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Oxidative Extractive Desulfurization System for Fuel Oil Using Acidic Eutectic-Based Ionic Liquid

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Abstract: The biggest challenge faced in oil refineries is the removal of sulfur compounds in fuel oil. The sulfur compounds which are found in fuel oil such as gasoline and diesel, react with oxygen in the atmosphere to produce sulfur oxide (SO_x) gases when combusted. These sulfur compounds produced from the reaction with oxygen in the atmosphere may result in various health problems and environmental effects. Hydrodesulfurization (HDS) is the conventional process used to remove sulfur compounds from fuel oil. However, the high operating conditions required for this process and its inefficiency in removing the organosulfur compounds turn to be the major drawbacks of this system. Researchers have also studied several alternatives to remove sulfur from fuel oil. The use of ionic liquids (ILs) has also drawn the interest of researchers to incorporate them in the desulfurization process. The environmental effects resulting from the use of these ILs can be eliminated using eutectic-based ionic liquids (EILs), which are known as greener solvents. In this research, a combination of extractive desulfurization (EDS) and oxidative desulfurization (ODS) using a photocatalyst and EIL was studied. The photocatalyst used is a pre-reported catalyst, Cu-Fe/TiO₂ and the EIL were synthesized by mixing choline chloride (ChCl) with organic acids. The acids used for the EILs were propionic acid (PA) and p-toluenesulfonic acid (TSA). The EILs synthesized were characterized using thermogravimetry analyser (TGA) differential scanning calorimetry (DSC) analysis to determine the physical properties of the EILs. Based on the TGA analysis, ChCl (1): PA (3) obtained the highest thermal stability whereas, as for the DSC analysis, all synthesized EILs have a lower melting point than its pure component. Further evaluation on the best EIL for the desulfurization process was carried out in a photo-reactor under UV light in the presence of Cu-Fe/TiO₂ photocatalyst and hydrogen peroxide (H₂O₂). Once the oxidation and extraction process were completed, the oil phase of the mixture was analyzed using high performance liquid chromatography (HPLC) to measure

the sulfur removal efficiency. In terms of the desulfurization efficiency, the EIL of ChCl (1): TSA (2) showed a removal efficiency of about 99.07%.

Keywords: desulfurization; hydrodesulfurization; eutectic-based ionic liquid; Cu-Fe/TiO₂

1. Introduction

Sulfur is one of the most commonly found impurities in crude oil. In fuel oils, sulfur compounds are undesirable and they tend to cause various problems during refining, as well as during their commercial use [1]. Sulfur compounds that are present can be classified into four main groups which are mercaptans, sulfides, disulfides, and thiophenes [2]. The increasing demand for fuel oil and the depletion of sweet (low sulfur content) crude reservoirs have increased the exploration and drilling of sour (high sulfur content) crude oil [3]. Sulfur is naturally found in crude oil in the form of free elemental sulfur or organosulfur compounds [4,5]. These compounds found in fuel oil can either be acidic or non-acidic by nature [5].

Sulfur, being a component in the fuel oil has been one of the biggest challenges faced by the oil refiners. There are various negative impacts towards the environment and human health caused by the combustion of fuel which emits sulfur oxide (SO_x) gases into the atmosphere. These gases can react with water in the atmosphere to form acid rain and sulfates [6–8]. Acid rain causes various adverse effects such as corrosion of metals, damage of buildings, destroying of paints and coatings, and acidifying of the soil and water, which results in the imbalance of the ecosystem.

Moreover, the emission of sulfur gases into the atmosphere also causes various chronic diseases to human beings such as respiratory problems, heart diseases, and asthma. A high content of sulfur in the atmosphere can also lead to the reduction of wildlife population, birds, mammals, and insects. Corrosion rates of metals and other materials would also be increased due to the presence of sulfur in the air.

