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EXTRACTIVE DESULFURIZATION OF FUEL OIL USING GLYCOL-BASED DEEP EUTECTIC SOLVENT MEDIATED BY HYDROGEN PEROXIDE AND GRAPHENE OXIDE

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ABSTRACT

Sulfur-containing compounds in fuel oil is one of the major pollutants that contributes to air pollution. To solve this issue, separation of sulfurs is crucial to produce ultra-clean fuel oil according to Euro V standard. Conventional method uses hydrodesulfurization to separate sulfur, however the system requires harsh conditions to operate in a separation unit. Morever, it is inefficient to remove sterically hindered sulfur compounds such as dibenzothiophene, benzothiophene and 4, 6-dimethyldibenzothiophene. An alternative to the current technology is using integrated extractive and catalytic-oxidative desulfurization. Many researchers has attempted to use ionic liquid as the extractant, however due to its complexity of synthesis and expensive starting material, the analogue of ionic liquid which is deep eutectic solvent (DES) could be a promising candidate to desulfurize fuel oil. In this work, four types of glycol-based DES (glycerol, ethylene glycol, tetraethylene glycol and poly(ethylene glycol) 400 (PEG)) with tetrabutylammonium chloride (TBAC) as salt have been synthesized in different mole ratios to study the effect of glycols towards desulfurization efficiency. Higher desulfurization can be achieved when using DES compared to glycol itself as solvent due to the synergistic effect of salt and glycols. The performance of desulfurization can reach as high as 66.24% when using TBAC:PEG in 1:2 mole ratio in ambient condition in the presence of hydrogen peroxide as oxidant and graphene oxide as catalyst. The hydrogen peroxide helps to oxidize dibenzothiphene into high polar dibenzothiophene sulfone so that it be easily extracted into the layer of DES and the process is mediated by the graphene oxide. The main reason for the enhanced performance is longer repeating ethoxy chains of polyethylene glycol which favoured the oxidized sulfur species to be extracted.

Keywords: *sulfur, desulfurization, deep-eutectic solvent, glycol, graphene oxide, oxidation*

INTRODUCTION

The Need Of Clean Oil

Fuel oil composed of hydrocarbons and some elemental species that exist as aliphatic and aromatic structure. About 0.03 – 6% of the content of fuel oil is composed of sulfur containing compounds (SCC) where it can be categorized into organic SCC and inorganic SCC. The burning process of fuel oil will convert SCC into SO_x particles. As it accumulates, it will react with the water vapor and lead to acid rain, which corrodes building [1]. An increase of SCC content may also lead to air pollution and haze, which give a catastrophic consequence towards health problem such as eyes cataract, skin disease and lung-related illness [2],[3]. To prevent the long terms effect of the current situation, production of sulfur-free fuel oil is a necessity to decrease the release of this toxic gas.

From Traditional Hydrodesulfurization To Non-Conventional Strategies

Stringent regulations have been in place prosecuted to achieve the minimum allowable sulfur content in fuel oil before commercialization. Some countries have

Table 1 The latest regulations of sulfur content in fuel oil [4]

Country	Regulations
United State Environmental Protection Agency (US EPA) Tier 3 vehicle emission and fuel standards	The allowed sulfur content in gasoline is lowered to 10 ppm by weight beginning in 2017
China V standard	The allowed sulfur content in gasoline is lowered to 10 ppm by weight beginning in 2016
European Union	Legal limit of 10 ppm on sulfur in gasoline since 2008
Malaysia	*Euro 5 Standards* fuel (10 ppm sulfur) for 95 RON and 97 RON gasoline by September 2025

agreed to implement Euro V standard production of fuel oil. A Euro V fuel oil contain only 10 ppm or less than 10 ppm of sulfur contents. The descriptions of the fuel oil specifications corresponding to selected countries can be referred in Table 1.

