in the 2Phenol:1ChCl eutectic system, while the 2o-cresol:1ChCl eutectic system has the lowest removal efficiency for sulfur, as demonstrated in Fig. 1. These data indicate that the extraction capability is different for each of the four systems, which could be related to the different types of functional groups present, the composition of the mixture, and how these mixtures are formed by the HBD and anion relation. Figure 1 shows that the extraction efficiencies for the sulfur contained in real diesel have the order: o-cresol + ChCl < catechol + ChCl < resorcinol + ChCl < phenol + ChCl.

Owing to the electron charge distribution in the phenol molecule, the maximum amount of sulfur removed (20%) was achieved using the DES containing phenol. Thus, with a decrease in the electron density on the oxygen, the bond between hydrogen and oxygen becomes weaker and then the proton can be weakly donated.

Another possible explanation, in addition to that given above, is that the mixture of o-cresol + ChCl showed the lowest extraction efficiency owing to the existence of the methyl ($-\text{CH}_3$) group on the HBD, which is a weak electron donating group and which

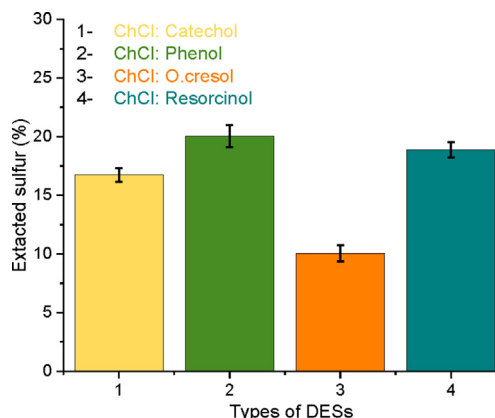


Fig. 1. Sulfur removal as a function of DES at 30 °C. The ratio of mass was 1 DES: 2 fuel for 1 h and the stirring rate was 500 rpm. The error bars have been taken for three readings.

increases the electron density on the phenolic ring. Therefore, the bond between hydrogen and oxygen becomes stronger. As a result, the sulfur removal efficiency was reduced. Chen and co-workers found that sulfur extraction by ILs can be achieved due to the π -electron density on the sulfur species [48]. This may suggest that the presence of inter- and intramolecular hydrogen bonding in catechol or resorcinol + ChCl weakened the interaction between π -electron density on the sulfur species and catechol- or resorcinol-based DESs. Therefore, the consequent extraction of sulfur is relatively low when using catechol + ChCl and resorcinol + ChCl mixtures compared to the phenol + ChCl mixture. Overall, we conclude that the functional groups and their positions play an essential role in the sulfur extraction processes.

3.2. Effect of H_2O_2 and $FeCl_3$ as catalysts on the sulfur extraction process

Yang et al. investigated the use of H_2O_2 in specific amounts, which was found to increase desulfurisation due to the formation amount of the species of catalytic present [49]. Similarly, Al-Shahrani and co-workers showed that H_2O_2 as a catalyst is suitable for the sulfur removal in fuel [50]. To investigate the effects of H_2O_2 as an oxidant on the desulfurisation of real diesel, experiments were achieved at 30 °C and under similar reaction circumstances as previously used with a diesel 8:1 oxidant molar ratio, as shown in Fig. 2.

The sulfur removed from the diesel increased with the adding of H_2O_2 and varied depending on the phenolic DES under consideration. A comparison of the two results from Figs. 1 and 2, respectively, it can be observed that owing to the reaction of H_2O_2 , as an

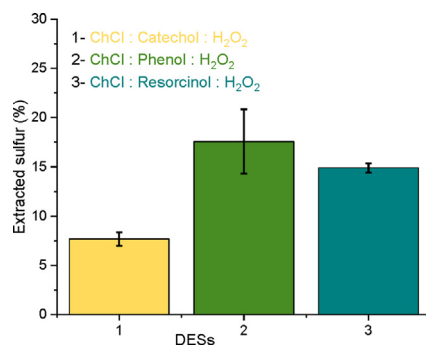


Fig. 2. Sulfur extraction from diesel fuel using DESs and H_2O_2 at 30 °C. The ratio of mass was 1 DES: 2 fuel, with the reaction allowed to continue for 1 h at a stirring rate of 500 rpm and a molar ratio of diesel: oxidant of 8:1. The error bars have been taken for three readings.

oxidizing agent, with all DES systems, the desulfurisation ability decreased due to the break down the hydrogen bond interaction between ChCl and HBDs, so a new product might be formed between H_2O_2 and HBD. The extraction of sulfur from diesel into mixtures of catechol + ChCl and phenol + ChCl with H_2O_2 is lower than that of those mixtures without H_2O_2 . This can be explained by the fact that the two adjacent hydroxyl groups existed in catechol forming an intramolecular interaction. Hence catechol-based DES weakly reacted with H_2O_2 . The extraction of sulfur is relatively similar using phenol + ChCl and resorcinol + ChCl with H_2O_2 .