Furthermore, according to researchers, a high content of sulfur compounds in fuel oil can be harmful to the environment as these sulfur compounds can prevent the use of catalytic diesel particulate filter to control diesel particulate emissions [9]. Most combustion engines and exhaust-cleaning catalyst used currently are quite sensitive to the presence of sulfur as the sulfur can cause deterioration of the engine and catalyst. Thus, this condition can also lead to the poisoning of catalyst which lowers the efficiency of catalytic converters in automobiles.

In addition, sulfur compounds can also contribute to the formation of engine deposits in diesel fuels [2]. During the process of refining, sulfur compounds tend to deactivate some catalyst used in fuel processing and cause corrosion problems in pumps, pipelines, and other refining equipment [1]. A high content of sulfur in fuel oil results in a high maintenance cost for oil refineries due to a regular wear and tear of steel pipes, storage tanks, pipelines for transportations of fluids, and also other metallic equipment [5].

Upon realizing the various effects of the presence of sulfur in fuel oil towards the human being and the environment, more stringent regulations have been imposed and implemented by mandating the use of fuel with low sulfur content [4]. In the year 2005, according to the European Union, the Euro IV standard was applied, where it specifies a maximum of 50 ppm of sulfur content in diesel [10]. In 2009, the European Union, again, adopted the Euro V standard where the allowable limit for sulfur content in fuel was reduced to 10 ppm for both diesel and gasoline for on-road vehicles, and in 2011, this was also implemented for the non-road vehicles [11]. Burned fuels are expected to have zero sulfur emissions in the near future along with stricter sulfur level requirements.

Gasoline and diesel fuel have been used for decades due to the high energy content and availability. Refineries have been working hard to produce gasoline and diesel that contains a permissible amount of sulfur. Due to the current situation of depleting sweet

crude oil, researchers are now focusing on treating the sour crude oil in order to use them [3]. It is a major operational and economic challenge for the petroleum refineries to fulfil the required low amount of sulfur content in fuel oil [1]. The removal of organic sulfur compounds from fuel has been the challenge since sulfur can only be removed from the organic molecule when a certain chemical bond is broken [9].

The conventional method used in most refineries for the purification of fuels from sulfuric compounds is hydrodesulfurization (HDS) [7]. HDS is highly effective in removing sulfur compounds such as thiols, sulfides, and disulfides [12]. However, it is difficult to remove organic sulfur compounds with steric hindrance on the sulfur such as dibenzothiophene (DBT) and its derivatives, especially, 4,6-dimethyldibenzothiophene (4,6-DMDBT) [6]. There is also some other unconventional method for desulfurization which includes biodesulfurization (BDS), oxidative desulfurization (ODS), and extractive desulfurization (EDS). These methods have become the research focus of many researchers by introducing various solvents, extractants, and catalysts for the desulfurization processes.

The most conventionally used solvents in refining industries involve alcohols, ethers, amines, and other volatile organic compounds (VOC). These solvents are currently facing challenges due to a low extraction ability or the negative impacts towards the environment [7].

Ionic liquids (ILs) have become increasingly popular for various applications in the electrochemical investigations. ILs are highly tuneable and can be designed with a specific task in mind and thus is known as a 'designer solvent' [3]. Most ILs tend to have a disadvantage of high cost as they are relatively expensive especially when applied in bulk conditions [9]. Some of them also tend to have low tolerance towards moisture in addition to still being further assessed to confirm its toxicology on being applicable as a green media. Therefore, refineries are looking for green solvents that do not harm the environment and are also reasonably priced. From this motivation, eutectic-based ionic liquids (EILs) have been developed. This solvent is developed by mixing a salt compound and a complexing agent or a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) until a homogenous mixture is formed [7,13]. EILs contain nonsymmetric ions that have low lattice energy and hence low melting points, as well [14]. EILs are defined as a new class of ILs formed as a result of eutectic mixture of Lewis or Bronsted acids and bases, which may consist of different anionic and/or cationic species [4]. EILs are also known as analogues of ILs that have many similar characteristics and physical properties with different chemical properties.

