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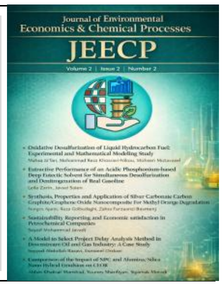

Extractive Performance of an Acidic Phosphonium-based Deep Eutectic Solvent for Simultaneous Desulfurization and Denitrogenation of Real Gasoline

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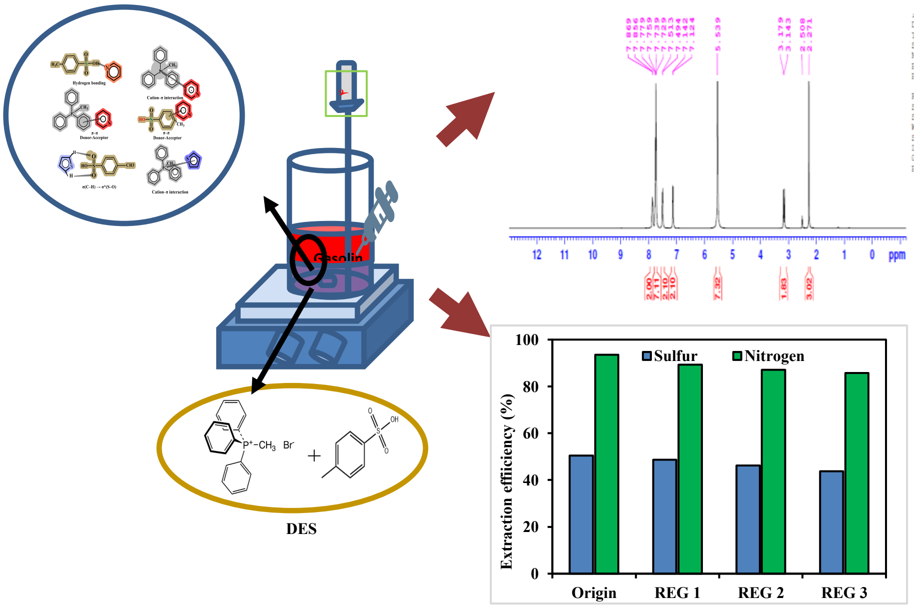
Hydrodesulfurization and hydrodenitrification in petroleum refinery are often associated with certain limitations of a huge energy consumption and restricted efficacy in removing total sulfur and nitrogen content. This study elucidates employing a selective liquid–liquid extraction process for desulfurization and denitrogenation of real gasoline using an efficient deep eutectic solvent (DES), obtained from methyltriphenylphosphonium bromide and para-toluensulfonic acid in a 3:7 molar ratio. The results show remarkable extraction efficiencies of 50.5% for the total sulfur compounds and 93.5% for the total nitrogen compounds in a single extraction step. After five extraction steps, these efficiencies were improved to 89.3% and 99.3%, respectively, using DES:gasoline volume ratio of 1:1 at 45 °C. In solvent regeneration via vacuum evaporation, 86.5% of its performance was retained after three stages in extracting sulfur and 91.0% in extracting nitrogen compounds. From NMR analysis, detailed information was obtained regarding the dominant interactions and the extraction mechanism involving acid-base interaction and π– π bonding, dominant for pyridine, and C–H···O hydrogen bonding for thiophene, examined by using the DES with a synthetic gasoline. The results totally demonstrate the benefits of utilizing such ecofriendly solvents for purifying fuels.



1. Introduction

Long-term energy studies indicate that fossil fuels will remain as the primary energy source for at least next 20 years [1]. This is because the world's growing energy needs are driven by factors such as population growth, economic development, and improved living conditions. Right now, fossil fuels make up about 88% of the world's energy consumption [1]. When these fuels are burned, they release sulfur and nitrogen-based substances, which create sulfur and nitrogen oxides with serious health issues such as headaches, coughing, eye problems, nausea, and vomiting [2]. These also cause environmental issues such as global warming, air and water pollution, acid rain, damage to equipment in oil refineries, and poisoning of catalysts [3]. To fix these issues, groups like the U.S. Environmental Protection Agency and the European Union have set limits on how much sulfur can be in fuel oils, usually keeping it below 10 to 15 ppm to protect the environment [4], and numerous countries have capped the nitrogen level at less than 1 ppm, a practice that has been in place since 2010 [5].

