Sustainable Solutions in Gas Separation: Exploring the Potential of Deep Eutectic Solvents

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Abstract: In the face of escalating environmental concerns, particularly related to greenhouse gas emissions, this study delves into the potential of Deep Eutectic Solvents (DESs) as a s ustainable alternative in gas separation technologies. Focusing on the significant emissions of CO2, SO2, and H2S from industrial processes, this work reviews the application of DESs for their capture and separation. We investigate the physical properties of DESs, such as solubility and viscosity, which are crucial for their efficacy as so rbents. This review includes a comprehensive analysis of various DES formulations, exploring their roles in CO2 absorption, SO2 removal, and the separation of other gases like H2S. Additionally, we extend our examination to the applicability of DESs in the oil and gas industry, highlighting their effectiveness in removing sulfur and nitrogen impurities, and their potential in the extraction of organic constituents. The study reveals that DESs, characterized by their biodegradability and environmental sustainability, offer promising performance in gas separation, aligning with the principles of green chemistry. However, challenges such as high viscosity and the need for further understanding of their solubility dynamics under different conditions are addressed. This work underscores the importance of DESs as novel sorbents for gas purification and sets a foundation for future research aimed at enhancing their application on a broader industrial scale.

Key-Words: Deep Eutectic Solvents (DESs), Ionic Liquids Green Chemistry, Sorbent, Carbon capture

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1 Introduction

In the contemporary landscape of industrial processes, the urgent need to address environmental challenges has become paramount. Among these, the emission of greenhouse gases such as sulfur oxides (SOx), nitrogen oxides (NOx), and carbon dioxide (CO2) from combustion processes stands as a critical concern, directly contributing to global warming and climate change. Traditional methods of gas separation and purification, employing Ionic liquids, Amino acid salts, and Potassium carbonate, have been at the forefront of research for the past two decades[1]–[4]. However, these methods are increasingly scrutinized for their environmental footprint, particularly regarding biodegradability, sustainability, and biocompatibility.

In response to these challenges, this paper introduces an innovative approach centered around Deep Eutectic Solvents (DESs). DESs emerge as a groundbreaking class of solvents, boasting a plethora of advantages over their traditional counterparts[1], [5]–[8]. Not only do t hey promise enhanced environmental compatibility, but they also offer a range of tunable physical properties that can be strategically tailored for specific gas separation processes. This paper endeavors to provide an in-depth analysis of the physical properties of various DESs, focusing on their solubility and viscosity, which are crucial for their efficacy as process solvents.

Through this comprehensive study, we aim to illustrate the potential of DESs in transforming the landscape of gas separation technologies. We will explore their applications in separating key gases like SO_2, CO_2, and H_2S from different oil and gas samples, under varied conditions of temperature and pressure. The paper also sheds light on the latest research regarding the role of viscosity in the practical deployment of these solvents, both at room and elevated temperatures. By presenting the thorough advancements of the applications of DESs in the oil and gas industry, this paper seeks to underscore their role as the next generation of sustainable and efficient gas separation agents.

2 Problem Formulation

Global warming, largely driven by emissions of CO_2, SO_2, and H_2S from large point sources like fossil-fueled power stations, poses a significant threat to the environment. Traditional methods of gas separation are either inefficient or environmentally detrimental. Furthermore, the rising need to manage SO_2 emissions, which contribute to acid precipitation affecting human health and infrastructure, underscores the urgency for more effective solutions. Similarly, the oil processing industry faces challenges in removing impurities like sulfur, nitrogen, and organic compounds from fuels. These problems demand innovative solutions that are both effective and sustainable.

3 Problem Solution

The application of DESs in gas separation processes offers a viable solution. Studies have shown that DESs, with their tunable properties, can effectively capture CO_2, with the absorption capacity influenced by factors like molar ratio and gas pressure. Similarly, DESs have demonstrated efficiency in SO_2 removal under various operational conditions, proving their potential in managing emissions. In the context of oil processing, DESs have been used successfully for the extraction of sulfur and nitrogen compounds and the separation of aromatics and aliphatics. These results indicate that DESs could serve as green and efficient alternatives to conventional solvents in gas separation and oil processing applications.

