

Choline-based Deep Eutectic Solvent for Extractive Oxidative Desulfurization of Model Oil

Theaveraj Ravi^{1,2}, *Asiah Nusaibah Masri*^{1,2,3*}, and *Izni Mariah Ibrahim*^{1,2,3}

¹UTM-MPRC Institute For Oil & Gas (IFOG), Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

²Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

³Energy Management Group, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

Abstract. One of the hardest processes encountered by petroleum refining is sulfur elimination from fuel oil. There are many traditional methods executed but they caused drawbacks such as poor selectivity of sulfur compounds and toxic raw materials. Extractive oxidative desulfurization (EODS) caught the interest of researchers due to high selectivity of sulfur compounds and great desulfurization. Currently, researchers are investigating the use of ionic liquids (ILs) as green extractant, unfortunately they are expensive. This research is proposing and comparing the use of cheap biodegradable solvents called deep eutectic solvents (DESs), as extractants in removing sulfur from fuel oil. The DESs are synthesized through a combination of choline chloride - orcinol and choline chloride - ethylene glycol, and their structure is confirmed through FTIR. Their thermal properties are characterized by DSC and TGA. Their desulfurization performance is evaluated by type of DESs, different ratios of DES and model oil, different ratios of oxidant and sulfone and various temperatures which these factors are found to influence the result. The optimum conditions are found to be at 1:1 for DES and model oil ratio, 4 for O/S ratio and temperature at 85 °C with the extraction efficiency of 99.98%. In conclusion, this DES has high potential to be the cheap green alternative to the conventional extractant for extractive oxidative desulfurization process.

1 Introduction

The elimination of sulfur compounds from fuel oil is the hardest process encountered by petroleum refining. When sulfur compounds in fuel oils like petrol and diesel undergo a combustion process, they react with oxygen in the air to form sulfur oxide (SO_x) gases. Sulfur compounds formed by reactions with oxygen in the air may cause a variety of health and environmental issues [1]. For instance, combines with vapor to produce acid rain and smog that affects building erosion, changes the pH of water in sea, and disrupts sea creatures [2].

* Corresponding author: nusaibah@utm.my

To put it another way, sulfur dioxide in the form of acid rain has everlasting effects for environmental stability. Crude petroleum refineries, industrial boilers, smelting industries, vehicles, volcanism, and power generation by coal power plants are all important sources of SO₂. Sulfur is found in fuel in a variety of forms, including thiophene, sulfides, sulfones and disulfides [3].

Bio-desulfurization (BDS), adsorptive desulfurization (ADS), hydrodesulfurization (HDS), extractive desulfurization (EDS), and oxidative desulfurization (ODS) are among the conventional and non-conventional sulfur removal methods currently being investigated [4]. In comparison to BDS, HDS, and ADS, EDS might be operated at mild conditions if an appropriate extractant was used to desulfurize the fuel oil [5]. BDS, HDS and ADS have various drawbacks such as costly raw material, require high temperature and pressure and poor selectivity of S-compounds. EDS and ODS have various advantages such as requiring low pressure and temperature, cheap raw materials and eliminating major sulfur compounds. However, these two technologies have some drawbacks including absence of oxidants for EDS and catalyst is required for ODS [6]. In order to overcome these drawbacks, integrating EDS into ODS which is called extractive oxidative desulfurization (EODS) is introduced. Benefits of EODS include higher sulfur efficiencies, eliminating all types of organosulfur compounds and catalyst is not required for deep desulfurization [2]. Even yet, choosing an extractant might be difficult because some traditional solvents are extremely flammable and volatile. Desulfurization performance could be considerably enhanced by using DESs in EODS [7].

Besides, EDS has also been used to investigate a number of other methods for removing sulfur from fuel oil. Researchers are interested in using ionic liquids (ILs) in the desulfurization process as they are known to be a designer solvent where their properties can be tuned through the correct formulation [8]. However, ILs have a number of significant disadvantages, including their high cost, difficulty in synthesis, high viscosity and in certain circumstances, toxicity and related biodegradability concerns [9]. Deep eutectic solvents (DESs), also called as greener solvents, can be used to solve the issue of environmental impacts caused by the use of these ILs. Deep eutectic solvents (DESs), which have several favorable properties equivalent to ILs, are made up of a hydrogen-bond acceptor (HBA) and hydrogen-bond donor (HBD) that produce a eutectic mixture [2]. DESs have a variety of benefits, including ease of synthesis and cheap cost, easy biodegradation, non-toxicity, and readily available raw materials [10].

Furthermore, there are two mechanisms by which DESs and sulfur atoms interact in EODS process, including the benzene ring from hydrogen bond acceptor (HBA) and the ring surrounding the sulfur atom [11]. Firstly, the strong interaction between DESs and sulfur atoms weakens the aromatic structure of the sulfur atom, making it vulnerable to oxidation. Secondly, sulfur atoms and metal ions can compound together [12]. Due to the reaction between metal ions and H₂O₂, sulfur will be oxidised to sulfones utilising H₂O₂. The next catalytic cycle, which results in a constant elimination of sulfur from the model, may be started by the peroxide oxidising the reduced acid in the DESs [13]. A major aspect that affects EODS is also the acidity of the DESs since more sulfur extraction results from stronger DES acidity. This was supported using the 5,5-dimethyl-1-pyrroline-1-oxide electron paramagnetic resonance spin-trap approach [14]. Additionally, it should be noted that sulfones have a higher tendency to dissolve in DES due to its bigger polarity than non-oxidized sulfur [15].

The objectives of this research are to synthesize and characterize deep eutectic solvents (DESs) as extractants for extractive oxidative desulfurization (EODS) application and to evaluate the performances of DESs as extractant. Scope and condition of the experiment includes to find out the characterization of deep eutectic solvents (DESs) using FTIR (Fourier Transformation Infrared Spectroscopy), TGA (Thermogravimetric analysis), DSC

(Differential Scanning Calorimetry), density meter and refractometer. Besides, UV-visible spectroscopy is used to find the efficiency of sulfur in fuel oil. Scope and condition of the experiment also includes model oil consisting of *n*-dodecane (model oil), thiophene (model sulfur) and oxidant as hydrogen peroxide (30wt %).

2 Experimental

2.1 Materials

Choline chloride ($C_5H_{14}ClNO$, Acros Organics, 99 %); ethylene glycol ($C_2H_6O_2$, QreC, 99 %) and orcinol ($C_7H_8O_2$, QreC, 99 %) are used for the synthesis of Deep Eutectic Solvents (DESs). Thiophene (C_4H_4S , Sigma-Aldrich, 99 %) and *n*-dodecane ($C_{12}H_{26}$, RCI Labscan, 99 %) are used for the synthesis of model oil. Hydrogen peroxide (H_2O_2 , Sigma-Aldrich, 30 %) are used as an oxidant in oxidative desulfurization.

2.2 Synthesis and Characterization of Deep Eutectic Solvents (DESs)

2.2.1 Synthesis of Deep Eutectic Solvents (DESs)

DESs will be created by combining the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) at the proper temperature. The first method involves melting low melting point components first, adding high melting point components subsequently, and then melting the mixtures together. These DESs contain choline chloride (ChCl) as HBA and orcinol and ethylene glycol (EG) as HBDs, mixed with a ratio of 1:2. The melting point for ChCl is 302 °C and the melting point for orcinol and EG is 109 °C and -12.9 °C respectively. Since orcinol and EG have a lower melting point, it has to be melted initially and ChCl is added, and the mixtures are mutually melted. The first DESs containing ChCl as HBA is mixed with orcinol as HBD at 80 °C for 4 hours while the second DESs containing ChCl as HBA is mixed with EG as HBD at 25 °C for 4 hours.