To deal with these problems, scientists are working on developing techniques that can effectively handle both the desulfurization and denitrogenation of fuels. Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are common methods for eliminating sulfur and nitrogen-based contaminants in fuels. However, these methods are not very effective in removing different types of sulfur and nitrogen compounds, like thiophene, dibenzothiophene,

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carbazole, pyridine, and their derivatives [6]. This is because these compounds are harder to break down due to their stable structure and undesirable interaction with the catalysts. In addition, these methods require intense heat and significant pressure to attain extremely minimal sulfur and nitrogen concentrations in fuel oils. Accordingly, to alter these methods, other approaches like liquid–liquid extraction [7], oxidation [8], adsorption [9], and bioprocessing [10] have been widely attempted.
Certain boundaries are still associated with the mentioned tactics; for example, the oxidation depends on expensive oxidizing agents, and the adsorption technique is constrained by the low capacity of adsorbents [11]. Nevertheless, extraction methods have gained much attention because of their ease and affordability. Nonetheless, conventional volatile solvents present numerous difficulties, such as concerns about toxicity and flammability. Accordingly, the advancements of deep eutectic solvents (DESs) have found much attention, known for their less volatile, heat-stable, and less flammable properties. In addition, the components used to prepare them, as hydrogen bond acceptors and donors, can be rather easily and inexpensively prepared [12].
One advanced use of DESs is cleaning fuels by extracting several sulfur and nitrogen aromatic compounds at once. Lima et al [13]. were among the first to investigate removing sulfur and nitrogen compounds from a model fuel using four different DESs from combining ammonium or phosphonium-based salts with (PEG400 and sulfolane). Simultaneous extractive desulfurization and denitrification (EDS/N) was demonstrated to be feasible, achieving the same level of extractive desulfurization as the EDS process alone. In the work by Rogošić and Kučan [14] on FCC gasoline, the highest sulfur compound removal was 1.32% using a DES of choline chloride (ChCl) and ethylene glycol (EG) at a molar ratio of 1:2, while 36.34% nitrogen compound removal was also achieved. In another study by Li et al. [15], the removal of sulfur and nitrogen compounds from real diesel fuel was achieved, at 10.5% and 58%, respectively, using a DES of choline chloride (ChCl) and mandelic acid with a molar ratio of 1:1.
Gasoline fuel is a well-known mixture of hydrocarbons with 4 to 12 carbons, additives (such as antifreezes and anti-rust agents), fine impurities such as heavy metals and water, and numerous sulfur and nitrogen compounds such as mercaptans, sulfides, disulfides, thiophene and its derivatives, totally with the boiling point range of (35 - ~200) °C [16,17]. The effectiveness of the extraction method may be influenced by the existence of such a diverse range of substances and reactions with the solvent. Therefore, evaluating the performance of a DES under real conditions is essential to prove the applicability of the method.
Notably, gasoline specifications vary in different regions of the world. Figure 1 shows several refining streams contributing to a typical gasoline pool, together with the major gasoline specifications [16]. Most of the sulfur in gasoline is from FCC (fluid catalytic cracking) naphtha, which contributes 30 – 40% of the pool content. Currently, the activity is concentrated more on cleaning FCC naphtha from sulfur and nitrogen [16]. Partially reprinted with permission from Ercan and Wang [16].

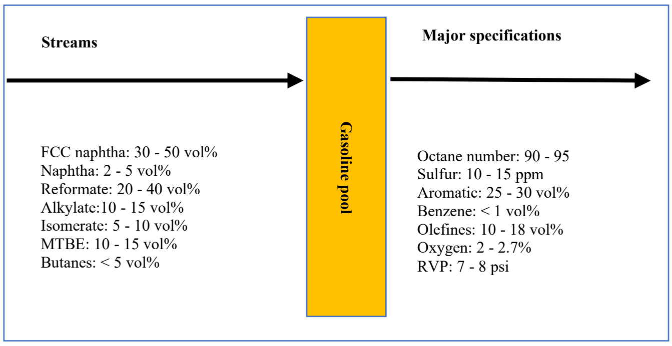
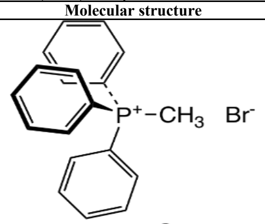
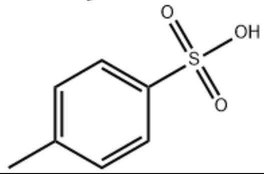


Figure 1. Blending of streams in the gasoline pool in refineries with major characteristics of the product. Partially reprinted with permission from Ercan et al [16].