3.1 Application of DESs in gas separation processes

Several studies have recently emerged on the use of DESs for gas separation, solubility studies, and capturing processes for different gasses. The current literature has mainly focused on emissions from different large point sources such as the flue gas from fossil-fueled power stations are the main contribution to global warming. These gasses mainly consist of CO_2 SO_2, and H_2S.

3.1.1 CO_2 Capture

Studying the CO_2 solubility is an important property for the sequestration of CO_2. In recent studies, different DESs are considered as an emerging alternative solvents for the CO_2 sorption process a promising green solvent candidates for improving the enhancement of CO_2 capture and also the capture process cost [9]. According to the conducted literature survey, the maximum CO_2 uptake performance was influenced by several factors effecting the DESs. For instance, Altamash et al. [10] research group studied the effect of increasing the mole ratio on choline chloride + phenylacetic acid at (1:2),(1:3), and (1:4) molar ratio for CO_2 capturing, using high-pressure gas absorption at post-combustion CO_2 capture conditions. This group found a general conclusion for the three mixtures, that solubility of CO_2 increases with increase of the gas pressure and consequently decreases with temperature on all the systems. However, an increase in the molar ratio to 1:3 from 1:2 showed relatively higher performance in CO_2 capture, but lower for 1:4 in comparison with 1:3. Therefore, further studies are required on the effect of molar ratio for CO_2 capture processing. The effect of molar ratio of a DES was also studied by Adeyemi et al., Lu et al., and Li et al. [11]–[13] In a different study by Altamash et al.[1], four novel choline chloride based DESs with altered HBDs.were evaluated .The group enhanced their studied on CO_2 solubility in DESs with rheological characterization on these solvents to furtherly investigate the bonding interactions between these NADES. Due to the low viscosity of choline chloride + lactic acid, CO_2 solubility in it was the best performing sorbent. Moreover, Deng et al. [14] considered addressing the effect of alternating the HBA using five different quarternary ammonium species for their study on CO_2 capture, using a fixed HBD of levulinic acid at a molar ratio of 1:3. They elaborated on the influence of the HBA on t he absorption capacity of the DESs, stating that the structure of HBA and weak related to that of HBA. The larger the HBA in the quarternary ammonium salt, the higher absorption ability of DES for CO_2.

3.1.2 SO_2 Removal

SO_2 emissions has rapidly increased over the past few years due do the burn in fossil fuels and the conversion of energy. Its adverse effect is mainly witnessed as a cause of acid precipitation on the health of humans and infrastructure. As a result, effective SO_2 management has been the forefront research of researchers in fields of gas capturing and separation.

Yang et al. [15] looked at the SO_2 absorption by tuning different parameters and operational conditions, such as the temperature, SO_2 partial pressure, and the molar ratio of choline chloride + glycerol (1:1 – 1:4). They concluded that the maximum sorption of SO_2 was obtained at the lowest molar ratio (1:1), lowest temperature (20ºC), and at atmospheric pressure, with a value of 0.678 g SO_2/ g absorbent. In another study on the conditions of SO_2 absorption, Zhang et al. [16], who studied the sorption capabilities of Betaine + Ethyl Glycol & L-carnitine + Ethyl Glycol under the effect of varied HBA/HBD mole ratios (1:3-1:5) and high temperatures. They concluded that the mole ratio had no effect on a bsorption, lower temperature (30ºC), and with the low SO_2 partial pressure was favored for SO_2 capturing. This analogy was also sensed in the study by Deng et al[17]. Moreover, Zhang et al investigated the potential abilities of regenerating DES after the SO_2 absorption, they have found and confirmed that SO_2 absorption is reversible and with increase the temperature, regeneration of DESs is achievable with capacities and stabilities. Furthermore, Sun et al.[18] also agreed with the findings of Zhang et al., where Sun et al. confirmed that all of the four investigated solvents of choline chloride + urea, choline chloride + ethyl glycol, choline chloride + malonic acid, choline chloride + urea are all suitable for sorption reuse and recycling, after regeneration 100% SO_2 molecule within a time frame of 15mins.