2. Materials and Methods

2.1. Materials

The main component, choline chloride, ChCl ($\geq 97\%$), propionic acid, PA (99%), *p*-toluenesulfonic acid, TSA (99%) and 5-sulfosalicylic acid, SSA (99%) were purchased from Sigma Aldrich. For the preparation of model oil, *n*-dodecane which was obtained from Merck was mixed with dibenzothiophene, DBT ($\geq 98\%$) and 4,6-dimethyldibenzothiophene, 4-6 DMDBT ($\geq 97\%$) which was obtained from Sigma Aldrich. As for the oxidative extractive desulfurization process, hydrogen peroxide (H_2O_2) (30%) purchased from Sigma Aldrich was used.

2.2. Synthesis of Acidic EIL

EIL was prepared by mixing choline chloride (ChCl) with different types of acid at different volumes based on the molar ratio. The details of the molar ratio used is summarized in Table 1. The choline chloride and alcohols were measured accurately according to the molar ratio and were added into a beaker. The mixture of ChCl and PA was heated at 80 °C for 2 h, whereas the mixture of ChCl and TSA was heated at 100 °C for 3 h with a stirring speed of 400 rpm until a homogenous liquid was achieved.

Table 1. Thermal characteristics of the synthesized acidic EILs.

| EIL | ChCl: HBD (Molar Ratio) | Onset Temperature/ T_{onset} (°C) | Weight Loss at 250 °C (%) | Complete Decomposition Temperature (°C) |
|-----------|----------------------------|--|------------------------------|---|
| ChCl: PA | 1:2 | 28.3 | 58.9 | 312.5 |
| ChCl: PA | 1:3 | 28.0 | 45.3 | - |
| ChCl: TSA | 1:1 | 25.2 | 34.9 | 444.1 |
| ChCl: TSA | 1:2 | 33.9 | 21.1 | - |

2.3. Characterization of EILs

EIL was characterized using the thermogravimetry analyser (TGA) and the differential scanning calorimetry (DCS) analyser to study the physical properties of the types of EILs synthesized. The TGA analysis gives a better understanding on the thermal decomposition of the acidic EILs synthesized in this research. The measurements were performed at temperatures ranging from 0 to 500 °C using the thermogravimetry analyser (Mettler Toledo, Selangor, Malaysia). The physical properties of the EILs were measured three times to ensure the accuracy of the readings. The DSC analysis is used to determine the melting point of the synthesized EIL. This is to ensure that the synthesized EILs fulfil the definition of EIL. The model of the analyser used is DSC822 (Mettler Toledo, Selangor, Malaysia).

2.4. Oxidative Extraction Desulfurization Method

A combination of extraction and catalytic oxidation desulfurization (OEDS) method using the EIL was applied to remove DBT as the sulfur compound from the model oil. This OEDS method was chosen since studies have reported that the combination of the extractive and oxidative method is able to give a high removal of sulfur compounds. OEDS using the synthesized EIL and Cu-Fe/TiO₂ was monitored for 6 h with sampling conducted every 1 h interval to determine the equilibrium of the reaction and the optimum reaction time. The experiment was conducted in a photo-reactor in the presence of H₂O₂ and under visible light from the halogen lamp with a power of 500 W. In addition, 0.01 g of photocatalyst was weighed and added into the model oil. A H₂O₂ to model the oil ratio of 2 was added to the mixture and was stirred well. Photo-oxidation was performed in a photo-reactor placed below a halogen light source. For extraction, the EIL synthesized was added to the oxidised model oil mixture in a certain volume ratio in a beaker. The mixture was stirred for 6 h at 25 °C until the equilibrium between the mixtures was achieved. The phase ratio of EIL to the model oil was 1:5. The samples of the residual sulfur in the model oil was collected every 1 h and was then analyzed using HPLC. HPLC was used to determine the concentration of sulfur species that remained in the *n*-dodecane layer before and after extractive desulfurization. The mobile phase for the column was a mixture of methanol, water, and isopropanol with a ratio of 90:8:2, and a flow rate of 5 mL per sample. The performance of the EIL was determined by calculating the extraction efficiency of sulfur compound in the model oil, using Equation (1).

$$\text{Extraction efficiency (\%)} = \frac{S_{BE} - S_{AE}}{S_{BE}} \times 100\% \quad (1)$$

where S_{BE} is the total concentration of sulfur species before OEDS and S_{AE} is the sulfur species in the model oil after OEDS.