The long-established technology to separate SCC from fuel employ hydrodesulfurization (HDS). The extensive reviews on the HDS strategies can be referred elsewhere [5]-[7]. In brief, HDS involves a chemical reaction to convert SCC into hydrogen sulfide which will be filtered from the separation unit. The typical conditions of the procedure require transition element catalyst such as $Co/Mo/Al_2O_3$ or $Ni/Mo/Al_2O_3$ with extreme pressure (20 – 100 atm hydrogen gas) and high temperature (300 – 340°C) [8]-[10]. Although it is efficient to remove most of the SCC in fuel oil, elimination of heterocyclic SCC which have a sterically-hindered chemical structure such as dibenzothiophene (DBT), benzothiophene (BT) and 4, 6-dimethyldibenzothiophene (4,6-DMDBT) is still a major challenge. Moreover, it also operates in harsh conditions which eventually decrease the quality of fuel oil production. Furthermore, the cost of hydrogen gas, heat supply and catalyst are expensive and not economy feasible. In lieu of the disadvantages of HDS technology, some of the alternative methods are now rapidly being discovered, including adsorptive desulfurization, biodesulfurization, extractive desulfurization, oxidative desulfurization, distillative desulfurization and precipitative desulfurization [11]. Among the mentioned approaches, extractive and oxidative desulfurization shows a promising substitute for HDS as it operates in low temperature and ambient pressure. Extraction requires solvent that can partition SCC from the fuel oil, while oxidation converts SCC into its oxidized form to increase the extraction capacity [11],[12]. Because of the absence of energy-extensive process and easy to separate procedure, the capital cost of this non-conventional method can be minimized, providing a cost-effective pathway to clean fuel. Integrating these two methods with the help of catalysis system will enhance the performance of SCC removal, providing an innovative approach for environment-benign desulfurization.

Deep Eutectic Solvent As Eco-Friendly Extractant

Most researchers use conventional organic solvents such as dimethylformamide, acetonitrile and formic acid to extract SCC from fuel oil [13],[14]. Due to the high volatility of organic solvents which is problematic while handling, ionic liquids was introduced which composed of cation and anion moeities. Although it has a lower vapor pressure and promising desulfurizing capability, the synthesis procedure is complex and the chemicals are expensive. A new generation of ionic liquid – deep eutectic solvent (DES) which consists of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) could be a proper choice as it is easy to synthesize, widely available and cheaper starting materials and biodegradable [15]. Many researchers utilize DES in separation and purification application such as carbon dioxide capture [16], bioactive compounds isolation [17],[18] and water osmosis [19]. A few findings on sulfur removal from fuel oil using DES was also published elsewhere [1],[16],[20]–[23].

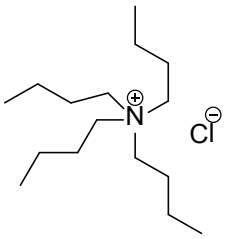
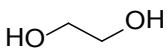
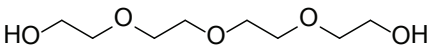
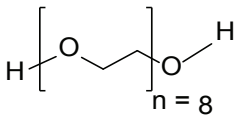
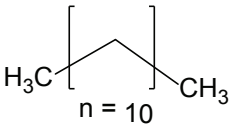
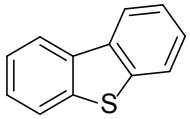
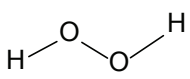
In recent times, glycol-based DES had caught attention on the potential as extractant for extractive desulfurization. Choline chloride:glycerol was used as solvent to desulfurize fuel oil in a photo-oxidative reaction using $Cu\text{-}Fe/TiO_2$ as photocatalyst with desulfurizing performance of almost 97.06% [1]. Besides that, a series of glycol-based DES were synthesized using several tetrabutylammonium salts for dibenzothiophene (DBT) removal from oil [24]. As high as 85% of DBT could be removed when tetrabutylammonium chloride:poly(ethylene glycol) (TBAC:PEG) used as extractor. Moreover,

tetrabutylammonium chloride:ethylene glycol (TBAC:EG) was utilized to remove sulfur from model oil and 99.5% of extraction efficiencies was reported [25]. Inspired by the performance of DES by previous literatures, 4 glycols namely glycerol, ethylene glycol, tetraethylene glycol and poly(ethylene glycol) 400 and TBAC as salt will be mixed in different mole ratios to synthesize glycol-based DES. The synthesized DES and individual glycols will we screened for the extraction capability through integrated extractive and catalytic-oxidative desulfurization (ECODS) system using hydrogen peroxide as oxidant and graphene oxide as catalyst. Graphene oxide serve as the catalyst surface which allows the oxidation of DBT to take place. It should be expected that an interdependent influence of HBA and HBD could be a major driven for the sulfur extraction in oil. Moreover, it is predicted that lengthy molecular chain of HBD can interact with more sulfur species resulting an increase in desulfurization performance.