In addition to using H_2O_2 , previous studies found that the use of ferric chloride ($FeCl_3$) as a catalyst also has an important role in desulfurization. For instance, sulfur compounds were significantly removed from diesel fuel using $FeCl_3$ when the amount of Fe^{3+} increased in the organic phase [51]. Therefore, Fe (III) has been utilised in this work. As can be shown from Fig. 3, the use of $FeCl_3$ has a relatively low influence on the extraction of sulfur species, where catechol- and o-cresol-containing DESs had extraction abilities of 9.2 and 1.3%, respectively. This might be due to the fact that these HBDs were blocked by H_2O_2 at this temperature. As a result, the colours of the DESs turned black after peroxide addition.

3.3. Optimization conditions

3.3.1. Influence of temperature

In general, temperature is one of the significant factors affecting sulfur removal efficiency. Caero et al. investigated the removal of aromatic sulfur-containing species from a fuel phase as achieved at a temperature

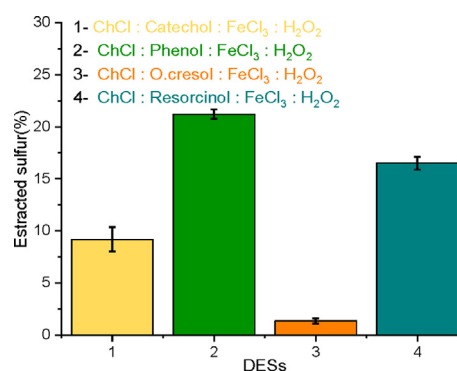


Fig. 3. Effect of $FeCl_3$ and H_2O_2 substances on the sulfur removal-based molecules. The mole proportion for DES: fuel was 1:2. The time of extraction process was 1 h at 30 °C whilst stirring at 500 rpm. The error bars have been taken for three readings.

of reaction of around 70 °C [52]. Similarly, Shiraishi et al. reported that the desulfurisation of fuel into the extractants phase increases as the reaction temperature increases [53]. To determine the optimal temperature for extractive desulfurisation, different temperatures were used for the extraction. Figure 4 illustrates the influence of temperature on the desulfurisation of the chosen DES (2 phenol:1 ChCl) from diesel oil. The diesel and DES phases were combined for 1 h utilising a continual stirring rate (500 rpm) and a 2 diesel fuel:1 DES (2 phenol:1 ChCl) mass ratio. From the resultant data, it can be shown that there were no significant differences in sulfur extraction efficiency from real diesel into a phenol-containing DES when increasing the extraction temperature from 30 to 55 °C. This study shows the extraction percentage is only slightly increased from 20% to 23.2% as a result of increasing the temperature of the solution.

3.3.2. Influence of reaction time

The influence of the time of extraction on sulfur species was probed in this study. The experiment was conducted at 30 °C with a 500 rpm stirring speed and a mass ratio of the phenol + ChCl to the fuel of 1:2. The data are given in Fig. 5, which shows that the equilibrium extraction probably can be obtained in 3 h for the DES-based extraction desulfurization process.

Obviously, it can be seen from the above figure that phenol:ChCl showed a comparatively low increase in sulfur removal performance. For instance, the total sulfur removal efficiency was 18.9% at a 30 min reaction time and became 23.2% after three (3) hours. The low increase in extraction ability could be

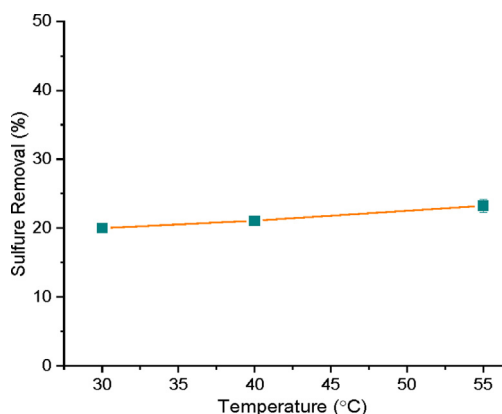


Fig. 4. Sulfur species' extraction efficiency as a function of temperature; the time of an interaction was 1 h and stirring speed was 500 rpm, and the molar ratio of the polar phase to the nonpolar phase was 1:2.