3. Results and Discussion

The results below are prepared to understand the physical characteristics of the acidic EILs that were synthesized and its influence towards desulfurization.

3.1. Characterization of EILs

3.1.1. Thermogravimetry Analysis

To understand the nature of the bonding between ChCl and the acids, the thermal behaviour of the acidic EILs was studied using the thermogravimetry analysis (TGA). It is important to study the thermal stability of the acidic EILs synthesized to avoid the thermal decomposition of the solvent when being used to extract the sulfur compounds [15]. The thermal stability of the HBD has a crucial impact on the maximum operating temperature of the EILs [16]. A comparison on the curves that shows the thermal stability of the synthesized EILs are shown in Figure 1. Whereas, Table 1 shows the onset temperatures, weight loss at 250 °C, and the temperature for complete decomposition of the acidic EILs synthesized.

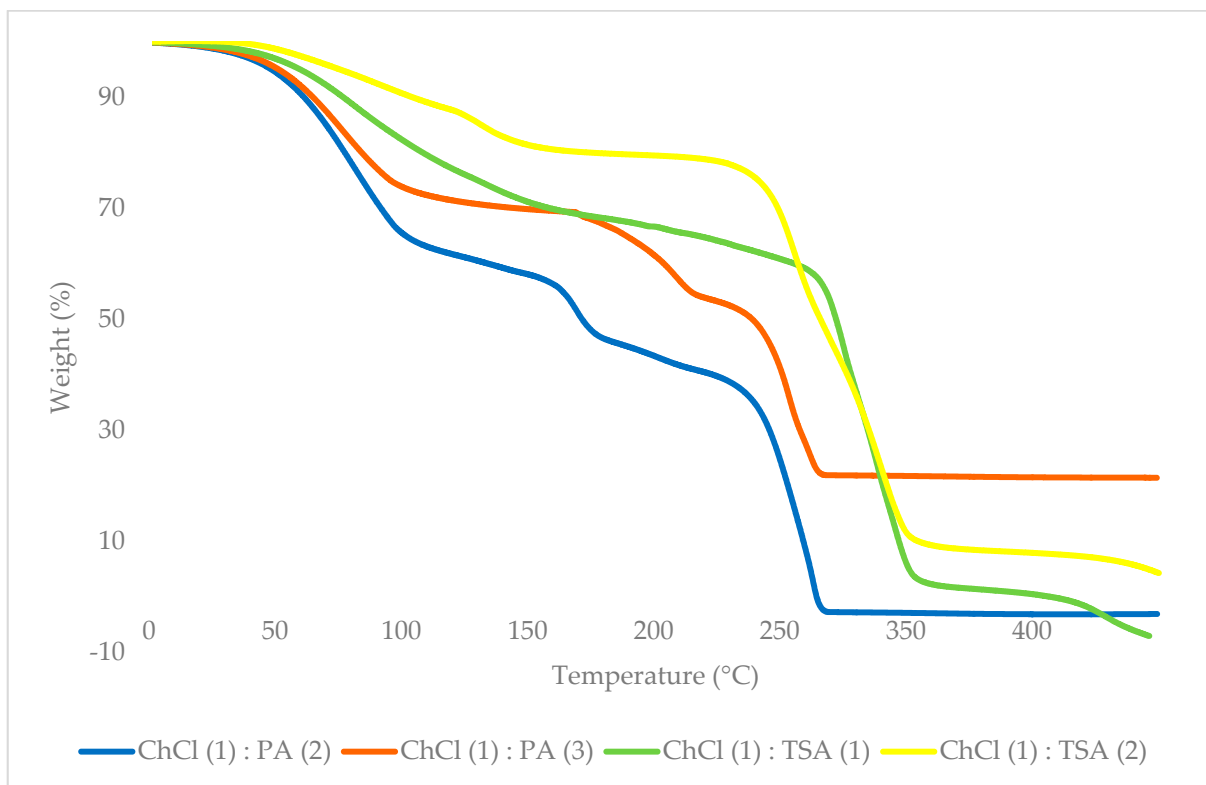


Figure 1. Weight content of EILs as a function of temperature for different types of acidic EILs.

The onset temperature (T_{onset}) is a very important property of an EIL as it determines the maximum temperature at which the EIL can maintain their complete liquid state without decomposing [14]. ChCl (1): TSA (2) has the highest T_{onset} . Thus, this EIL takes the longest time and highest temperature for decomposition to happen compared to the other synthesized EILs. In addition, at the temperature of 250 °C, ChCl (1): PA (2) has the highest weight loss, which is about 58.865%. The lowest weight loss of 21.114% was observed for the EIL of ChCl (1): TSA (2). However, only ChCl (1): PA (2) and ChCl (1): TSA (1) achieved a complete decomposition at 500 °C. As for ChCl (1): PA (3), at 500 °C, the weight loss achieved was 78.523%, followed by ChCl (1): TSA (2) with 95.693% weight loss. The decomposition of the EIL occurs at different steps or stages during the analysis at different temperatures [16]. The first step of mass loss, that