2.2.2 Characterization of Deep Eutectic Solvents (DESs)

- Fourier Transformation Infrared Spectroscopy (FTIR)

With a four-time scanning repetition and a wavenumber range of 450–4000 nm, a Perkin Elmer FTIR spectrometer was used to measure the carbon samples' FTIR prior to and following the treatment. Both DESs were analysed under the same conditions. In this case, ChCl - orcinol and ChCl - EG will be the DESs analysed in FTIR analysis.

- Thermogravimetric analysis (TGA)

One approach of characterizing DES is thermogravimetric analysis, which measures the weight change that occurs when a sample is heated steadily to a higher temperature in order to ascertain the amount of volatile components and the thermal stability of the material. Both DESs are used to analyse in TGA analysis. The temperature range used in this analysis is from 50 °C to 700 °C whereas the heating rate is used at 10 °C/min.

- Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter analysis is used as one of the characterizations of DES to determine its melting point (T_m). The DSC Mettler-Toledo model SC822 was used to determine the melting point of DES. Approximately 15 mg of samples were weighed in a pan before exposed to flowing liquid nitrogen. The heating range was set from -50 °C to 150 °C for ChCl - orcinol and -50 °C to 80 °C for ChCl - EG at a heating/cooling rate of 10 °C/min.

Four heating cycles have been implemented to the sample, beginning with cooling and ending with heating to remove thermal history.

- Computational characterization of DESs using COSMO-RS

COnductor-like Screening Model for Realistic Solvation (COSMO-RS) is used for the computational study. TmoleX3.1 (Turbomole Version 6.2) quantum mechanics package performed the structural optimization of all DESs and thiophene. Then, the geometry optimizations are performed using density functional theory (DFT) approach by employing the Becke-Perdew-86 (BP86) functional through resolution of identity (RI) approximation and a triple- ξ valence polarized basis set (TZVP). The analysis is carried out with the COSMOthermX software Version 2.1, whereby the viscosity and thiophene extraction capability of the DESs are extracted.

2.3 Extractive Oxidative Desulfurization (EODS)

Thiophene was first used as an organosulfur chemical to prepare model oil. The initial content of a 250 ml volumetric flask was filled with dissolved thiophene in n-dodecane, as per the production technique for 30 ppm thiophene model oil. A flask with a round bottom will be filled with a few millilitres of model oil. To conduct the extraction process, several millilitres of DES will be introduced to the model oil and stirred. A suitable volume of upper oil was removed using a micropipette after 15 minutes in order to assess the effectiveness of extractive desulfurization. A single neck flask containing the above-prepared DES would typically be filled with multiple portions of 30% hydrogen peroxide, and the mixture would then be stirred on a hot plate. Then, the upper model oil sample will then be analysed to calculate the sulfur efficiency.

During the period of this research, DESs were used in a comprehensive effort to optimize the EODS process. The experimental design involved four key factors, beginning with the evaluation of two DES options in two initial experiments. Desulfurization efficiency was measured as the primary variable, providing valuable insights into the performance of each DES which consisting of glycol-based DES (ChCl - EG) and aromatic based DES (ChCl - orcinol). Following this initial assessment, one DES was selected for further optimization, forming the basis for the second phase of the study. The optimization process encompassed three factors consisting of different ratios of DES and model oil, different ratios of oxidant and sulfone and various temperatures. This study included 15 experiments for the optimization phase after the first 2 experiments for the DES comparison. The primary variable, desulfurization efficiency, was measured in each experiment, resulting in a total of 17 data points across the entire study.

2.4 Sulfur Content Analysis

High-performance UV-Visible spectroscopy (1200 Series, Agilent Technologies) is used to analyse the efficiency of sulfur removal from the model fuel. Using an external standard approach, the UV-vis wavelength is set at 200 nm to 700 nm to determine the sulfur concentration. Initially, calibration curve will be obtained by using different concentrations of sulfur in accordance with the ISO 8466-1 standard. Extraction efficiency (EE) is calculated using Equation (1):

$$\text{Extraction Efficiency \% (EE \%)} = \frac{s_i - s_f}{s_i} \times 100 \% \quad (1)$$

where s_i and s_f are the initial and final concentration of sulfur, accordingly.

3 Results and Discussion

3.1 Characterization of Deep Eutectic Solvents (DESs)

3.1.1 Fourier Transformation Infrared Spectroscopy (FTIR)

The structural changes on the carbon surface were first identified after a thorough investigation was performed to identify the functional groups of DES as functionalizing agents. Consequently, FTIR spectra were examined for each of the two DESs (ChCl - EG and ChCl - orcinol). Each DES is a mixture of two or more components, and its spectrum was interpreted using the recognizable and well-known peaks of those components. Fig. 1 shows the FTIR spectra for DES (ChCl - orcinol) whereas Fig. 2 shows the FTIR spectra for DES (ChCl - EG).

Based on Fig. 1, only four of the functional groups that existed in this DES contained ChCl and orcinol. C = C was the most common group found in all orcinol-based DESs. The remaining two peaks, on the other hand, were found in trace amounts in this DES which are of O-H and C-N bonds from ChCl and orcinol source. Thus, the functional groups that present in ChCl - orcinol are mainly alcohol, amine and alkene as refer to Fig. 1.

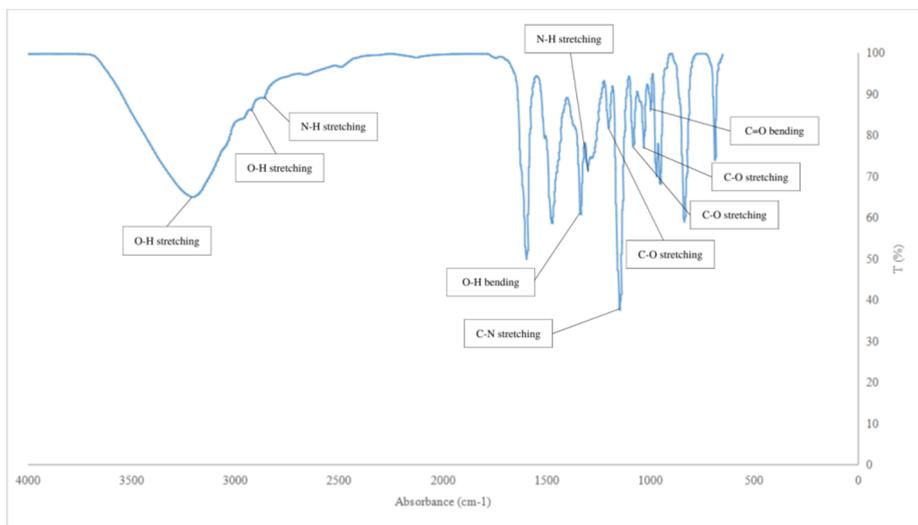


Fig. 1. FTIR spectra for DES (ChCl - Orcinol).

Based on Fig. 2, there are also four functional groups that exist in this DES containing ChCl and EG. The two peaks were found in trace amounts in DES (ChCl - EG) which are of O-H and C-N bonds. Thus, the functional groups that present in ChCl - EG are mainly alcohol and amine as refer to Fig. 2. This summarizes that both types of DES contain the same functional groups which are O-H and C-N bonds. ChCl - orcinol has C = C bond due to the aromatic structure of orcinol whereas ChCl - EG does not have C = C bond.