Acidic phosphonium-based DESs have been widely utilized for extracting aromatic compounds with sulfur and nitrogen heteroatoms [18,19]. Impressive performance has been accordingly achieved in terms of extraction efficiency, distribution coefficient, and selectivity. In our recent study [20], a DES comprising methyltriphenylphosphonium bromide (MTPPBr) and para-toluenesulfonic acid (PTSA) (Table 1) at a molar ratio of 3:7 was utilized for desulfurization and denitrogenation of a synthesized gasoline. The same compound was used, in the present study, for the simultaneous extraction of sulfur and nitrogen from real gasoline (Euro 1) with sulfur and nitrogen contents of 878.7 and 654.8 ppm, respectively. The practical reusability via a low-energy regeneration protocol confirms the high potential of the solvent for scalable continuous fuel-upgrading processes. This work thus establishes a new paradigm in green extractive refining by integrating real-fuel applicability and mechanistic understanding into a unified framework. To distinguish the dominant non-covalent interactions with sulfur and nitrogen compounds, a comprehensive molecular-level elucidation of the synergistic extraction mechanism has been done through ^{1}H NMR spectroscopic analysis on synthesized gasoline.

Table 1. The molecular Schematic of the (DES) components.

DES component	Linear formula	Molecular structure
methyltriphenylphosphonium bromide (HBA)	[(C6H5)3PCH3] Br	
para-toluenesulfonic acid (HBD)	CH3C6H4SO3H	

2. Materials and methods

2.1. Materials

Table 2 details the inventory of the utilized chemical substances, all of which were sourced from Merck and possess well-documented properties. These substances encompass both hydrogen bond donors and hydrogen bond acceptors that are necessary for formulating the DES, as well as the constituents of synthetic gasoline. All substances underwent utilization in their as-received state, with no refinement procedures. Experiments were conducted using the Euro 1 gasoline.

Table 2. The chemicals used in the study.

Chemical	Cas No	Linear formula	Purity (%)
methyltriphenylphosphonium bromide	1779-49-3	$[(C_6H_5)_3PCH_3]Br$	≥ 98
para-toluenesulfonic acid	6192-52-5	$CH_3C_6H_4SO_3H$	≥ 98
***n*-heptane**	142-82-5	C_7H_{16}	99
***n*-hexane**	110-54-3	C_6H_{14}	99
***i*-octane**	111-65-9	C_8H_{18}	99
thiophene	110-02-1	C_4H_4S	99
pyridine	110-86-1	C_5H_5N	99

To follow the extraction mechanism, a synthetic gasoline was prepared following a previously documented formulation, made up of 0.3 mass fractions of *n*-hexane, 0.4 *n*-heptane, and 0.3 *i*-octane [13,21]. This formulation has a boiling point range of approximately 69 °C (boiling point of *n*-hexane) to 99 °C (boiling point of *i*-octane), which aligns closely with the usual mean boiling point of commercial gasoline [22,23].

2.2. Preparation of the DES

The DES used in this study was prepared through the thermal process [20,24]. Each mixture, with a specified molar concentration, was carefully heated within a sealed glass vial equipped with a jacket till achieving a maximum temperature of 240 °C. After that, the heat was slowly lowered up to early signs of a cloudy mixture appeared at a certain temperature. The deep point temperature of the DES, which appeared at 2.2 °C, was strongly lower than the freeze point of MTPPBr (233.7 °C) and PTSA (104.5 °C). The FTIR spectra of the DES and its components show specific peaks indicating various vibrations in MTPPBr and PTSA [20]. Key peaks confirm the presence of major functional groups such as $-CH_3$ stretching vibrations in MTPPBr and asymmetric SO_3 stretching motions at 1117 cm^{-1} before and after DES synthesis, indicating the formation of hydrogen bonds between DES components. The hydrogen bond formed during the synthesis was confirmed by the shifts in peak locations and changes in the intensity of the –OH group.
The moisture level in the prepared solvent was determined through Karl Fischer titration coulometric titrator (KIANSHAR DANESH, KFT50), revealing insignificant water content of only 0.0073 wt%. Additionally, the viscosity of the DES was assessed with a Brookfield DV2T Gel Timer Viscometer, yielding a measurement of 938.7 mPa·s at 20 °C. The density of the DES was determined via pycnometry, indicating a value of 1.40 g·cm^{-3} at 20 °C. As a result, the solvent used in this study displayed moderate viscosity and density, which are favorable for an efficient extraction process [25].