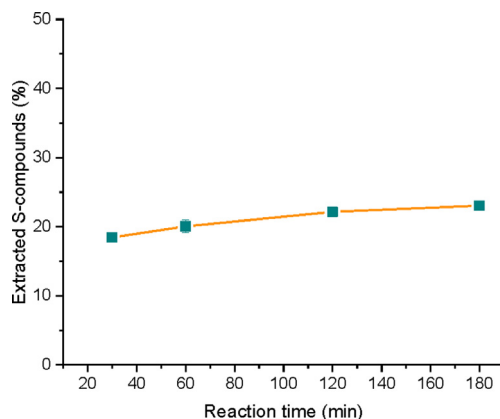


Fig. 5. Elimination of sulfur species as a function of reaction time. DES:fuel molar ratio was 1:2; extraction time 1 h; and stirring speed was 500 rpm at a constant 30 °C.

attributed to the following aspects. Firstly, the extraction reaction probably reaches to equilibrium state at around 1 h, and therefore the efficiency of the desulfurisation becomes relatively slow, as noted by Abbott and co-workers [30]. Moreover, the major reasons for the lack of extractive desulfurisation in treated real diesel fuel are explained in this study. As mentioned in Table 1, 25.6% of diesel is aromatic compounds, some of which might be presented like phenanthrenes as polyaromatic compounds which hinder or prevent extractive desulfurisation, as shown by Xiao and co-workers [54]. This is due to the high aromatic compounds in diesel reducing the cetane number to 52.3434, which has a negative effect on the fuel quality.

Similarly, Xu and Yu and co-researchers found that the comparatively high quantity of water in real diesel fuel requires additives to remove it. However, these additives have a negative influence on desulfurisation [54,55]. In addition, owing to the complicated conformation of commercial diesel, including impurities made up of various aromatic species, organic nitrogen and oxygen species, the sulfur removal efficiency decreases. Moreover, the existence of olefins and aromatic materials in real diesel makes the fuel more complex which has a direct negative impact on the extraction of sulfur species [56,57].

3.3.3. Influence of DES/fuel mass ratio

In terms of industrial application, reducing the mass of the S-extractants to a minimum is essential. To increase the removal efficiency of the sulfur molecules, four various mass ratios of “deep eutectic solvents” (phenol + ChCl)/fuel were investigated in terms of

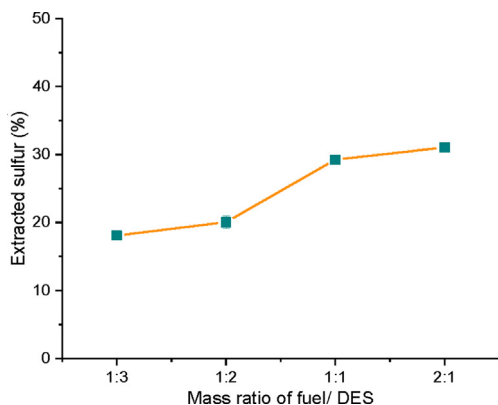


Fig. 6. Influence of stoichiometry of DESs: fuel (different mass ratio) on sulfur removal efficiency at 30 °C and a 500 rpm stirring rate; extraction time was 1 h.

their desulfurization capabilities, as found in Fig. 6. As indicated in this figure, the percentage of sulfur materials extracted from the diesel fuel into the phenol-ChCl solvent was 18% when the ratio of mass of the fuel:DES was 1:3. The extraction efficiencies reached 29% and 31% when the ratio of extractant: fuel was 1:1 and 2:1, respectively. This clearly shows that as the amount of the extractant became larger, the extraction efficiency increases.