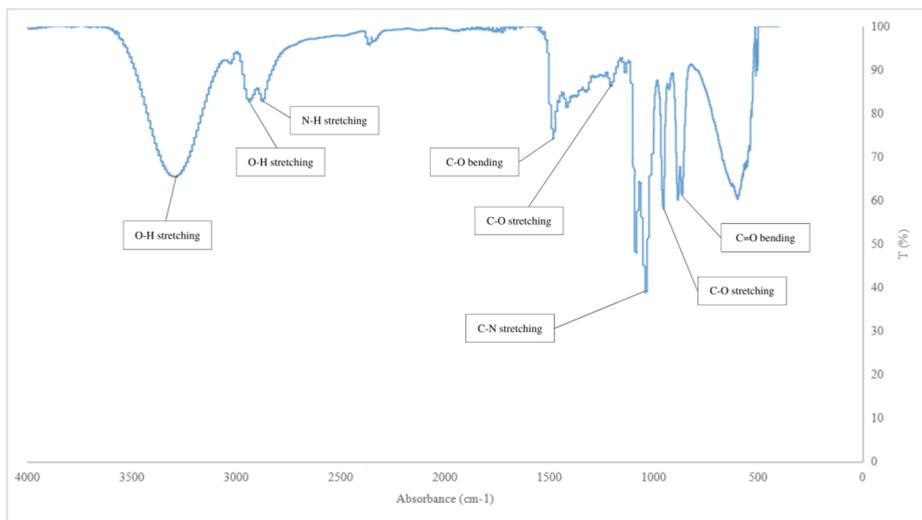
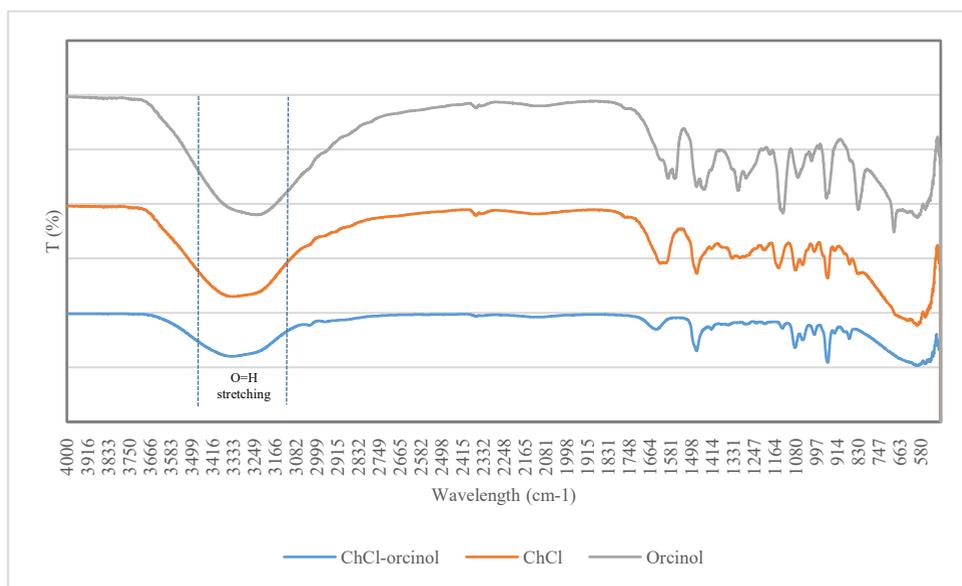
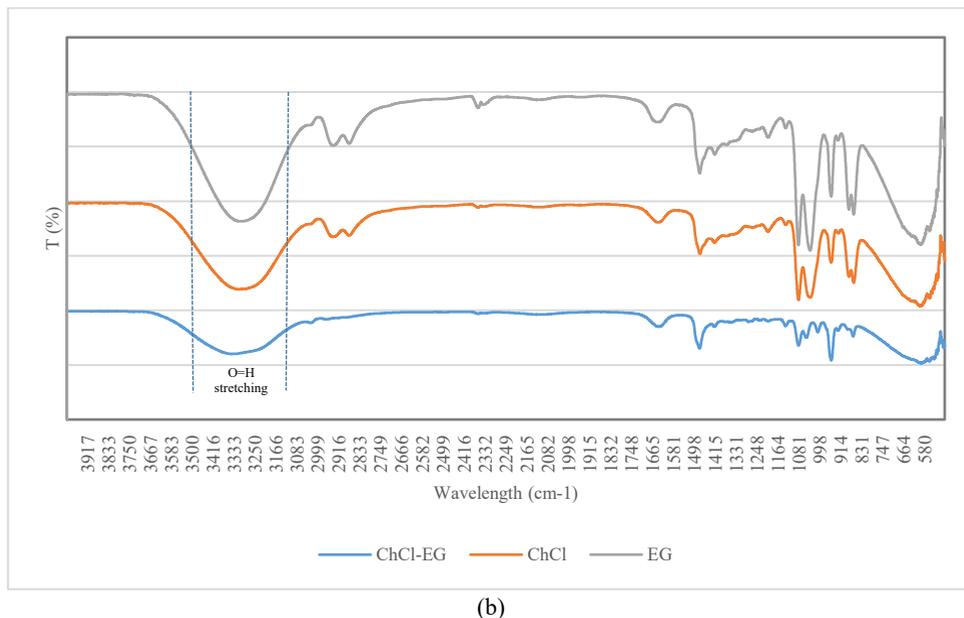


Fig. 2. FTIR spectra for DES (ChCl - EG).

The Fourier Transform Infrared (FTIR) analysis of DES and its individual components, ChCl (choline chloride), EG (ethylene glycol), and orcinol were conducted as illustrated in Fig. 3. It reveals distinct peaks indicative of functional groups and hydrogen bond interactions within the DES matrix. The observed shifts and intensities of specific bands in the FTIR spectra offer valuable insights into the nature and strength of hydrogen bonding among ChCl, EG, and orcinol, playing a pivotal role in the enhanced extractive oxidative desulfurization performance of the DES system.



(a)



(b)

Fig. 3. FTIR spectra of DES and individual components of (a) ChCl - orcinol and (b) ChCl – EG.

For instance, in the O-H stretching region, typically occurring between 3200 and 3700 cm^{-1} in Fourier Transform Infrared (FTIR) spectra, the presence and characteristics of hydrogen bonding can be elucidated [5]. Hydroxyl groups (O-H) exhibit stretching vibrations in this region, and the extent of hydrogen bonding can influence the intensity and shape of these peaks. A distinctive feature of hydrogen bonding is the broadening and reduction in peak intensity observed in the FTIR spectra. Based on Fig. 1 to Fig. 3, the O-H stretching region of both DES exhibits a lower peak intensity (higher transmittance, T %) compared to the spectra of individual components which includes choline chloride (ChCl), ethylene glycol (EG), and orcinol. This decrease in peak intensity suggests the formation of hydrogen bonds within the DES matrix. The higher peak intensity in the O-H stretching region of the individual components indicates stronger O-H stretching vibrations in the absence of hydrogen bonding. Majid et al. has provided valuable insights into this finding; he discussed that he found the decrease in O-H peak intensity for the formation of TBAC - EG based DESs which confirms the formation of DES through hydrogen bonding [16]. Fig. 4 shows the intermolecular interactions of synthesized DES. This observation supports the notion that hydrogen bonding plays a crucial role in the molecular interactions within the DES, influencing its potential application in EODS process.

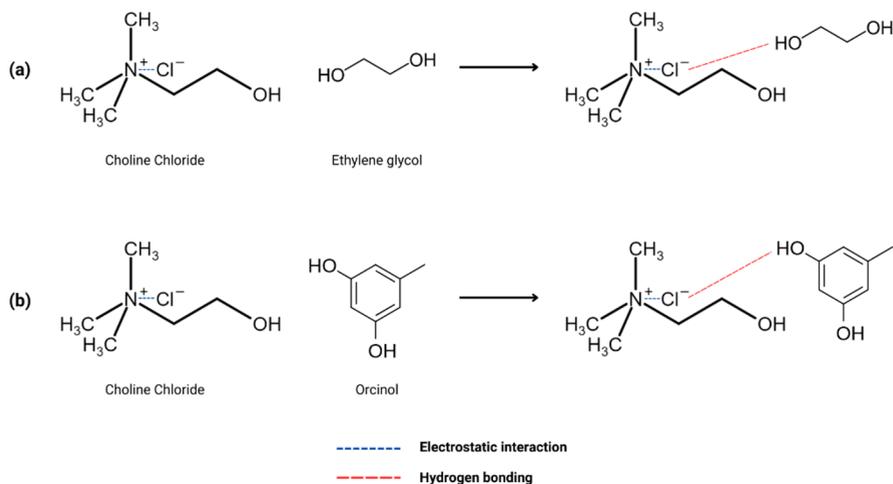


Fig. 4. Intermolecular interactions of synthesized of (a) ChCl – EG and (b) ChCl – orcinol.