2.3. Analytical method

The total sulfur and nitrogen amounts in the real Euro 1 gasoline and each of the samples obtained from extraction experiments were assessed by means of an Analytic Jena EA 5100 micro-elemental analyzer, which operates through oxidative combustion and electrochemical detection coulometric titration using iodine for total sulfur and a chemiluminescence detector for total nitrogen.
To conduct experiments, sample-filled equilibrium cells were utilized, guaranteeing accurate measurements using a DES to oil volume ratio of 1:1. The containers underwent careful sealing and were immersed in a shaking water bath, experiencing consistent agitation at 175 rpm at a defined temperature for 4 h. Following this agitation phase, the solutions rested undisturbed for over 24 hours, allowing for stabilization and phase separation to confirm equilibrium attainment. Subsequently, a syringe was employed to separate the solvent and fuel layers, extracting the fuel layer situated on top, referred to as raffinate, for subsequent analysis [26].
The performance of the solvent and extraction process was accordingly evaluated from the extraction efficiency, defined as

$$E_i(\%) = \frac{w_{i,feed} - w_{i,raffinate}}{w_{i,feed}} \times 100 \quad (1)$$

where the subscript i indicates either sulfur or nitrogen; $w_{i,feed}$ and $w_{i,raffinate}$ signify the ppm of the considered element in the feed (before extraction) and in the raffinate (post-extraction), respectively.

3. Results and discussion

3.1. Effect of temperature

Temperature is a crucial factor in the extraction process. Figure 2 shows that the extraction efficiency initially rose with temperature but tended to decrease after 45 °C. Hence, extraction efficiencies of 50.5% and 93.6% could be achieved for the total sulfur and total nitrogen compounds, respectively. Thus, temperature was maintained at 45 °C after this observation. In a recent study by Tahir et al. [27], the best extraction efficiency was reported within the temperature range of (25 - 45) °C. This observation can be linked to how the viscosity of DESs changes with temperature. As the viscosity decreases with temperature, it allows for better movement of materials during the extraction process, improving mass transfer and efficiency of the extraction process. However, if the temperature becomes too high, it can damage the organosulfur compounds in the fuel, which lowers the extraction efficiency [27], attributed to the role of hydrogen bonds in the extraction and the exothermic nature of the interactions. In another research by Warrag et al. [28], the removal of thiophene and quinoline exhibited various sensitivities to temperature. The efficiency of thiophene extraction changed slightly with temperature; however, quinoline was found to be temperature sensitive. This was attributed to the hydrogen bonding interactions in the quinoline extraction.

Considering nitrogen compounds, specifically small and mobile molecules like pyridine, the electronegativity of the nitrogen atom and acid-base interactions help to improve the extraction efficiency [29]. Meanwhile, better mass transfer can compensate for the exothermic nature of hydrogen bonding formation with nitrogen compounds, which has reduced the sensitivity of the process to temperature. However, for sulfur compounds, due to dominant hydrogen bonds and their exothermic nature, the sensitivity to temperature is higher, evident in Figure 2 as evidenced from previous inveistagtions [29,30].