METHODOLOGY

The methodology descriptions are divided into two parts. The first part is the synthesis of glycol-based DES, while the second part is the desulfurization experiment. The chemicals used along the experiment can be referred in Table 2.

Table 2 List of chemicals used in the experiment

Name	Abbreviation	Chemical structure	Purity (%)	Supplier
Tetrabutylammonium chloride	TBAC		95	Acros
Ethylene glycol	EG		99.5	Merck
Tetraethylene glycol	TEG		98	Merck
Poly(ethylene glycol) 400	PEG		-	Sigma Aldrich
n-dodecane	DOD		99%	Acros
Dibenzothiophene	DBT		-	Merck
Hydrogen peroxide (30%)	H_2O_2		-	Merck
Graphene oxide dispersed in water (2 mg/mL)	GO	-	-	Sigma

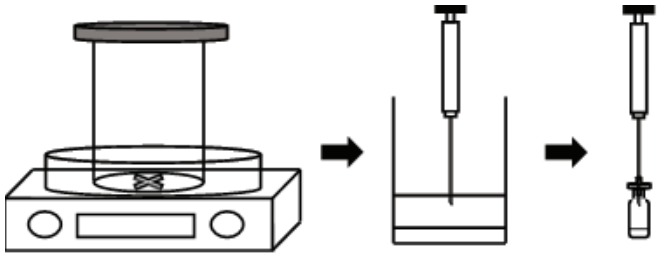


Figure 1 The schematic procedure of sulfur extraction. For each finished desulfurization experiment, a syringe is used to collect the model oil on the bottom layer of the mixture. The model oil is then transferred into capped vial for sulfur analysis. Reprinted with permission from [26]. Copyright 2020 Elsevier

The preparation of glycol-based DES was carried out by mixing the TBAC salt and glycolic HBD (glycerol, ethylene glycol, tetraethylene glycol and poly(ethylene glycol)) in mole ratio of 1:1 to 1:4 for 1 hour at a fixed temperature of 50°C with stirring speed of 500 rpm. To test the desulfurization ability, batches of ECODS was utilized where model oil (100 ppm DBT), solvent, oxidant (hydrogen peroxide, *n*(O): 3) and catalyst (graphene oxide, 1/25) were mixed together in a glass reactor at constant stirring speed and temperature as shown in Figure 1. Sample of model oil was analyzed via gas chromatography with sulfur chemiluminescence as the detector.

The desulfurization efficiency was calculated based on the following Equation 1,

$$Desulfurization\ efficiency\ (\%) = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

where C_i and C_f are the initial and final concentrations of DBT, respectively.

RESULT AND DISCUSSION

TBAC:GLY, TBAC:EG, TBAC:TEG and TBAC:PEG were prepared with mole ratios of 1:1 to 1:4. The appearance of all DES were clearly homogenous liquid when left to room temperature except for glycerol and ethylene glycol with mole ratio of 1:1 to 1:2. Table 3 shows the appearance of each synthesized DES. The formation of DES began as heat being applied to melt the HBA and HBD. As chloride anion and hydrogen atom bonded to the electronegative oxygen in the HBD, hydrogen bond was formed which eventually enhanced the complexation of the HBA to form molten mixture [27].

Solvent screening was then performed to assess the ability of DES to remove SCC from model oil. The screening was conducted together with the pure component to see the effect of HBA towards desulfurization efficiency. As can be seen from Figure 2, the trend of desulfurization performance for pure component was GLY < EG < TEG < PEG. It can be referred that as the ethoxy chain of the HBD increases,

Table 3 Physical appearance of synthesized DES

HBD	HBA to HBD Ratio	Appearance
Glycerol (GLY)	1:1	Solid
	1:2	Translucent slimy liquid
	1:3	Clear liquid
	1:4	
Ethylene glycol (EG)	1:1	Solid
	1:2	Translucent slimy liquid
	1:3	Clear liquid
	1:4	
Tetraethylene glycol (TEG)	1:1 – 1:4	Clear liquid
Poly(ethylene glycol) 400 (PEG)	1:1 – 1:4	Clear liquid