occurs before reaching the boiling point of any one component is due to the evaporation of the acid below its boiling point. That explains why the trend gradually decreases during this stage. The second step of mass loss is known to be due to the vaporization of the acid once the boiling point is reached and exceeded. Lastly, the third step of mass loss is due to the decomposition of the salt compound, ChCl at the highest temperature. Therefore, the relative thermal stability

observed is: ChCl (1): PA (3) > ChCl (1): TSA (2) > ChCl (1): TSA (1) > ChCl (1): PA (2). Thus, from these results, it could be inferred that the EILs with a higher amount of acid or the HBD has a better thermal stability compared to the ones with lower amounts. From here, it could be concluded that ChCl (1): PA (3) has the highest thermal stability and thus also has the strongest hydrogen bonds of all the synthesized EILs.

3.1.2. Differential Scanning Calorimetry Analysis

Eutectic based ionic liquids are defined by the fact that the synthesized solvent has a lower melting point compared to both the components that are mixed together in their pure form. Table 2 shows the melting points of the acidic EILs synthesized and their pure components at room temperature.

Table 2. Melting points of components.

| Component | ChCl: HBD (Molar Ratio) | Melting Point (°C) |
|-----------|-------------------------|--------------------|
| ChCl | Pure | 302 |
| PA | Pure | −21 |
| TSA | Pure | 38 |
| ChCl: PA | 1:2 | −23 |
| ChCl: PA | 1:3 | −24 |
| ChCl: TSA | 1:1 | 24 |
| ChCl: TSA | 1:2 | 30 |

According to the results in Table 2, the synthesized EILs have a lower melting point than its pure constituent. This is known as the advantage of using EILs since it can be used at room temperature and atmospheric pressure during the desulfurization method compared to the conventional method of HDS that requires a high operating temperature and pressure [3]. Based on these results, it can be said that the acidic EILs were successfully synthesized as EILs.