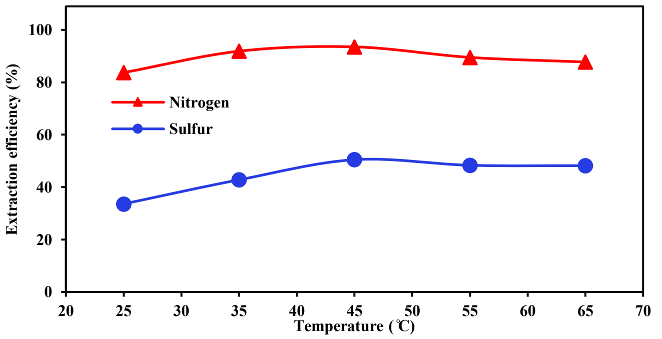


Figure 2. Influence of temperature on the extraction efficiency of total sulfur and nitrogen from the real gasoline using a V_{DES}: V_{oil} ratio of 1:1.

3.2. Effect of the number of extraction stages

Results indicate that single-stage extraction fails to lower the sulfur levels adequately. Accordingly, by utilizing multistage extraction, deep desulfurization can be achieved, resulting in sulfur concentrations less than 10 ppm. Despite this, the effectiveness of this method relies on two important factors: the specific type of sulfur compounds and how well a **deep eutectic** solvent is able to extract them. In a series of experiments in this step, after each extraction step, the raffinate phase was again treated with a new solvent to extract more of the desired compounds. Accordingly, a total of five extraction stages were performed. As depicted in Figure 3, the efficiency of the solvent in extracting sulfur compounds from real fuel reached to 89.3%, and for nitrogen compounds, 99.3%.

As was pointed in the previous section, numerous interactions are possible in the extraction of nitrogen compounds due to the acidic nature of the used DES, for which the most dominant interactions are acid-base type, while weak hydrogen interactions correspond to the extraction of sulfur compounds. In basic nitrogenous species such as pyridine and quinoline, the electron pair resides in the sp^2-hybridized orbital lying in the molecular plane, making it highly accessible for strong interactions with the Brønsted acidic component of the PTSA in the deep eutectic solvent [15]. Additionally, nitrogen compounds exhibit a more negative electrostatic potential on their ring faces and provide a larger molecular dipole moment (~2.2 D for pyridine) than sulfur compounds (~0.5 D for thiophene) [31]. Consequently, nitrogen compounds exhibit higher extraction efficiencies in the early stages. In addition, because part of the solvent capacity is coved by non-targeted hydrocarbons at each stage, the interactions become weaker, requiring more extraction steps for sulfur compounds.

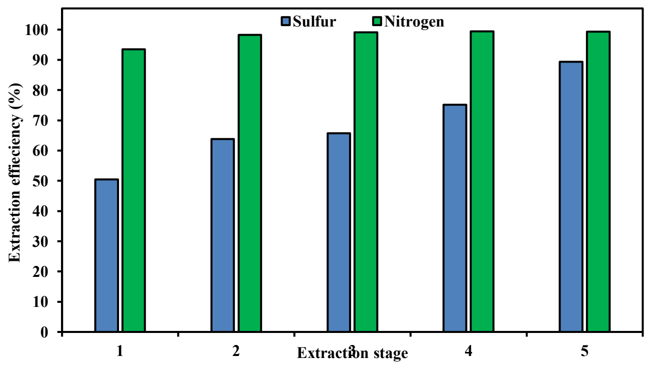


Figure 3. Influence of extraction stages on the extraction efficiency of total sulfur and nitrogen from real gasoline using a V_{DES}: V_{oil} ratio of 1:1 and temperature of 45 °C.

3.3. Solvent regeneration

Deep eutectic solvents are often considered as "green solvents," and their regeneration is important due to reducing the cost and preventing waste of resources. In this section, two series of experiments were conducted to enable the reuse of the solvent. In the first series, the solvent was used without recovery by a specific method to be used in the subsequent extraction. As presented in Figure 4(a), the performance of the DES for nitrogen compounds was maintained at an acceptable level, whereas for the sulfur compounds, decreased to below 30% after five stages.

In addition to the above case, DESs can be regenerated by washing with water, diethyl ether, and vacuum evaporation, as explained in our previous report [11]. However, with the advance of providing a practical and easy method, the vacuum evaporation method was used in the second series of solvent regenerating experiments, thus minimizing the use of solvent using a vacuum rotary evaporator set at 50 °C and 35 mbar for six hours [32]. As presented in Figure 4(b), using this regeneration method provides no significant diminishing in extraction efficiency, e.g., after three stages, it retains 86.5% of its performance in extracting sulfur compounds and 91.0% in extracting nitrogen compounds.