3.2 DESs for separation of other gases

Guo et al. [19] explored the solubility of H_2S at different temperatures ranging from 303.2 – 363.2 K on tetrabutyl ammonium bromide + caprolactam with different molar ratios of from 1:1 to 1:7. They found that the solubility of the 1:1 mole ratio was at performing the best out of the other molar ratios, where the highest capacity was 5.4 wt% of at 303.15 K and atmospheric pressure. The effect of incrementing the amount of HBA: HBD has shown an adverse effect to the solubility capacitance, as it decreased with increase HBA: HBD. Moreover, the regeneration and reusability has also shown promising capacities of DESs on H_2S. The absorption process taken place was by the physical interactions between the DESs and H_2S, as the H_2S was noticed to remain in its molecular state after regeneration of six cycles. Further approaches and studies on the use of DESs for their use in H_2S capture were only limited to a single paper, as the lack of literature studies hinder the evaluation of their field applicability. Other predictions on D ES absorption for different gases such as CH_4, H_2, CO, and N_2 were applied on several choline-chloride based deep eutectic solvents by Xie et al. [20]. A computational based study by Kamgar et al. [21] using COMSO-RS and NTRL models to theoretically evaluate the solubility of CH_4, CO, N_2, H_2.The general gas solubilities in DESs were reported by Zhang et al. [22], stating that choline chloride DESs are usually selective in the order of $SO_2 > CO_2 > CH_4 > N_2 > CO > H_2$. However, the authors also noted that this trend may differ for certain DES systems.

3.3 Applications of DESs in oil processing

3.3.1 Desulphurization of fuel oils (Removal of mercaptans)

The extraction of mercaptans from fuels has become a frontier topic in research that requires special attention. DESs have shown to become an emerging route for their application in desulfurization of different fuels with different sulfur impurity. Li et al. [23] Reported the use of tetrabutyl ammonium chloride-based DESs with the use of a series of well-recognized HBA: glycerol, ethylene glycol, propionate, and malonic acid to extract Benzothiophene from a n-octane based fuel matrix. The maximum extraction in their study has shown higher removal rates than conventional ILs ones. In one cycle, the 82.23%. In another study by Li et al.[24] , The highest removal efficiency per cycle was recorded, a maximum removal efficiency of 89.53%. Their study involved enhancing the DES mixture with a metal ion of $FeCl_3$. The group explained the effect of the metal ion on the extraction mechanism by exploring the interactions from IR spectra. The FT-IT peaks have shown that the interactions between the DESs hydrogen bond and the metal ion were weak, yet almost destroyed. However, the hydrogen bonding interactions between the DESs mixture and the sulphur impurity of dibenzothiophene was enhanced gradually, resulting in a network breakdown between the intramolecular forces between the DESs itself. Therefore, improving and extraction process. Tang et al. [25] suggested two possible explanations on the extraction excellence in DESs (tetrabutylammonium bromide + sulfolane) with thiophenic sulfur in a heptane based fuel. The first factor is the $\pi - \pi$ interactions between the aromatic functional group in the DES and the thiopheic sulphur. The second reason is the complexation of the thiphenic sulfur with the HBD in the DES system. The mechanism of DES/sulphur extraction was also represented by the Tang et al., shown by Figure 1.

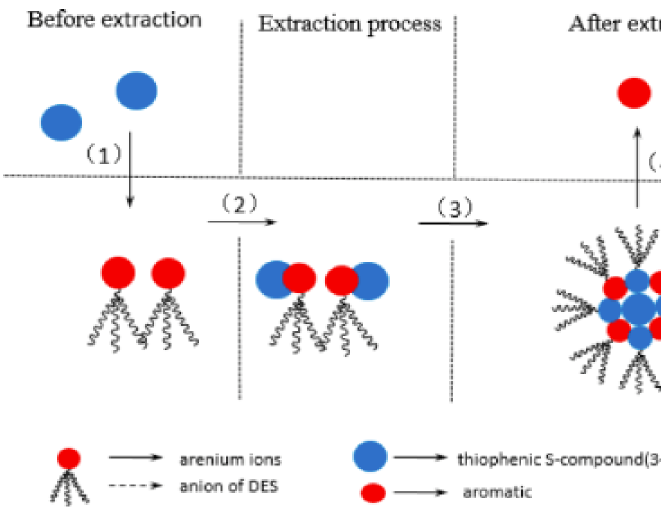

Figure 1: The extraction process of sulphur from an oil mixture using DESs [25]