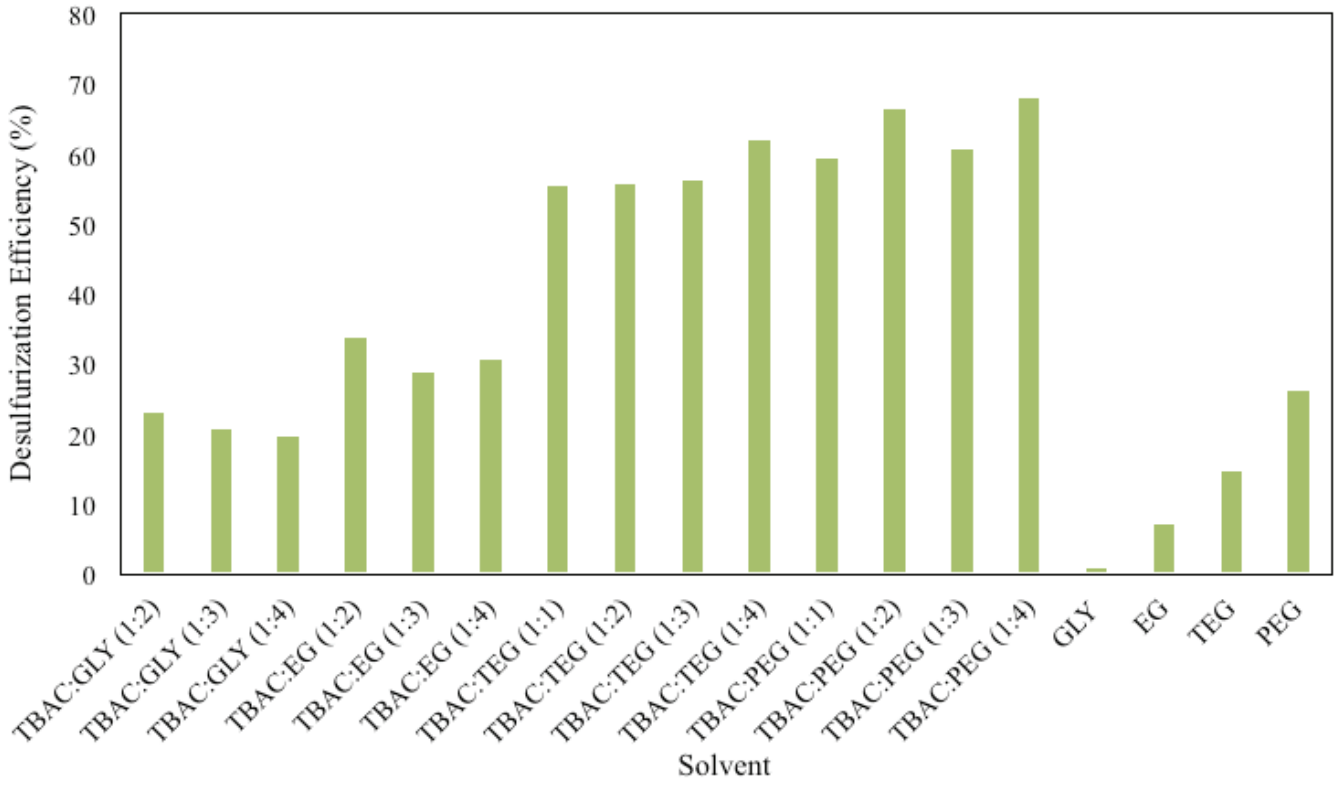


Figure 2 Solvent screening for ECODS performance. Temperature: 25°C, oxidant ratio: 3, catalyst ratio (Graphene oxide 2 mg/mL in H_2O): 1/25, time: 1 h, solvent to model oil ratio: 1:5, speed: 300 rpm, model oil: 100 ppm DBT

more DBT can be extracted into the extractant phase. This trend was also the same when each HBD bonded with TBAC to form DES (TBAC:GLY < TBAC:EG < TBAC:TEG < TBAC:PEG). Surprisingly, the efficiency of the desulfurization capacity increases when using synthesized DES. The role of the TBAC as HBA has a significant effect on the extraction of DBT due to its longer alkyl chain of ammonium salt [24].