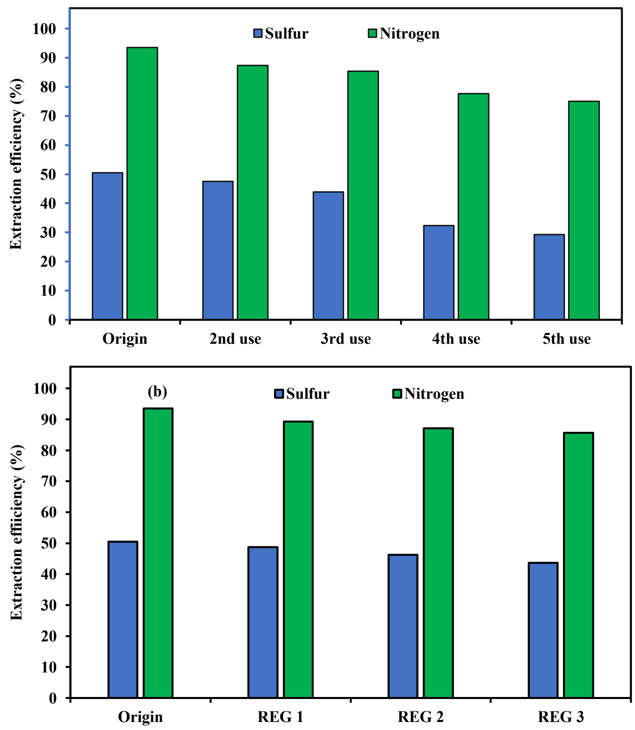


Figure 4. Effects of reusing (a) and regenerating of the DES (b) on total sulfur and nitrogen extraction from real gasoline with V_{DES}: V_{oil} of 1:1 and temperature of 45 °C.

3.4. Comparison with previous studies

A comparison of the extraction efficiency of the used DES with several other solvents, examined for extractive desulfurization and denitrogenation from different fuels and under different conditions, is provided in Table 3. Amazingly, higher extraction efficiencies correspond to the use of the utilized DES compared with other DESs. The involved cases are for different temperatures and different molar ratios of solvent to fuel, and of course, the initial amounts of sulfur and nitrogen compounds. Further, as presented, rather mild extraction conditions and unique results are corresponding to the results of the present study.

Table 3. Extractive desulfurization and denitrogenation by different DESs from different feeds at different conditions.*

DES (HBD: HBA)	Fuel	Extraction conditions	Extraction efficiency (%)		Ref.
			Sulfur	Nitrogen	
ChCl:EG (1:2)	FCC gasoline	25 °C; DES:Fuel 1:1; TS = 760 ppm; TN = 72 ppm; time = 60 min	1.32	36.34	[14]
ChCl:Mandelic acid (1:1)	catalytic cracking	50 °C; DES:Fuel 1:1; TS = 3650 μg/g; TN = 426 μg/g; time = 60 min	10.5	58.0	[15]

DES (HBD: HBA)	Fuel	Extraction conditions	Extraction efficiency (%)		Ref.
			Sulfur	Nitrogen	
ChCl:PTSA (1:2)		50 °C; DES:Fuel 1:1; TS = 3650 µg/g; TN = 426 µg/g; time = 60 min	13.2	60.0	[15]
TBACl:PEG400 (1:2)	diesel	70 °C; DES:Fuel 1:1; TS = 2300 ppm; time = 120 min	35.6	–	[33]
ChCl:PEG200 (1:2)	diesel	70 °C; DES:Fuel 1:1; TS = 2300 ppm; time = 120 min	4.1	–	[33]
TBACl:EG (1:2)	gasoline	30 °C; DES:Fuel 1:1; TS = 406 ppm; time = 20 min	38.7	–	[34]
TBACl:Gl (1:2)	gasoline	30 °C; DES:Fuel 1:1; TS = 406 ppm; time = 20 min	31.5	–	[34]
TBACl:MA (1:2)	gasoline	30 °C; DES:Fuel 1:1; TS = 406 ppm; time = 20 min	26.3	–	[34]
TBABr:HCOOH (1:1)	FCC gasoline	30 °C; DES:Fuel 2:1; TS = 500 ppm; time = 45 min	40.9	–	[35]
TBABr:HCOOH (1:1)	diesel	30 °C; DES:Fuel 2:1; TS = 500 ppm; time = 45 min	35.2	–	[35]
TBABr:imidazole (1:1)	diesel	30 °C; DES:Fuel 1:2; TS = 286 ppm; time = 95 min	47.0	–	[36]
TBABr:imidazole (1:1)	diesel	30 °C; DES:Fuel 1:2; TS = 255 ppm; time = 95 min	48.0	–	[36]
MTPPBr:PTSA (3:7)	gasoline	45 °C; DES:Fuel 1:1; TS = 879 ppm; TN = 654.8 ppm; time = 60 min	50.4	93.5	present work