3.1.2 Thermogravimetric analysis (TGA)

Fig. 5 shows the dynamic TGA curves with a heating of 10 °C/min on DES (ChCl - orcinol) whereas Fig. 6 shows the dynamic TGA curves with a heating of 10 °C/min on DES (ChCl - EG). It summarizes the value of T_{max} which is the decomposition temperature of both DES. One of the most notable characteristics of deep eutectic solvents is their melting and decomposition temperatures, particularly when considering their potential use as substitute solvents. These characteristics establish the temperature range within which a DES can retain its liquid state and, in turn, its range of use.

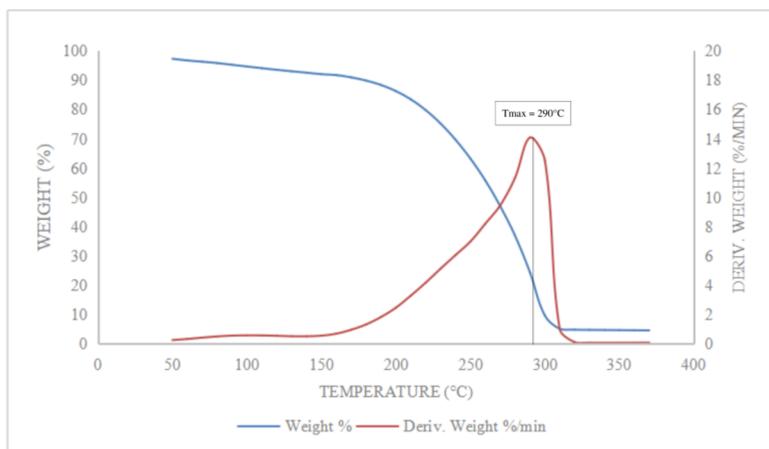


Fig. 5. Dynamic TGA curves with a heating of 10 °C/min on DES (ChCl - orcinol).

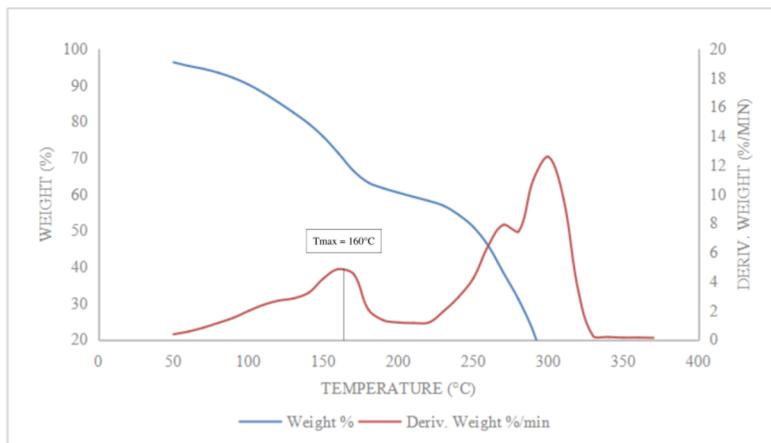


Fig. 6. Dynamic TGA curves with a heating of 10 °C/min on DES (ChCl - EG).

In Fig. 5, the T_{max} value of the DES obtained is 290 °C. In Fig. 6, the T_{max} value of the DES obtained is 160 °C. Since the decomposition temperatures of both DES is high, it is a very stable solvent. This is because the stability of a substance increases when its decomposition temperature increases. Additionally, this DES can be used at high temperature. This may decrease the limitation of the DES towards more applications.

Furthermore, weight loss analysis is made for both ChCl - EG and ChCl - orcinol. Almost no weight loss was observed for both DES until 50 °C. At a range from 50 °C to 150 °C, there is a small weight loss of 5 % was observed for ChCl - orcinol, followed by around 20 % for ChCl - EG. The weight loss decrease drastically for both DES only after around 150 °C. These analysis indicate that the investigated DESs are relatively stable up to upper temperature of current study (150 °C), suggesting that these DESs could be used for desulfurization process at low reaction temperature without degrading DES.

3.1.3 Differential Scanning Calorimetry (DSC)

The synthesis of DES led to the creation of a eutectic point, which is the point at which a combination melts below the melting point of its pure elements. To determine the eutectic point, the phase transitions of DES were thermally characterized at ChCl - orcinol and ChCl - EG via DSC. Fig. 7 shows the heating curve of ChCl - orcinol whereas Fig. 8 shows the heating curve of ChCl - EG.

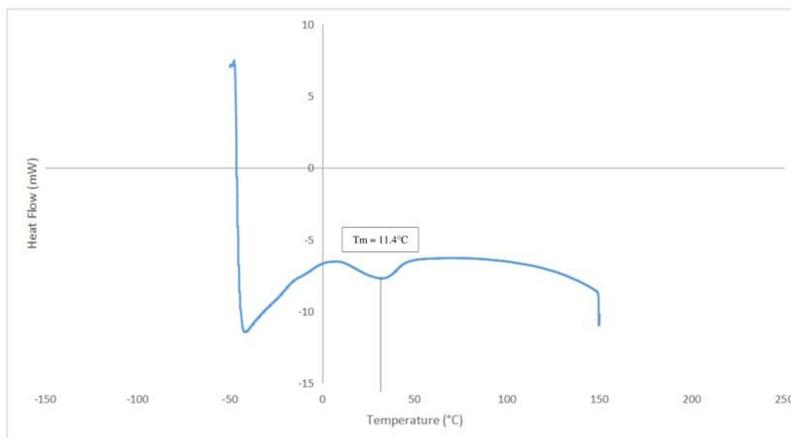


Fig. 7. Heating curve of ChCl – orcinol.

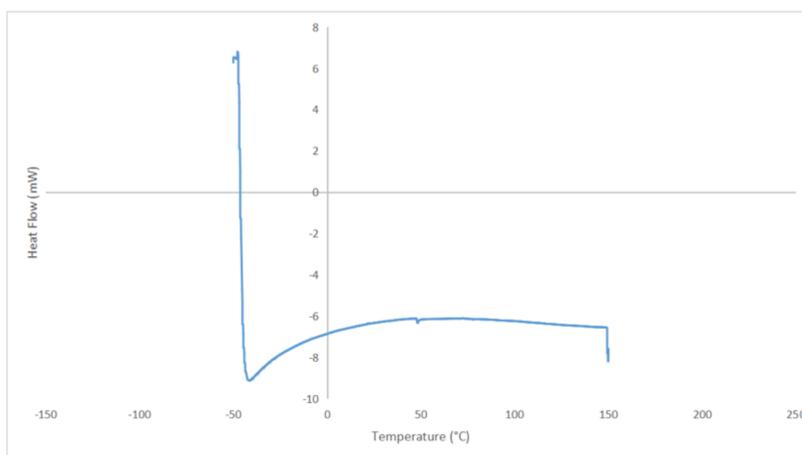


Fig. 8. Heating curve of ChCl – EG.