3.2. Removal Efficiency of Sulfur Compounds

3.2.1. Effect of Catalyst Dosage

Previous researchers have proven that the amount of catalyst used has a vital effect on the removal of sulfur compounds. Figure 2 shows the effect of different amounts of the catalyst on desulfurization. When no catalyst was used for the process, ChCl (1): PA (2), ChCl (1): PA (3) and ChCl (1): PA (4) resulted in the highest removal efficiency of 79.17%, 84.30%, and 11.29%, respectively. This was caused by the EIL itself which is effective in removing sulfur compounds without the presence of any catalyst. However, for ChCl (1): TSA (1) and ChCl (1): TSA (2), the use of 0.01 g of catalyst resulted in the highest desulfurization of 95.76% and 99.06%, respectively. A high amount of catalyst may result in more active sites for the reaction to take place, thus resulting in a better and higher efficiency. However, further increasing the catalyst dosage to 0.015 and 0.020 g, decreased the efficiency. The reduction in the efficiency might be caused by the overdosing of catalyst, which has a negative influence on the DBT conversion since at a high amount of catalyst, they tend to agglomerate and settle down.

3.2.2. Effect of H₂O₂:DBT Ratio

According to the stoichiometry equation, two moles of H₂O₂ are consumed for every mole of DBT oxidised [17]. Figure 3 shows the data obtained for the amount of sulfur removed from the model oil against the amount of H₂O₂ used. Based on the experiment conducted on four different ratios for the amounts of H₂O₂ against DBT, the ratio of 2:1 achieved the highest desulfurization for all five different types of EILs, followed by 4:1 and 6:1. When no oxidant was present in the process, the desulfurization efficiency was the lowest. Moreover, using a high amount of H₂O₂ reduced the desulfurization efficiency for all the types of EIL. Thus, the optimum ratio of H₂O₂ to DBT was 2:1 since it has the

highest removal efficiency of sulfur compounds. These results satisfy a study performed by researchers, where the findings demonstrated that a ratio of H_2O_2 to DBT of more than 3 leads to the slow rate of oxidation and promotes the decomposition of H_2O_2 [18].