* PEG: Polyethyleneglycol; GL: Glyserol; MA: Malic acid; ChCl: Cholinchloride; TS: total sulfur content before extraction;
TN: total nitrogen content before extraction

3.5. The extraction mechanism

The synergistic interactions collectively enhance the efficiency of DESs for desulfurization and denitrogenation of refractory heteroatomic compounds [37]. In order to investigate the mechanism, an extraction experiment was performed on the synthetic gasoline containing 1500 ppm thiophene and 1500 ppm pyridine at a temperature of 45 °C and the DES:oil volume ratio of 1:1 in one step. The 1H NMR tests on the DES were obtained before and after extraction. The results give compelling evidence for the proposed non-covalent interactions. Aromatic signals within the range of δ ~7.1–8.00 ppm (Figures 5a) indicate the protons of the phenyl rings of the phosphonium (15H) at 7.84–7.67 ppm and the aromatic protons of the PTSA (4H) at 7.53 and 7.17 ppm [38]. This region appears complex due to the overlap of several signals. The signals at 2.3 ppm and 3.3 ppm correspond to the methyl groups in PTSA and MTPPBr, respectively [38].

Following the extraction test, the peak that appeared in the 1H NMR spectrum (Figure 5b) at δ ~7.88 ppm is mainly due to phenylphosphonium protons, which are shifted downfield from their usual position (δ ~8.00 ppm) after extraction due to electrostatic interactions and hydrogen bonding. The emergence of a distinct signal at 8.94 ppm was unambiguously assigned to the ortho-protons of pyridine, exhibiting a significant downfield shift relative to free pyridine (~8.5 ppm) [38], which directly confirms strong hydrogen bonding between the nitrogen electron pair and the acidic proton of PTSA [39]. Concurrently, the aromatic protons of the DES, particularly those of the p-toluenesulfonate ring, undergo a noticeable up-field shift e.g., from (7.47–7.51) ppm to (7.47–7.50) ppm, with subtle but consistent changes across multiple signals, indicative of magnetic shielding induced by π–π stacking with extracted heterocycles [40]. The appearance of an additional resonance at 8.10 ppm, absent in the pristine DES (Figures 5a), further supports the involvement of thiophene or perturbed aromatic environments through C–H⋯O or cation–π interactions. Collectively, these spectral shifts corroborate a synergistic extraction mechanism involving acid-base interactions and hydrogen bonding for pyridine, and cation–π/C–H⋯O contacts for thiophene, in agreement with the theoretical expectations for phosphonium-based deep eutectic solvents. Similar interpretation of the 1H NMR results has been reported by Hadj-Kali et al. [41] and Li et al. [42].

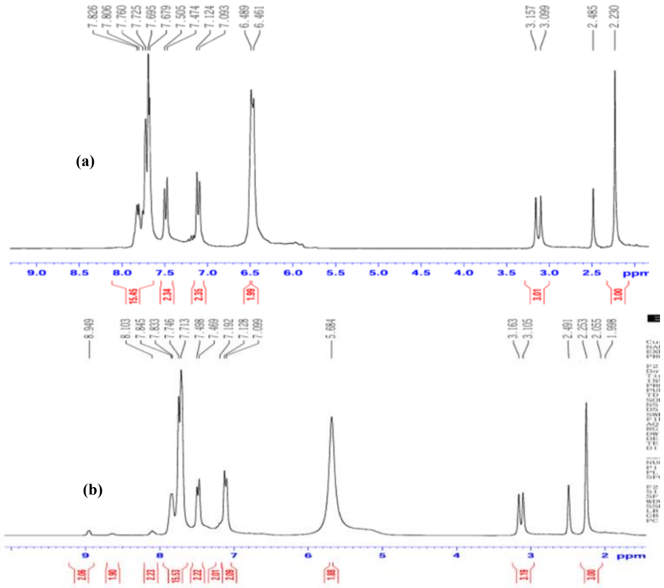


Figure 5. The [1]HNMR of DES (a) before and (b) after extraction process.