Besides, the interaction of sulfur is mainly driven by the presence of TBAC salt which is verified by molecular dynamics simulations [28]. On the other hand, the HBD helps to reduce the melting point of the DES mixture. By comparing the mole ratio of each synthesized DES, it was noted that the high DBT can be extracted as low as 1:2 mole ratio. As HBD increases, the efficiency decreases in TBAC:GLY and TBAC:EG. This shows that TBAC itself play an important role in SCC removal. In the case of TBAC:TEG and TBAC:PEG, the desulfurization efficiency was 55.47% and 66.24% at mole ratio of 1:2 respectively. A slight increase of desulfurization percentage was observed at mole ratio of 1:4. However, when considering economical value, the mole ratio of 1:2 was chosen to minimize chemical consumption. By looking at TBAC:PEG, when the ratio of PEG was increased, the dominant factor was now perceived by the PEG itself as higher ethoxy chain of HBD enhances the desulfurization capability.

The extraction process of DBT into DES is visualized in Figure 3. The model oil and DES were mixed to begin the extraction process. The DBT from *n*-dodecane was extracted to the DES layer via solvent polarity. The interaction of aromatic DBT with DES is one of the driving forces for the removal process [3]. Some of the DBT will be converted to its oxidized form which is dibenzothiophene sulfone ($DBTO_2$). The oxidation process was initiated by the hydrogen peroxide as oxidant and it was further catalyzed by graphene oxide. The graphene oxide also serves as the surface support to allow the rapid adsorption and oxidation of DBT. Oxidized DBT is more easily extracted to the DES layer compared to the unoxidized species, leaving less DBT in the oil phase.