3.3.2 Denitrification of fuel oil

Ali et al. [26] were the first to report the experimental study on the use of choline chloride + phenylacetic acid using a the molar ratios of 1:1 and 1:2 as an extractants for a promising denitrification technique from fuels. Among these two molar ratios, the 1:2 showed superior performance in denitrifying basic and non-basic nitrogen-based compounds. Pyridine and carbazole nitrogen compounds were separated from an n-heptane fuel sample by physical extraction at ambient temperature and atmospheric pressure. The removal efficiencies of pyridine and carbazole were 99.2% and 98.2%, respectively. Ali et al. group had also mentioned that the extraction efficiency was not affected by the choline chloride + phenylacetic acid, even after four sets of regeneration, oil mass ratios, and elevated temperatures. A screening of 94 sets of different DESs using COMSO-RS and NTRL correlations was reported by Hizaddin et al.[27] for the predication of potential extraction candidates of nitrogen from diesel. Accordingly, an experimental approach was conducted on a n ammonium and phosphonium hydrogen bond a cceptor based based DESs at 1:2 molar ratio based on t he preliminary study. The experimental data had come into an agreement with the experimental data by using the NTRL model with an root mean square value of 0.6% However, no nitrogen removal efficiencies were recorded in this study. The use of ^{1}H NMR was used to access compositional analysis of the nitrogen in the experimental studies [28] .

3.3.3 Removal of BTEX

The removal of aromatics and aliphatic compounds is a co mplicated process in the petrochemical industry. The minimal difference in boiling points between the extract and the extractant hinder the process of BTEX removal from gas streams. Moreover, the formation of azeotrope combinations is also a challenge in their removal. The use of DESs in the separation of different BTEX.

Rodriguez et al. [29] compared the extraction of a hexane + benzene mixture using ammonium based DESs with glycerol and ethylene glycol with of mole ratio (1:2) with the extraction performance of sulfolane. After characterizing both solvent's viscosity and density, the ethylene glycol based deep eutectic solvent was favored glycerol, due to the lower magnitudes in viscosity and density that enhanced the extraction of benzene. The liquid-liquid equilibria (LLE) was determined at 298,308 K and at atmospheric pressure. The solute distribution coefficients of the solfolane were higher than DESs, and the selectivity values were also higher for solfolane. Moreover, the group of researchers apprised to that the performance of DESs in extraction was comparable to ILs and may be considered as the new generation of solvents.

Mukhtar et al. [30] studied the extraction of an aromatic/aliphatic mixture from a n aptha steam cracking unit a series of phophonium based DESs at Methyltriphinylphosphonuim bromide + ethylene glycol with three different molar ratios of 1:4,1:6, 1:8 at elevated temperatures of 300,308,318 K. The authors described their satisfaction with the performance of the 1:6 molar ratio DESs in comparison with sulfolane. Moreover, the authors also compared the study with N-formylmorpholine, stating that the 1:4 DESs showed better separation in comparison with it. The effective extraction temperature was recorded at 318 K. Furthermore, a complementary study by Mukhtar et al. [31]. discussed the removal of aromatics from ethylene cracking unit using LLE using two novel DESs: tetrabutylphosphonium bromide + ethylene glycol and tetrabutylphosphonium bromide + sulfolane. This study altered the HBD molar ratio of 1:4,1:6,1:8 and operated at temperatures of 313,323,333 K. This group suggested that more investigation on this particular group requires further investigation prior applying and using these two DESs in the separation of aromatics.