Based on Fig. 7, a distinctive endothermic was observed for ChCl - orcinol, which corresponds to melting temperature (T_m). One of the important characteristics of DES that we were primarily interested in studying here was the melting point depression. As anticipated, DES (ChCl – orcinol) showed a drop in melting point. The DES obtained a melting point of 11.4 °C which represents the eutectic point of this DES. This eutectic point is proved by the melting point of the individual components. ChCl has a melting point of 302 °C whereas orcinol has a melting point of 109 °C. Based on Fig. 8, there is no distinctive endothermic observed for ChCl - EG. This might be because it could be less than 50 °C. This is proven by literature which uses ChCl - EG as the DES. The melting point T_m is found to be at around -55 °C [17]. This eutectic point is also proved by the melting point of the individual components. ChCl has a melting point of 302 °C whereas EG has a melting point of -12.9 °C. As a result, this summarizes that the eutectic point of both DES is below than of its respective melting points.

3.1.4 Computational Capacity and Viscosity of DESs

COSMO-RS is used for the computational study to find out the capacity, hydrogen bonding and the viscosity of the DESs. As shown in Table 1, the computational capacity of ChCl - EG is slightly higher compared to ChCl - orcinol indicating ChCl - EG has slightly higher desulfurization rate than ChCl - orcinol. Viscosity plays a crucial role at this point where ChCl - EG is less viscous than ChCl - EG which is the reason to promote desulfurization rate. Decreasing the viscosity of DES by adding other low viscous solvents might be an effective method to promote desulfurization efficiency. Fig. 9 demonstrates 3D and surface model using COSMO-RS of both DESs.

Table 1. Computational capacity, hydrogen bonding energy and viscosity of DESs.

DES	Capacity	Hydrogen Bonding Energy (kcal/mol)	Viscosity (cP)
ChCl - orcinol	0.8679	-30.5577	1.099×10^{12}
ChCl - EG	0.8712	-14.4362	5.893×10^6

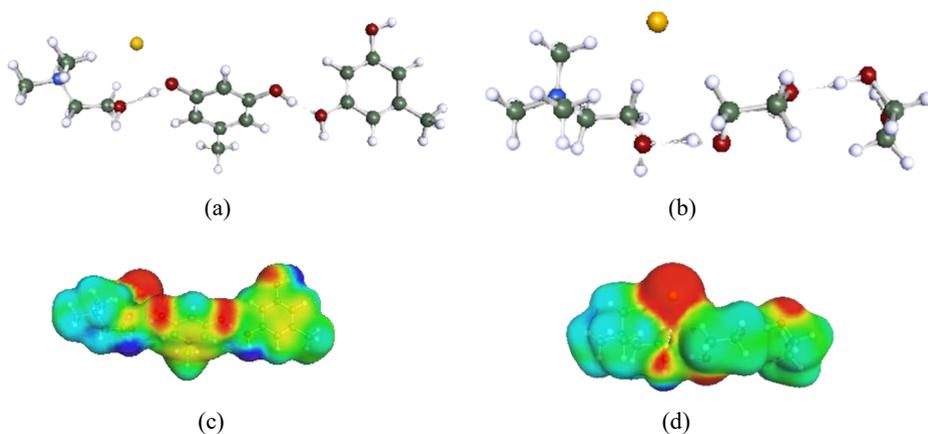
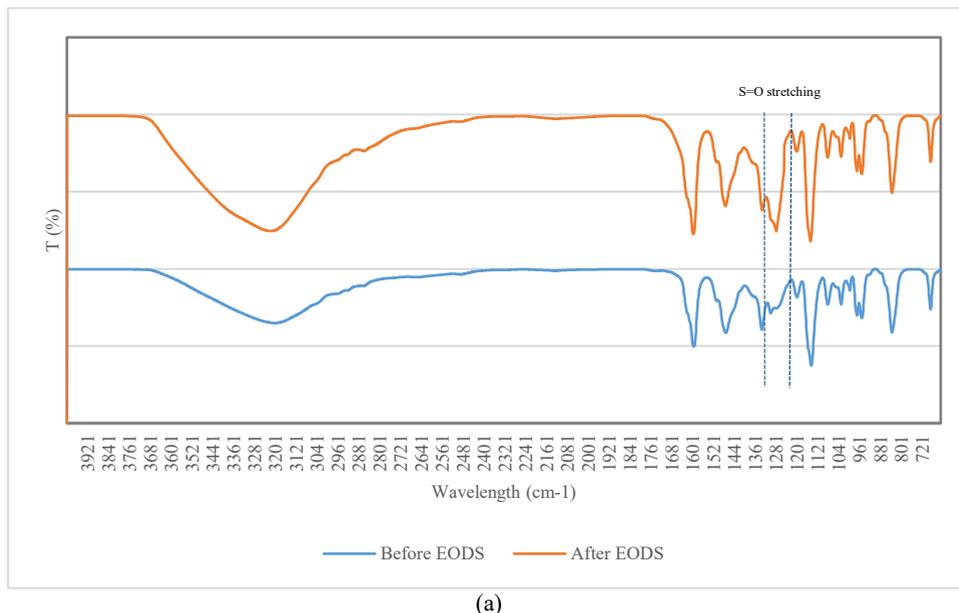
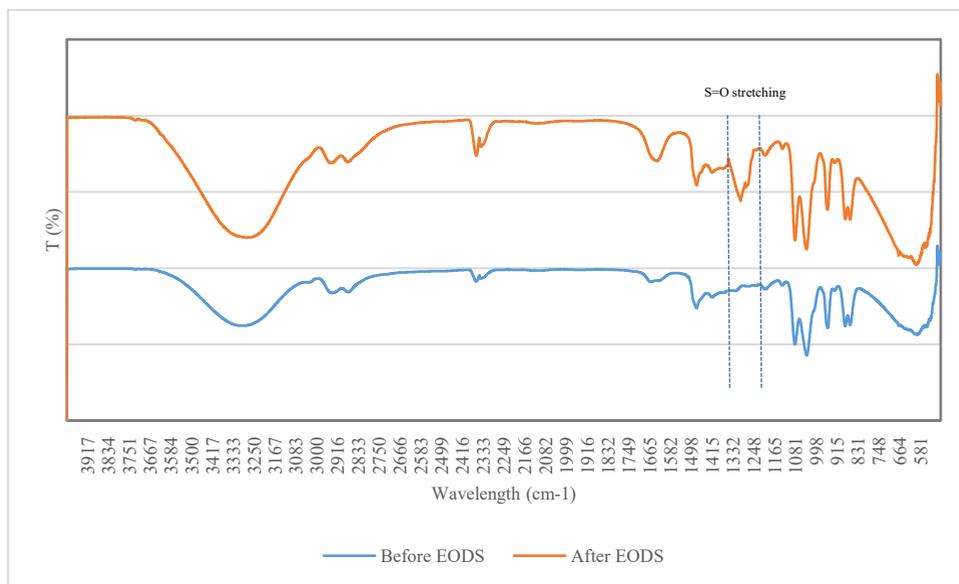


Fig. 9. 3D and surface model using COSMO-RS of (a,c) ChCl - orcinol and (b,d) ChCl - EG.

Furthermore, the FTIR spectra presented in Fig. 10 depict the outcomes of the EODS process applied to both DESs. A comparative analysis of the spectra before and after the EODS treatment reveals notable changes, particularly in the range associated with S = O stretching vibrations. Notably, no significant peaks were observed prior to EODS within the wavelength range of approximately 1250 to 1350 cm^{-1} [5]. After the EODS process, there are some peaks in the range of S = O stretching confirming that DESs have extracted thiophene dioxide from model oil. The observed shifts in the S = O stretching region lend support to the occurrence of oxidative desulfurization. This spectral evidence underscores the transformative impact of EODS on the molecular structure of the DESs, affirming its potential as a viable method for sulfur removal.



(a)



(b)

Fig. 10. FTIR spectra of DESs before and after EODS process. (a) ChCl - orcinol and (b) ChCl – EG.