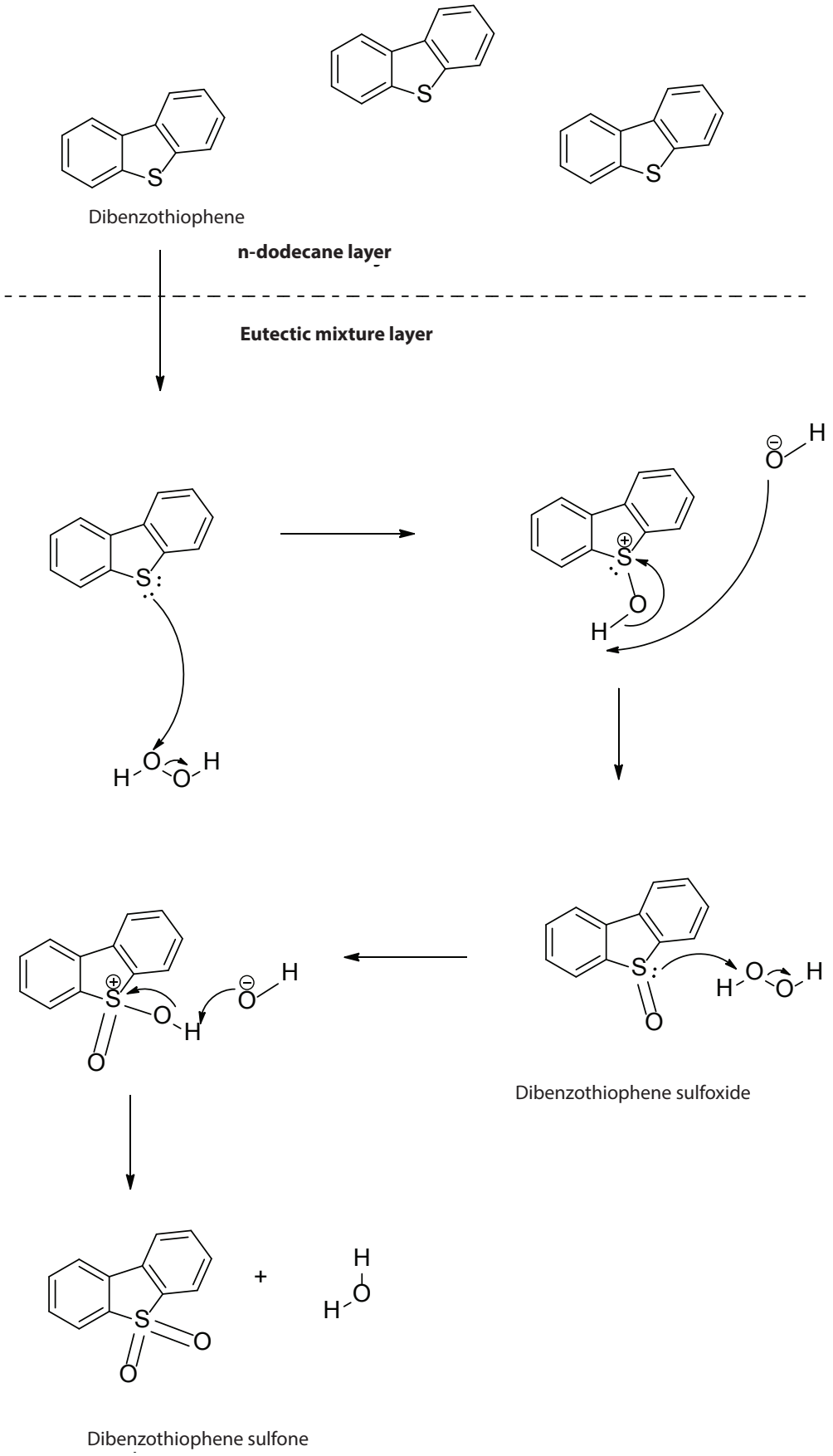


Figure 3 The proposed process of DBT extraction

CONCLUSION

Four glycol-based DESs were synthesized at low temperature and short period of time with a mole ratio from 1:1 to 1:4. The ability to form eutectic mixture was influenced by the ethoxy chain of the HBD. Long ethoxy chain provide more sites for complexation which simultaneously enhance the hydrogen bonding. When DES used as solvent, the performance of SCC removal was higher compared with using HBD alone. TBAC:PEG shows an excellent desulfurization performance due to its longer ethoxy chain. It can be concluded that utilizing DES as alternative solvent for fuel oil desulfurization provide a future direction on the potential of ECODS to produce ultra-low sulfur fuel oil.

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REFERENCES

[1] H. F. Mohd Zaid, F. K. Chong, & M. I. Abdul Mutalib, "Photooxidative-extractive deep desulfurization of diesel using Cu-Fe/TiO_2 and eutectic ionic liquid," *Fuel*, 156, pp. 54–62, 2015.

[2] F. R. Moghadam, S. Azizian, E. Kianpour, M. Yarie, M. Bayat, & M. A. Zolfigol, "Green fuel through green route by using a task-specific and neutral phosphonium ionic liquid: A joint experimental and theoretical study," *Chem. Eng. J.*, 309, pp. 480–488, 2017.

[3] C. Li et al., "Extraction desulfurization of fuels with 'metal ions' based deep eutectic solvents (MDESs)," *Green Chem.*, 18, 13, pp. 3789–3795, 2016.

[4] M. F. Majid, H. F. Mohd Zaid, C. F. Kait, K. Jumbri, L. C. Yuan, & S. Rajasuriyan, "Futuristic advance and perspective of deep eutectic solvent for extractive desulfurization of fuel oil: A review," *Journal of Molecular Liquids*, 2020.

[5] R. Shafi & G. J. Hutchings, "Hydrodesulfurization of hindered dibenzothiophenes: an overview," *Catal. Today*, 59, 3, pp. 423–442, 2000.

[6] S. Brunet, D. Mey, G. Pérot, C. Bouchy, & F. Diehl, "On the hydrodesulfurization of FCC gasoline: A review," *Appl. Catal. A Gen.*, 278, 2, pp. 143–172, 2005.

[7] R. Prins, M. Egorova, A. Röthlisberger, Y. Zhao, N. Sivasankar, & P. Kukula, "Mechanisms of hydrodesulfurization and hydrodenitrogenation," in *Catalysis Today*, 111, 1–2, pp. 84–93, 2006.

[8] X. Chen et al., "Extractive Desulfurization and Denitrogenation of Fuels Using Functional Acidic Ionic Liquids," *Sep. Purif. Technol.*, 133, pp. 187–193, 2014.

[9] M. Ja'fari, S. L. Ebrahimi, & M. R. Khosravi-Nikou, "Ultrasound-assisted oxidative desulfurization and denitrogenation of liquid hydrocarbon fuels: A critical review," *Ultrason. Sonochem.*, 40, pp. 955–968, 2018.

[10] P. Wu et al., "Graphene-like boron nitride anchored BrÖnsted acid ionic liquids as metal-free catalyst for advanced oxidation process," *Mol. Catal.*, 436, pp. 53–59, 2017.

[11] M. N. Hossain, H. C. Park, & H. S. Choi, "A comprehensive review on catalytic oxidative desulfurization of liquid fuel oil," *Catalysts*, 9, 3, p. 229, 2019.

[12] A. W. Bhutto, R. Abro, S. Gao, T. Abbas, X. Chen, & G. Yu, "Oxidative desulfurization of fuel oils using ionic liquids: A review," *J. Taiwan Inst. Chem. Eng.*, 62, pp. 84–97, 2016.