The influence of the H_2O_2 substance as an oxidizing agent to the sulfur composition that exist in diesel was also studied in different molar ratio at 50 °C. Figure 7 illustrates the sulfur removal as a function of nH_2O_2/nS at 50 °C using 2diesel: 1(phenol + ChCl + acetic acid

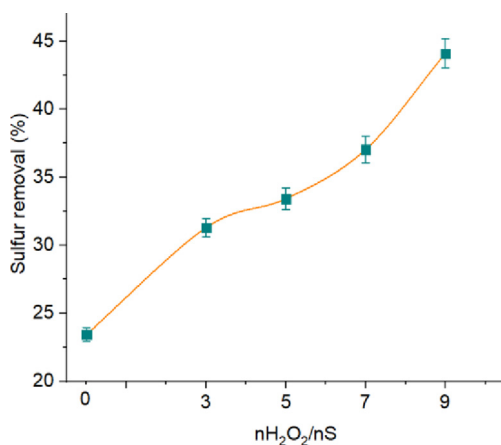


Fig. 7. Influence of nH_2O_2/nS on the extracted sulfur in diesel. The conditions of an interaction: 2 diesel - 1 ChCl-phenol system; $T = 55$ °C; no. of moles of H_2O_2 for nH_2O_2/nS equal to 3, 5, 7 and 9, respectively, reaction time: 1 h and stirring rate of 500 rpm. The error bars have been taken for three readings.

at 1:1:1 M ratio) as catalyst. In this experiment, we added acetic acid into DES in order to form polar sulfone and sulfoxide via H_2O_2 which strongly interact with phenol-based DES and enhance the extraction process of sulfur from diesel as has been reported in the literature. It can be noted that the extractive desulfurization process increased as the mole (n) ratios of H_2O_2 to sulfur increased from 3 to 9.

As indicated in Fig. 7, the best result for sulfur extraction was 44.1%, obtained for the nH_2O_2/nS of 9 at 55 °C. Owing to the transfer restriction in liquid-liquid-phase reaction systems, the oxidant is commonly employed in additional of the stoichiometric ratio. In addition, some of the hydrogen peroxide decomposes to O_2 , H_2O and some side reactions will occur in the oxidation of N-compounds present in diesel [58]. As mentioned in Table 1, 25.6% of diesel contains aromatic compounds. Therefore, according to Kok-Giap's group, some oxidants are consumed in epoxy formation with aromatic hydrocarbons, and therefore the influence of H_2O_2 on the oxidation of sulfur species is relatively slow [59].

3.4. Regeneration of DESs

Recycling of the consumed DESs after extractive desulfurization is clearly essential [60]. This experiment was carried out at 30 °C at a stirring rate of 500 rpm for 1 h and with a mass ratio of phenol + ChCl: fuel of 1:2.

After completed extraction process for each sample, the ChCl: phenol was regenerated and was reutilised up to three times. This indicates that the liquid can be regenerated without any reduction in the removal potential over all three cycles. Regeneration of the used phenol:ChCl solvent was achieved by extraction using diethyl ether in a rotary evaporator and, after recycling, the DES composition was found to have remained unchanged in each instance. It can be observed that the phenol:ChCl as DES could be used at least three times without decreasing extraction efficiency.

4. Conclusions

In this research, the extraction of sulfur materials from real diesel into a number of DESs was carried out by liquid-liquid extraction. Four hydrogen bond donors, namely phenol, catechol, resorcinol, and o-cresol, were used to form DESs in different molar ratios with ChCl as a quaternary ammonium salt. The HBDs used in this work have an essential role in extraction processes in different practical areas. Studies on the effect

of functional group positions in HBDs, oxidant (H_2O_2) and FeCl_3 to diesel molar ratio on desulfurization were performed. In the optimization conditions, we also studied the effect of temperature, reaction time, DES/fuel mass ratio. It was found that extraction was preferred for molecules which could strongly form hydrogen bond. The results have shown that that the maximum amount of sulfur was removed by using phenol + ChCl due to low steric hindrance and no intramolecular hydrogen bonding.

The extraction process of sulfur species occurs with Cl^- ion from ChCl via the charge dipole interaction. This interaction is stronger than the hydrogen bonding between the chloride of the DESs and HBDs.

The results of this investigation show that the desulfurization efficiency, enhanced by increasing temperature due to an increase of the mass transfer rate between DES and diesel phases. Desulfurization efficiency is increased from 20% to 44% by adding H_2O_2 as the oxidant supported by acetic acid in Phenol-based DES at a temperature of 50 °C. This is due to formation of sulfone/sulfone oxides from oxidation of sulfur components which lead to increasing solution conductivity. It was found that the extraction efficiency was ordered o-cresol + ChCl < catechol + ChCl < resorcinol + ChCl < phenol + ChCl . In addition, it can be shown that the species of the solutes are controlled by the HBDs as the main constituents of the DESs. This favours the transfer of sulfur molecules into such DESs. The findings of this study have a number of important implications for future practice; for instance, they could be useful in an environmental sense in the removal of carcinogenic and corrosive molecules in industrial processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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