Hydrogen peroxide is a powerful oxidizing agent that can react with sulfur compounds including thiophene in the feedstock. As in Fig. 15, oxidizing thiophene with hydrogen peroxide involves a chemical reaction where oxygen atoms from hydrogen peroxide replace some hydrogen atoms in the thiophene molecule [15]. This process results in the formation of thiophene oxide, and further oxidation leads to thiophene dioxide. The addition of oxygen increases the polarity of the thiophene ring, making the molecules more reactive and polar [9]. Thiophene oxide and dioxide have different properties compared to the original thiophene due to the presence of oxygen atoms, which can be important in various applications in chemistry and biology [15].

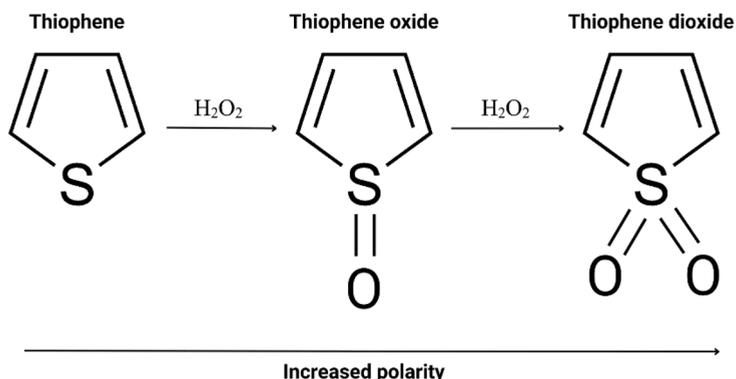


Fig. 15. Oxidation process of thiophene.

3.2 Extractive Oxidative Desulfurization (EODS) process

This experiment has been carried out using different parameters which are types of DES, different ratios of DES and model oil, different ratios of oxidant and sulfone and different temperatures. The extraction efficiencies will be analysed by UV-vis spectroscopy. Before that, a calibration curve needs to be plotted using different sulfur concentrations (10 ppm, 15 ppm, 20 ppm, 25 ppm, 30 ppm) using UV-vis spectroscopy. Using linear regression, in accordance with the ISO 8466-1 standard, the average (of 5 calibration curves) regression parameters obtained are presented in Fig. 11 [18].

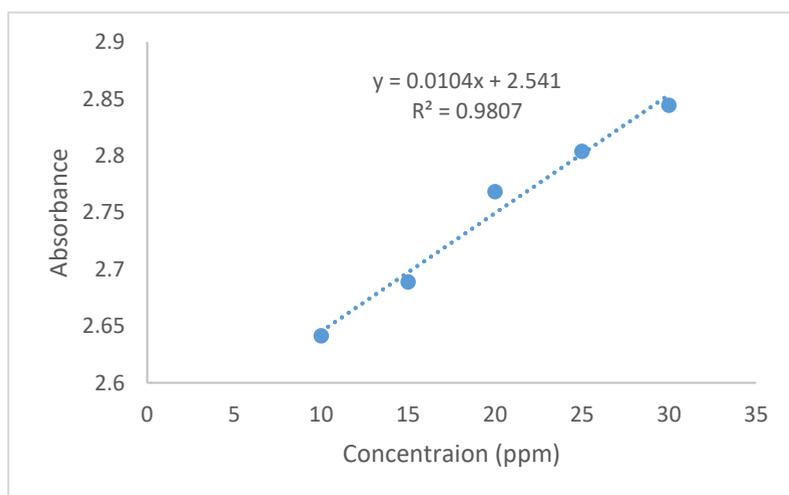


Fig. 11. Calibration curve of sulfur concentration in model oil.

3.2.1 Types of Deep Eutectic Solvents (DESs)

In this experiment, both DESs (ChCl - orcinol and ChCl - EG) are analysed and compared with its desulfurization efficiencies. ChCl - orcinol is categorized as aromatic based DES and

ChCl - EG is categorized as glycol based DES. Fig. 12 shows desulfurization efficiencies of both DESs.

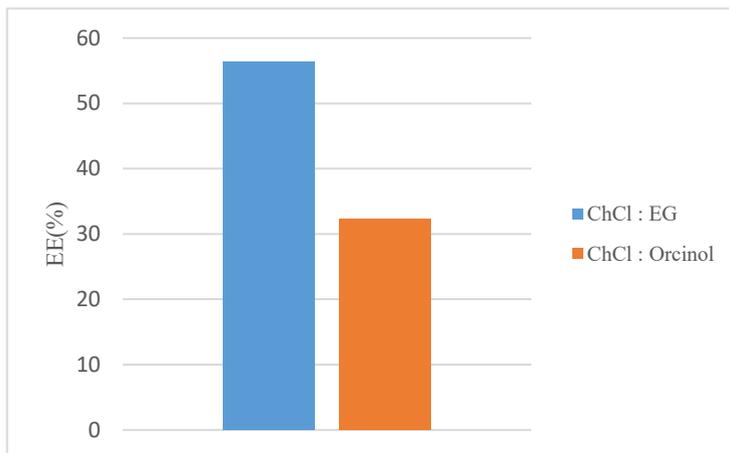


Fig. 12. Extraction efficiencies (EE %) of DESs (ChCl - EG and ChCl - orcinol).

Based on Fig. 12, DES (ChCl - EG) has higher desulfurization efficiencies which is 56.33 % compared to DES (ChCl - orcinol) which is 32.33 %. The lower performance of ChCl - orcinol is because of the ability to form hydrogen bonding by aromatic compounds as compared to aliphatic compounds [19]. In this case, EG is an aliphatic compound whereas orcinol is an aromatic compound. As per literature, it is stated that the hydrogen bonding capability or Brønsted acid character of aliphatic hydroxyl group is more than that of aromatic hydroxyl group. DES with high hydrogen bonding capability will easily create a bond with sulfur compound and extract it from oil phase to DES phase [19]. Besides that, this finding can be further explained by the influence of viscosity of the DESs in the EODS process. The viscosity of ChCl - orcinol and ChCl - EG are reported to be 195cP and 36cP, respectively [20]. The lower viscosity of ChCl - EG as compared to ChCl - orcinol promotes the desulfurization process by facilitating the dispersion of the DES inside the model oil, thus giving higher tendency of possible collision and extraction of sulfur by the DES [21]. Thus, it is proven that EG has more hydrogen bond capability and high desulfurization efficiency than orcinol. DES (ChCl - EG) is selected and will proceed to be further optimized.

As per literature, the desulfurization efficiency of EDS process using the same DES (ChCl - EG) on removing thiophene from fuel oil ranges from 15 % to 40 % using different DES : fuel oil ratios [21]. Since the highest EE of EDS can get up to 40 %, it still has lower desulfurization efficiency than EODS process. As we compare the extraction efficiency (EE) of DES (ChCl - EG) in EODS process to EDS process, it is proven that EODS has more sulfur removal efficiencies than EDS.

Oxidative desulfurization enhances extractive desulfurization by converting thiophene compounds into more polar forms. As a result, thiophene dioxide becomes more soluble in the DES, improving the efficiency of the extraction process and facilitating the removal of thiophene from model oil [10]. In ChCl-EG and ChCl-orcinol, thiophene dioxide likely interacts with the choline chloride component through Lewis acidic sites. The chloride ions in choline chloride coordinate with thiophene dioxide, aiding in their extraction. Meanwhile, the EG and orcinol portion contributes through hydrogen bonding interactions, enhancing the solubility of sulfur-containing compounds in the DES [19]. The specific sulfur-DES interactions involve a combination of Lewis acid-base interactions and hydrogen bonding, contributing to the effectiveness of extractive oxidative desulfurization.