[13] W. N. A. W. Mokhtar, W. A. W. A. Bakar, R. Ali, & A. A. A. Kadir, "Optimization of extractive desulfurization of Malaysian diesel fuel using response surface methodology/Box-Behnken design," *J. Ind. Eng. Chem.*, 30, pp. 274–280, 2015.

[14] X. Zeng, X. Xiao, Y. Li, J. Chen, & H. Wang, "Deep desulfurization of liquid fuels with molecular oxygen through graphene photocatalytic oxidation," *Appl. Catal. B Environ.*, 209, pp. 98–109, 2017.

[15] W. Jiang et al., "Biodegradable choline-like deep eutectic solvents for extractive desulfurization of fuel," *Chem. Eng. Process. Process Intensif.*, 115, pp. 34–38, 2017.

[16] S. E. E. Warrag, C. J. Peters, & M. C. Kroon, "Deep eutectic solvents for highly efficient separations in oil and gas industries," *Curr. Opin. Green Sustain. Chem.*, 5, pp. 55–60, 2017.

[17] A. Paiva, R. Craveiro, I. M. Aroso, M. Martins, R. L. Reis, & A. R. C. Duarte, "Natural Deep Eutectic Solvents - Solvents for the 21st Century," *ACS Sustain. Chem. Eng.*, pp. 1–9, 2014.

[18] Y. Liu, J. B. Friesen, J. B. McAlpine, D. C. Lankin, S.-N. Chen, & G. F. Pauli, "Natural Deep Eutectic Solvents: Properties, Applications, and Perspectives," *J. Nat. Prod.*, 81, pp. 679–690, 2018.

[19] A. Mahto et al., "Sustainable Water Reclamation from Different Feed Streams by Forward Osmosis Process Using Deep Eutectic Solvents as Reusable Draw Solution," *Ind. Eng. Chem. Res.*, 56, 49, pp. 14623–14632, 2017.

[20] W. Jiang et al., "Synthesis of Ionic-Liquid-Based Deep Eutectic Solvents for Extractive Desulfurization of Fuel," *Energy and Fuels*, 30, 10, pp. 8164–8170, 2016.

[21] L. Hao et al., "L-proline-based deep eutectic solvents (DESs) for deep catalytic oxidative desulfurization (ODS) of diesel," *J. Hazard. Mater.*, 339, pp. 216–222, 2017.

[22] K. H. Almashjary, M. Khalid, S. Dharaskar, P. Jagadish, R. Walvekar, & T. C. S. M. Gupta, "Optimisation of extractive desulfurization using Choline Chloride-based deep eutectic solvents," *Fuel*, 234, pp. 1388–1400, 2018.

[23] A. K. Dwamena, "Recent advances in hydrophobic deep eutectic solvents for extraction," *Separations*, 6, 1, pp. 1–15, 2019.

[24] F. Lima, J. Gouvenaux, L. C. Branco, A. J. D. Silvestre, & I. M. Marrucho, "Towards a sulfur clean fuel: Deep extraction of thiophene and dibenzothiophene using polyethylene glycol-based deep eutectic solvents," *Fuel*, 234, pp. 414–421, 2018.

[25] C. Shu & T. Sun, "Extractive desulfurisation of gasoline with tetrabutyl ammonium chloride-based deep eutectic solvents," *Sep. Sci. Technol.*, 51, 8, pp. 1336–1343, 2016.

[26] M. F. Majid, H. F. Mohd Zaid, C. F. Kait, N. A. Ghani, & N. Saidon, "Physical properties of dihydric Alcohol-based deep eutectic solvent for integrated fuel oil desulfurization," in *Materials Today: Proceedings*, 2020, 29, pp. 68–74, November 2018.

[27] Q. Zhang, K. De Oliveira Vigier, S. Royer, & F. Jérôme, "Deep eutectic solvents: Syntheses, properties and applications," *Chem. Soc. Rev.*, 41, 21, pp. 7108–7146, 2012.

[28] D. Shah, D. Gapeyenko, A. Urakpayev, & M. Torkmahalleh, "Molecular dynamics simulations on extractive desulfurization of fuels by tetrabutylammonium chloride based Deep Eutectic Solvents," *Journal of Molecular Liquids*, 274, pp. 254–260, 2019.