Gonzalez et al. [32] investigated the use of two choline chloride based DESs:lactic acid and glycerol with molar ratios of 1:2 on LLE for the purpose of extracting benzene and acetate mixtures from a hexane based fuel model at 298,308,318 K. In their comparison with ILs, both choline chloride based DESs have shown higher selectivity and showed no signs of decomposition with time. The favored temperature of the extraction process was at 308 K. They concluded that the choline chloride + glycerol DESs showed the best separation at room temperature and lactic acid was more soluble to benzene.

4 Conclusion

This comprehensive review has underscored the pivotal role of Deep Eutectic Solvents (DESs) in revolutionizing gas separation technologies and addressing environmental challenges associated with industrial emissions. Our exploration revealed that DESs are not only effective in capturing and separating key greenhouse gases like CO_2, SO_2, and H2S but also hold significant potential in various applications within the oil and gas industry. The studies reviewed highlight the advantageous physical properties of DESs, particularly in terms of solubility and viscosity, which are critical for their performance as novel sorbents.

The research into CO_2 absorption, SO_2 removal, and H_2S separation using DESs has demonstrated their capacity for efficient gas capture under a range of conditions, emphasizing their versatility. Furthermore, the application of DESs in the removal of sulfur and nitrogen impurities, as well as the extraction of organic compounds from oil samples, positions them as a p romising green alternative to conventional solvents.

However, this review also identifies key challenges that need to be addressed to fully harness the potential of DESs. The high viscosity of some DES formulations and the need for a deeper understanding of their solubility and polarity dynamics are areas requiring further research. Additionally, while laboratory and bench-scale studies show promising results, scaling up these applications to industrial levels remains a critical step for the future.

In conclusion, DESs emerge as a beacon of hope in the quest for sustainable industrial processes. As we continue to seek solutions that align with environmental sustainability and green chemistry principles, DESs offer a promising path forward. Their adaptability and efficiency in gas separation and purification, combined with their eco-friendly properties, pave the way for their expanded use and development in future industrial applications.

References:

[1] T. Altamash *et al.*, “Gas solubility and rheological behavior study of betaine and alanine based natural deep eutectic solvents (NADES),” *J Mol Liq*, vol. 256, pp. 286–295, 2018, doi : 10.1016/j.molliq.2018.02.049.

[2] T. Altamash *et al.*, “Gas Solubility and Rheological Behavior of Natural Deep Eutectic Solvents (NADES) via Combined Experimental and Molecular Simulation Techniques,”

ChemistrySelect, vol. 2, no. 24, pp. 7278–7295, 2017, doi: 10.1002/slct.201701223.

[3] Y. Elhamarnah *et al.*, "An Experimental Investigation on the Thermo-Rheological Behaviors of Lactic Acid-Based Natural Deep Eutectic Solvents," *Materials*, vol. 15, no. 11, p. 4 027, Jun. 2022, doi : 10.3390/ma15114027.

[4] Y. Elhamarnah, H. Qiblawey, M. S. Nasser, and A. Benamor, "Thermo-rheological characterization of Malic Acid based Natural Deep Eutectic Solvents," *Science of the Total Environment*, vol. 708, 2020, doi : 10.1016/j.scitotenv.2019.134848.

[5] Y. Elhamarnah, "Thermo-Rheological Characterization of Natural Deep Eutectic Solvents (Nades) Used In CO2 Capture," *Master Thesis*, vol. 8, no. 5, p. 55, 2019, [Online]. Available: https://qspace.qu.edu.qa/bitstream/handle/10576/12383/Yousef Adel Elhamarnah_OGS Approved Thesis.pdf?sequence=1&isAllowed=y

[6] Y. Elhamarnah, T. Hey, F. Lipnizki, and H. Qiblawey, "Investigating the impact of stormwater fouling on polysulfone ultrafiltration membranes modified with deep eutectic solvents," *Journal of Water Process Engineering*, vol. 56, p. 104362, Dec. 2023, doi: 10.1016/j.jwpe.2023.104362.

[7] Y. Elhamarnah, H. Qiblawey, M. S. Nasser, and A. Benamor, "Thermo-rheological characterization of Malic Acid based Natural Deep Eutectic Solvents," *Science of the Total Environment*, vol. 708, p. 134848, 2020, doi: 10.1016/j.scitotenv.2019.134848.