3.2.2 DES and model oil volume ratio

The second parameter to analyse the desulfurization efficiency is DES and volume oil volume ratios. In this research, the volume ratios of DES to model oil that have been investigated are 1:5, 2:5, 3:5, 4:5 and 5:5. Fig. 13 shows the desulfurization efficiencies of DES (ChCl : EG) on different volume ratios of DES and model oil.

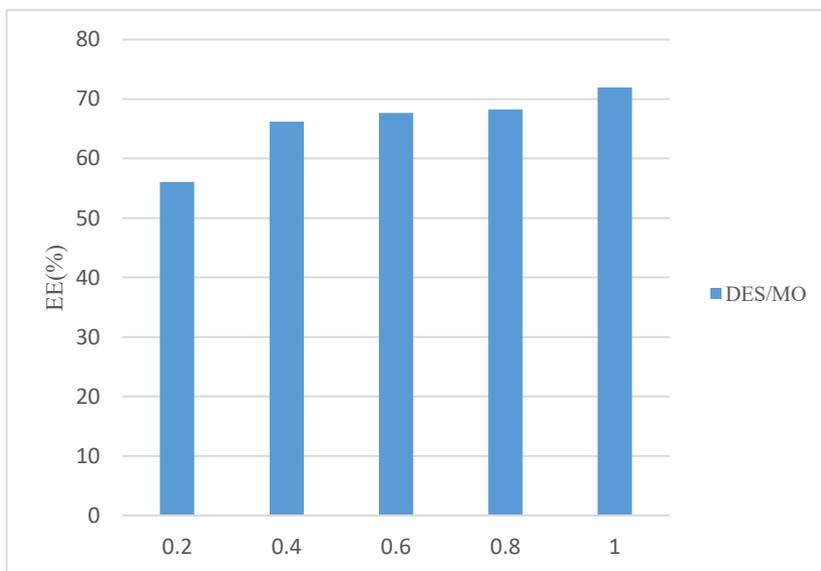


Fig. 13. Extraction efficiencies (EE %) of DES (ChCl - EG) on different volume ratios of DES and model oil.

Based on Fig. 13, by increasing the volume ratio of DESs to model oil, the desulfurization performance will increase. At a volume ratio of 1 : 5 between DES and model oil, the sulfur removal of thiophene was only 56.05 %. The desulfurization efficiency increase to 66.18 % and 67.64 %, respectively, for 2 : 5 and 3 : 5 volume ratios. Because more DES could aid in extracting more T from the upper phase and oxidizing it in the lower phase, that was the rationale. The efficiency of desulfurization rise to 71.92 % when the volume ratio of DES to model oil is increased to 5 : 5. This happened as a result of the ability of more DES to produce extractive active sites that could target S atoms. Therefore, the best appropriate condition for this experiment is a 5 : 5 ratio.

As per literature, by using TBAB and PEG-200 as DES, the desulfurization performance also increases as the ratio of DES towards model oil increases. This happened as a result of the ability of more DES to produce extractive active sites that could target S atoms. However, in the brief period of 15 minutes, the force of hydrogen bonding was unable to entirely remove all DBT from the oil phase. As a result, numerous researchers used multi-stage extraction or extraction combined with oxidation to accomplish desulfurization, and they produced excellent results [21]. Thus, it has the same trend as Fig. 13 as when the volume ratios of DES and model oil increases, the desulfurization efficiency also increases.

3.2.3 Oxidant and sulfone volume ratio

The third parameter to analyse the desulfurization efficiency is volume ratios of oxidant and sulfone. In this research, the volume ratios of oxidant to sulfone that have been investigated

are 1:1, 2:1, 3:1, 4:1 and 5:1. Fig. 14 shows the desulfurization efficiencies of DES (ChCl : EG) on different oxidant and sulfone volume ratios.

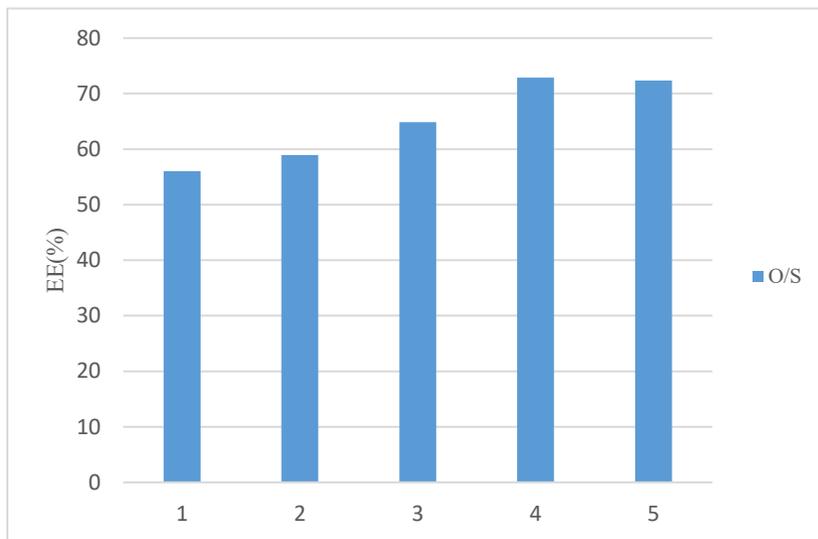


Fig. 14. Extraction efficiencies (EE %) of DES (ChCl - EG) on different volume ratios of oxidant and sulfone.

Based on Fig. 14, by increasing the volume ratios of oxidant to model oil, the desulfurization performance will increase until it achieves a certain volume ratio. The sulfur removal of thiophene was only 56.03 % when the O/S volume ratio was 1. This is because the H_2O_2 addition was not enough to oxidize too much thiophene to thiophene dioxide, and the force of desulfurization was mainly extracted by the hydrogen bonding between the DES and the S atoms in thiophene. As the O/S volume ratio increases to 4, the desulfurization efficiency reaches 72.85 % due to the synergistic effect of sufficient oxidant and the hydrogen bonding force; therefore, thiophene will be removed to achieve deep desulfurization. When the O/S volume ratio increased to 5, the desulfurization rate did not increase significantly. This might have been because the oxidation reaction of thiophene to thiophene dioxide had reached equilibrium. This has been proven from the literature which has the same trend as in Fig. 14. The desulfurization rate did not considerably increase when the O/S molar ratio increased to 10 in the literature that employed TBAB: PEG-200 as the DES. This could have happened as a result of a tiny quantity of water being added by the oxidant, which diluted the DES and weakened the hydrogen bonding interactions between molecules [22]. Because of its higher desulfurization effectiveness, an O/S volume ratio of 4 is chosen as the ideal reaction condition for the subsequent processes.

As per literature, experiments with different O/S molar ratios (2.0, 2.5, 3.5, and 5.0) were employed at 25 °C. According to stoichiometry, 2 mol of hydrogen peroxide is required to oxidize 1 mol dibenzothiophene (DBT) to dibenzothiophene dioxide. Based on the previous research, desulfurization capacity increases with enhancing oxidants. Surprisingly, the sulfur removal of DBT can achieve a maximum at 95 % [23]. Thus, it is proven that the oxidant dosage also plays an important role in affecting the performance of desulfurization. Thus, it has the same trend as Fig. 14 as when the O/S volume ratio increases, the desulfurization efficiency also increases at a certain volume ratio.

3.2.4 Temperature

The fourth parameter to analyse the desulfurization efficiency is temperature. In this research, the temperatures that have been investigated are 25 °C, 40 °C, 55 °C, 70 °C and 85 °C. Fig. 16 shows the desulfurization efficiencies of DES (ChCl - EG) on different temperatures.