Based on the above mechanism analysis, the schematic of the dominant interactions in the extraction of thiophene and pyridine with the used DES is presented in Figure 6. The illustrated molecular interactions are a chemically intuitive representation of the key non-covalent forces governing the extraction mechanism. For pyridine, representing nitrogen-containing compounds, four plausible interactions with the DES composed of MTPPBr and PTSA are proposed as: (i) a hydrogen bond between the electron pair on pyridinic nitrogen and the acidic hydroxyl proton of PTSA, which is favorable due to the high proton-donating ability of PTSA; (ii) a cation–π interaction between the positively charged phosphonium center and the electron-rich π-system of pyridine; (iii) and (iv) two distinct π–π stacking interactions involving the aromatic rings of pyridine with either a phenyl ring of the phosphonium cation or the toluene moiety of PTSA, driven by dispersion forces and orbital overlap in planar aromatic systems [19, 43].

In the case of thiophene, sulfur-containing species include: (i) cation–π interaction between the phosphonium and the electron-rich thiophene ring, and (ii) weak hydrogen bonding between the acidic α-hydrogens of thiophene (slightly acidic due to the electron-withdrawing sulfur) and the sulfonyl oxygen atoms of PTSA, consistent with literature reports on C–H⋯O interactions in sulfur-aromatic systems [44, 45].

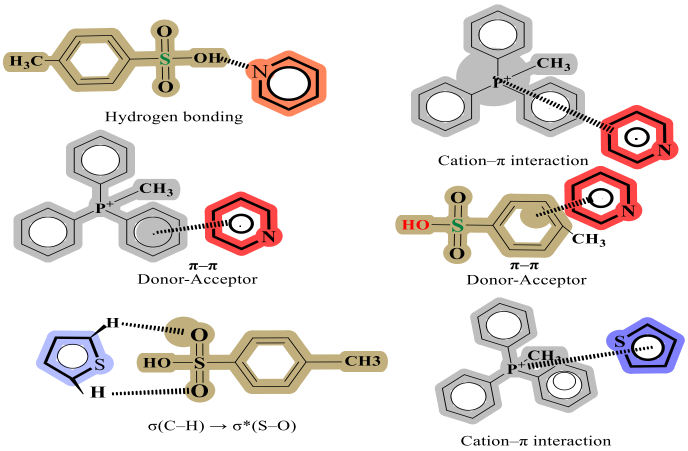


Figure 6. The schematic of the dominant interactions in the extraction of thiophene and pyridine with the used DES.

4. Conclusions

In this study, the performance of an acidic phosphonium-based deep eutectic solvent was evaluated for the simultaneous removal of sulfur and nitrogen compounds from real gasoline via liquid–liquid extraction process. Interestingly, a rather perfect separation of the total nitrogen content was achieved in five stages, but the efficiency for nitrogen was not as strong as for sulfur. The extraction capacity of the deep eutectic solvent was slightly decreased upon repeated use without regeneration. Consequently, solvent regeneration via vacuum evaporation was quite beneficial to maintain efficacy even after several operational cycles.

The consistently higher extraction efficiency observed for the nitrogen-containing compounds compared to sulfur-containing analogs can be rationalized by the energetically favorable non-covalent interactions with the used DES. Pyridine's planar aromatic structure compounds possess a localized electron pair on nitrogen that facilitates strong interactions with the Brønsted acidic component, with the acidic proton of p-toluenesulfonic acid. In contrast, thiophenic compounds lack strong hydrogen-bonding sites, and their sulfur-centered lone pairs are partially delocalized in the aromatic group, limiting their availability for specific interactions .

Additional studies may focus on effective regeneration methods to retrieve DES from different precursors with distinct characteristics. DFT calculations to evaluate the proposed forming molecular interactions would also be beneficial.

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