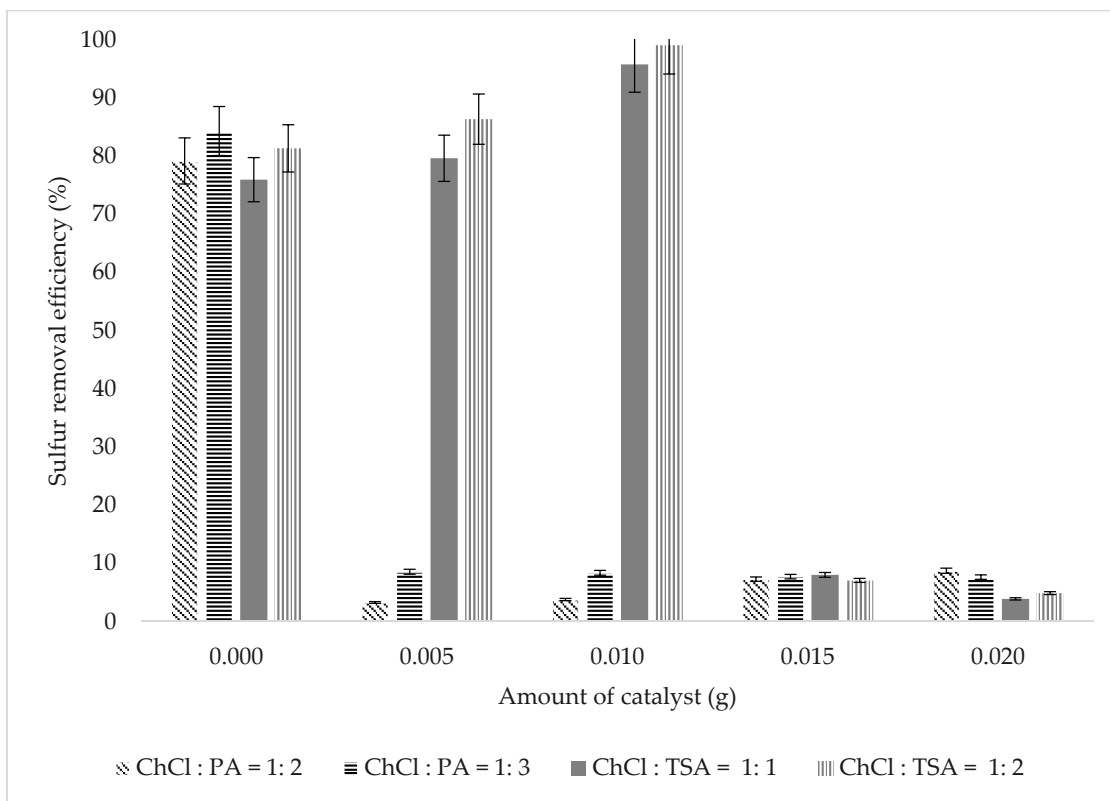


Figure 2. The effect of catalyst dosage on the sulfur removal efficiency (H_2O_2 as an oxidant with a ratio to DBT of 1:2, 10 mL of 100 ppm model oil (DBT), room temperature, EIL to model oil ratio of 1:5, and 300 rpm stirring speed).

3.2.3. Effect of Stirring Speed

The stirring speed studied was 300, 600, and 900 rpm, respectively. Figure 4 shows the sulfur removal efficiency based on different stirring speeds for different EILs. As can be seen in Figure 4, when the stirring speed was 300 rpm, the sulfur removal efficiency achieved was lower than when the speed is 600 and 900 rpm. A comparison between 600 and 900 rpm, there is not much difference in terms of the removal efficiency of sulfur compounds. This is due to the fact that increasing the speed did not affect the process of interfacial extraction between the model oil and EIL [19]. Thus, the best stirring speed chosen for all the different types of EILs is 600 rpm.

3.2.4. Effect of Oil to EIL Ratio

Researchers have proven that the removal efficiency of sulfur compounds decreases with the decreasing mass of IL to oil ratio [1]. The model oil and EIL are immiscible, thus the mass transfer between the model oil and EIL can affect the desulfurization [18]. As can be seen in Figure 5, the ratio of 1:1 EIL to model oil gave the highest removal efficiency for all the different types of EILs used. This was followed by the ratio of 1:2 and 1:5 of model oil to EIL. The higher the amount of EIL, the higher the removal efficiency. The reason may probably be due to the fact that the increase in the volume of EIL enhances the transfer of sulfur species from the oil phase to the EIL phase and also increases the rate of reaction [20]. However, the difference in the sulfur removal efficiency is very small when comparing the ratio of 1:1, 1:2, and 1:5 for the EIL to model oil ratio. Previous research has also stated that the mass ratio of EIL to model oil is not a universal rate and that it depends on the

types of EIL being used. Thus, for further experiments, the ratio of 1:5 EIL to model oil would be used since it requires the lowest volume of EIL for the highest amount of sulfur removal efficiency.