[8] Y. A. Elhamarnah, M. Nasser, H. Qiblawey, A. Benamor, M. Atilhan, and S. Aparicio, "A comprehensive review on the rheological behavior of imidazolium based ionic liquids and natural deep eutectic solvents," *J Mol Liq*, vol. 277, pp. 932–958, 2019, doi : 10.1016/j.molliq.2019.01.002.

[9] A. Yadav and S. Pandey, "Densities and viscosities of (choline chloride + urea) deep eutectic solvent and its aqueous mixtures in the temperature range 293.15 K to 363.15 K," *Journal of Chemical and Engineering Data*, vol. 59, no. 7, pp. 2221–2229, 2014, doi : 10.1021/je5001796.

[10] T. Altamash, M. Atilhan, A. Aliyan, R. Ullah, M. Nasser, and S. Aparicio, "Rheological, Thermodynamic, and Gas Solubility Properties of Phenylacetic Acid-Based Deep Eutectic Solvents," *Chemical Engineering and Technology*, vol. 40, no. 4, pp. 778–790, 2017, do i: 10.1002/ceat.201600475.

[11] I. Adeyemi, M. R. M. Abu-Zahra, and I. Alnashef, "Experimental Study of the Solubility of CO2 in Novel Amine Based Deep Eutectic Solvents," *Energy Procedia*, vol. 105, pp. 1394–1400, 2017, doi: 10.1016/j.egypro.2017.03.519.

[12] M. Lu, G. Han, Y. Jiang, X. Zhang, D. Deng, and N. Ai, "Solubilities of carbon dioxide in the eutectic mixture of levulinic acid (or furfuryl alcohol) and choline chloride," *Journal of Chemical Thermodynamics*, vol. 88, pp. 72 –77, 2015, doi: 10.1016/j.jct.2015.04.021.

[13] G. Li, D. Deng, Y. Chen, H. Shan, and N. Ai, "Solubilities and thermodynamic properties of CO2 in choline-chloride

based deep eutectic solvents," *The Journal of Chemical Thermodynamics*, vol. 75, pp. 58 –62, 2014, doi : 10.1016/j.jct.2014.04.012.

[14] D. Deng, Y. Jiang, X. Liu, Z. Zhang, and N. Ai, "Investigation of solubilities of carbon dioxide in five levulinic acid-based deep eutectic solvents and their thermodynamic properties," *Journal of Chemical Thermodynamics*, vol. 103, pp. 212–217, 2016, doi : 10.1016/j.jct.2016.08.015.

[15] D. Yang, M. Hou, H. Ning, J. Zhang, G. Yang, and B. Han, "Efficient SO2 absorption by renewable choline chloride–glycerol deep eutectic solvents," pp. 2261–2265, 2013, doi : 10.1039/c3gc40815a.

[16] K. Zhang, S. Ren, Y. Hou, and W. Wu, "Efficient absorption of SO2 with low-partial pressures by environmentally benign functional deep eutectic solvents," *Journal of Hazardous Materials*, 2016, doi: 10.1016/j.jhazmat.2016.11.012.

[17] D. Deng, X. Liu, and B. Gao, "Physicochemical Properties and Investigation of azole-based deep eutectic solvents as efficient and reversible SO2 absorbents Physicochemical Properties and Investigation of Azole-Based Deep Eutectic Solvents as Efficient and Reversible SO 2 Absorbents," 2017, doi: 10.1021/acs.iecr.7b02478.

[18] S. Sun, Y. Niu, Q. Xu, Z. Sun, and X. Wei, "E ffi cient SO 2 A bsorptions by Four Kinds of Deep Eutectic Solvents Based on Choline Chloride," 2015, doi : 10.1021/acs.iecr.5b01789.

[19] B. Guo, E. Duan, Y. Zhong, L. Gao, X. Zhang, and D. Zhao, "Absorption and Oxidation of H2S in Caprolactam Tetrabutyl Ammonium Bromide Ionic Liquid," no. 11, pp. 159 –161, 2011, doi: 10.1021/ef1012006.