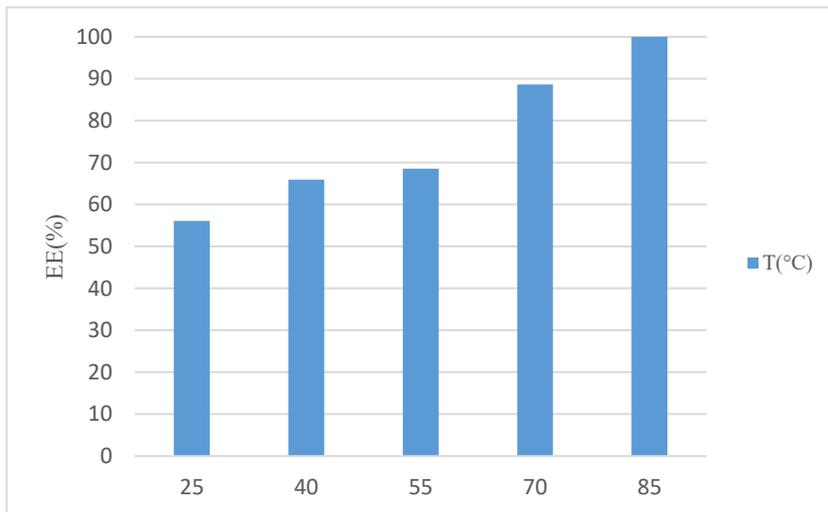


Fig. 16. Extraction efficiencies (EE %) of DES (ChCl - EG) on different temperatures.

Based on Fig. 16, by increasing the temperature, the desulfurization performance will increase. At 25 °C, the desulfurization efficiency is only 56.11 % because at this temperature, the active oxygen components' oxidation capacity was too low to show significant desulfurization efficiency. Another explanation could be that most of the thiophene (T) remained in the upper oil phase because the interaction between the sulfur atoms and hydrogen bonds in T was too weak at comparatively low ambient temperature. When the temperature was raised to 40 °C and 55 °C, the desulfurization efficiencies significantly improved, because only hydrogen bonding was the driving force in the extraction stage. As the temperature is raised to 85 °C, the desulfurization efficiency reaches 99.98 %. During the extractive oxidative reaction, the power of T conversion was derived from the synergistic action of hydrogen bonding and oxidation. Generally, at higher temperature, when the kinetic energy increases, viscosity decreases and mass can be transferred between two immiscible DES and model oil. Moreover, this will increase the possible collision between thiophene in model oil with the DES. Hence, the amount of thiophene extracted increases as temperature increases. Thus, reaction temperature at 85 °C is the most suitable condition in this experiment.

As per literature, a series of experiments at different reaction temperatures (25 °C, 35 °C, and 50 °C) was carried out to investigate the effect of temperature on dibenzothiophene (DBT) removal. The sulfur removal of DBT at 25 °C, 35 °C, and 50 °C increases dramatically to 81.4 %, 93.5 %, and 96.6 %, indicating that 5-SSA/3 FA DES has high catalytic activity in this EODS system. Sulfur removal of DBT can reach up to 99.8 %, suggesting that the desulfurization capacity is at the highest when reaction temperature increases to 50 °C [24]. Thus, it has the same trend as Fig. 16 as when the temperature increases, the desulfurization efficiencies also increase.

4 Conclusion

In conclusion, all the four factors under study that are types of DESs, different ratios of DES and model oil, different ratios of oxidant and sulfone, and temperature will influence the performance of removal of sulfur from model oil. Glycol-based DES has higher efficiency of sulfur removal compared to aromatic-based DES due to their high hydrogen bonding capability. Desulfurization performance is also improved as the volume ratio of DES to model oil rises. When the volume ratio of oxidant to sulfone increases, the sulfur desulfurization also increases. Besides, when the temperature increases, the desulfurization performance also increases. As a result, it's clear that a variety of factors influence the desulfurization process. Besides, the proposed DES is a potential alternative extractant with the benefits of being a cheap biodegradable solvent that improves the EODS process.

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Reference

1. S. Rajasuriyan, H.F. Mohd Zaid, M.F. Majid, R.M. Ramli, K. Jumbri, J.W. Lim, M. Mohamad, P.L. Show, B. Yulianto, *Processes*, **9**(6) 1050 (2021).
2. S. Tahir, U.Y. Qazi, Z. Naseem, N. Tahir, M. Zahid, R. Javaid, I. Shahid, *Fuel*, **305** 121502 (2021).
3. E.L. Smith, A.P. Abbott, and K.S. Ryder, *Chem Rev*, **114**(21) 11060 (2014).
4. P. Makoś, and G. Boczkaj, *J Mol Liq*, **296** 111916 (2019).
5. H. Xu, Y. Kong, J. Peng, X. Song, Y. Liu, Z. Su, B. Li, C. Gao, W. Tian, *Bioresour Technol*, **319** 124209 (2021).
6. Y. Guo, X. Liu, J. Li, B. Hu, *RSC Adv*, **11**(50) 31727 (2021).
7. D. Chandran, M. Khalid, R. Walvekar, N.M. Mubarak, S. Dharaskar, W.Y. Wong, T.C.S.M. Gupta, *J Mol Liq*, **275** 312 (2019).
8. Mohammed, S. A. S., Yahya, W. Z. N., Bustam, M. A., Kibria, M. G., Masri, A. N., & Kamonwel, N. D. M, *J Mol Liq*, **359** 119219 (2022).
9. Sulaimon, A. A., Masri, A. N., Shahpin, M. H. A., Zailani, N. H. Z. O., Baharuddin, S. N. A., Moniruzzaman, M., . . . Saaid, I. M, *J Mol Liq*, **319** 114092 (2020).
10. M.F. Majid, H.F. Mohd Zaid, F.K. Chong, K. Jumbri, C.Y. Lim, S. Rajasuriyan, *J Mol Liq*, **306** 112870 (2020).
11. B. Wang, J. Zhu, H. Ma, *J Hazard Mater*, **164**(1) 256 (2009).
12. W. Liu, W. Jiang, W. Zhu, W. Zhu, H. Li, T. Guo, W. Zhu, H. Li, *J Mol Catal A Chem*, **424** 261 (2016).
13. C.F. Mao, R.X. Zhao, X.P. Li, *Fuel*, **189** 400 (2017).
14. S.A. Dharaskar, K.L. Wasewar, M.N. Varma, D.Z. Shende, *Sep Purif Technol*, **155** 101 (2015).
15. H. Lü, P. Li, C. Deng, W. Ren, S. Wang, P. Liu, H. Zhang, *Chem Comm*, **51**(53) 10703 (2015).
16. Majid, M. F., Zaid, H. F. M., Kait, C. F., Abd Ghani, N., & Jumbri, K, **294** 111588 (2019).
17. M. Hayyan, A. Abo-Hamad, M.A. AlSaadi, M.A. Hashim, *Nanoscale Res Lett*, **10**(1) 1 (2015).
18. Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration

- function (1990), International Organization for Standardization, method ISO 8466-1.
<https://www.iso.org/obp/ui/#iso:std:iso:8466:-1:ed1:v1:en>
19. Y. Nie, X. Gong, H.S. Gao, X.P. Zhang, S.J. Zhang, *Sci China Chem*, **57**(12) 1766 (2014).
 20. H. Qin, M.J. Panzer, *Chem Electro Chem*, **4**(10) 2556 (2017).
 21. W. Jiang, K. Zhu, H. Li, L. Zhu, M. Hua, J. Xiao, C. Wang, Z. Yang, G. Chen, W. Zhu, H. Li, S. Dai, *Chem Eng J*, **394** 124831 (2020).
 22. X. Wang, W. Jiang, W. Zhu, H. Li, S. Yin, Y. Chang, H. Li, *RSC Adv*, **6**(36) 30345 (2016).
 23. N. Jose, S. Sengupta, J. Basu, *Fuel*, **90**(2) 626 (2011).
 24. T.A. Saleh, *Trends Environ Anal Chem*, **25** e00080 (2020).