[20] Y. Xie, H. Dong, S. Zhang, X. Lu, and X. Ji, "THERMOPHYSICAL PROPERTIES AND GAS SOLUBILITIES IN CHOLINE CHLORIDE / UREA FOR CO 2 SEPARATION," pp. 1–8, 2013.

[21] A. Kamgar, S. Mohsenpour, and F. Esmaeilzadeh, "Solubility prediction of CO2, CH4, H2, CO and N2in Choline Chloride/Urea as a eutectic solvent using NRTL and COSMO-RS models," *Journal of Molecular Liquids*, vol. 247, pp. 70–74, 2017, doi: 10.1016/j.molliq.2017.09.101.

[22] Y. Zhang, X. Ji, and X. Lu, "Choline-based deep eutectic solvents for CO2separation: Review and thermodynamic analysis," *Renewable and Sustainable Energy Reviews*, vol. 97, no. August, pp. 436 –455, 2018, doi : 10.1016/j.rser.2018.08.007.

[23] C. Li *et al.*, "Extraction desulfurization process of fuels with ammonium-based deep eutectic solvents," *Green Chemistry*, vol. 15, no. 10, pp. 2793–2799, 2013, doi: 10.1039/c3gc41067f.

[24] C. Li *et al.*, "Extraction desulfurization of fuels with 'metal ions' based deep eutectic solvents (MDESs)," pp. 3789–3795, 2016, doi: 10.1039/c6gc00366d.

[25] X. Tang, Y. Zhang, J. Li, Y. Zhu, D. Qing, and Y. Deng, "Deep Extractive Desulfurization with Arenium Ion Deep

Eutectic Solvents," 2015, doi : 10.1021/acs.iecr.5b00291.

[26] M. C. Ali *et al.*, "Efficient removal of both basic and non-basic nitrogen compounds from fuels by deep eutectic solvents," *Green Chemistry*, vol. 18, no. 1, pp. 157–164, 2015, doi: 10.1039/c5gc01823d.

[27] H. F. Hizaddin, A. Ramalingam, M. A. Hashim, and M. K. O. Hadj-kali, "Evaluating the Performance of Deep Eutectic Solvents for Use in Extractive Denitri fi cation of Liquid Fuels by the Conductor-like Screening Model for Real Solvents," 2014, doi: 10.1021/je5004302.

[28] H. F. Hizaddin, M. K. Hadj-Kali, A. Ramalingam, and M. Ali Hashim, "Extractive denitrogenation of diesel fuel using ammonium- and phosphonium-based deep eutectic solvents," *Journal of Chemical Thermodynamics*, vol. 95, pp. 164–173, 2016, doi : 10.1016/j.jct.2015.12.009.

[29] N. R. Rodriguez, P. F. Requejo, and M. C. Kroon, "Aliphatic − Aromatic Separation Using Deep Eutectic Solvents as Extracting Agents," 2015, doi : 10.1021/acs.iecr.5b02611.

[30] M. A. Kareem, F. S. Mjalli, M. Ali, and I. M. Alnashef, "Liquid–liquid equilibria for the ternary system (phosphonium based deep eutectic solvent–benzene–hexane) at different temperatures: A new solvent introduced," *Fluid Phase Equilibria*, vol. 314, pp. 52 –59, 2012, doi: 10.1016/j.fluid.2011.10.024.

[31] M. A. Kareem *et al.*, "Fluid Phase Equilibria Phase equilibria of toluene / heptane with tetrabutylphosphonium bromide based deep eutectic solvents for the potential use in the separation of aromatics from naphtha," *Fluid Phase Equilibria*, vol. 333, pp. 47–54, 2012, doi: 10.1016/j.fluid.2012.07.020.

[32] A. S. B. Gonzalez, M. Francisco, G. Jimeno, S. L. G. De Dios, and M. C. Kroon, "Liquid-liquid equilibrium data for the systems {LTTM+benzene+hexane} and {LTTM+ethyl acetate+hexane} at different temperatures and atmospheric pressure," *Fluid Phase Equilib*, vol. 360, pp. 54–62, 2013, doi: 10.1016/j.fluid.2013.09.010.

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Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.