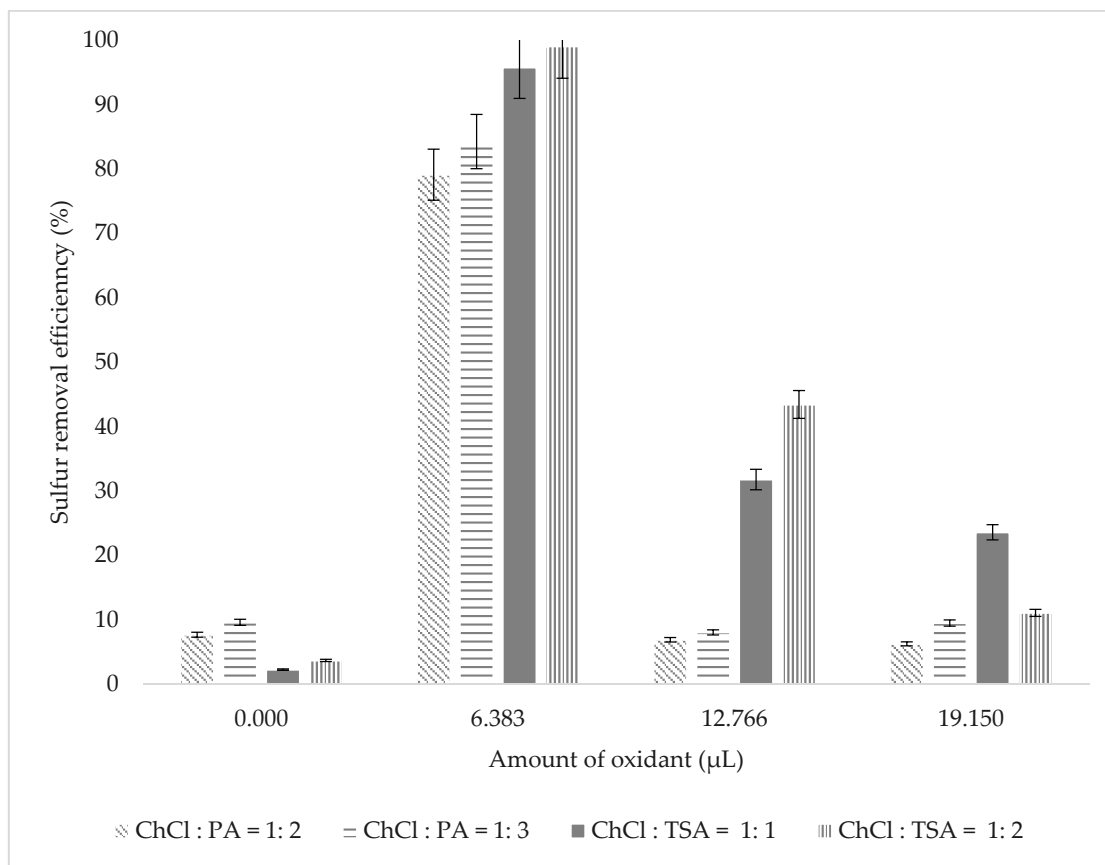


Figure 3. The effect of ratio of the oxidant to DBT in the model oil on the sulfur removal efficiency (0.01 g Cu-Fe/TiO₂, 10 mL of 100 ppm model oil (DBT), room temperature, EIL to model oil ratio of 1:5, and 300 rpm stirring speed).

3.2.5. Effect of Types of EIL

The suitable choice of EIL is important for the desulfurization process. Unfortunately, not all EILs synthesized can be used to remove sulfur compounds from gasoline/oil. During desulfurization, the sulfur element in the compound is removed via extraction to the extractant phase from the oil phase. This process can only be effective when the suitable type of extractant is used. Thus, proper research and experiments are required to determine how effective the EILs are in terms of desulfurization. In this research, different types of HBDs with different ratios were used to determine the EIL with the highest sulfur removal efficiency. Since HBD has a greater influence on the desulfurization process compared to the HBA, ChCl was used as the only HBA and different types of acids were used as the HBD [20]. The extraction of DBT by a series of salt and acid mixtures were carried out with the initial concentration of DBT at 100 ppm, as can be seen in Figure 6. From Figure 6, it can be seen that ChCl:TSA = 1:2, demonstrates the highest sulfur removal efficiency of 99.07%, with just one cycle. It is higher than using the equal amount of salt to acid, which resulted in the removal efficiency of about 96%. The higher the amount of acid, the better the desulfurization efficiency [20]. This explains why the ratio of ChCl:TSA of 1:2 gave a better desulfurization efficiency compared to the ratio of 1:1. The same observation can be made from the EILs of ChCl and PA. The order of desulfurization efficiency is listed as follows: ChCl (1): TSA (2) > ChCl (1): TSA (1) > ChCl (1): PA (2). In terms of the comparison between the type of acids: the TSA higher acidity compares to PA. Thus, EILs synthesized with TSA have a higher acidity, resulting in a higher sulfur removal efficiency.

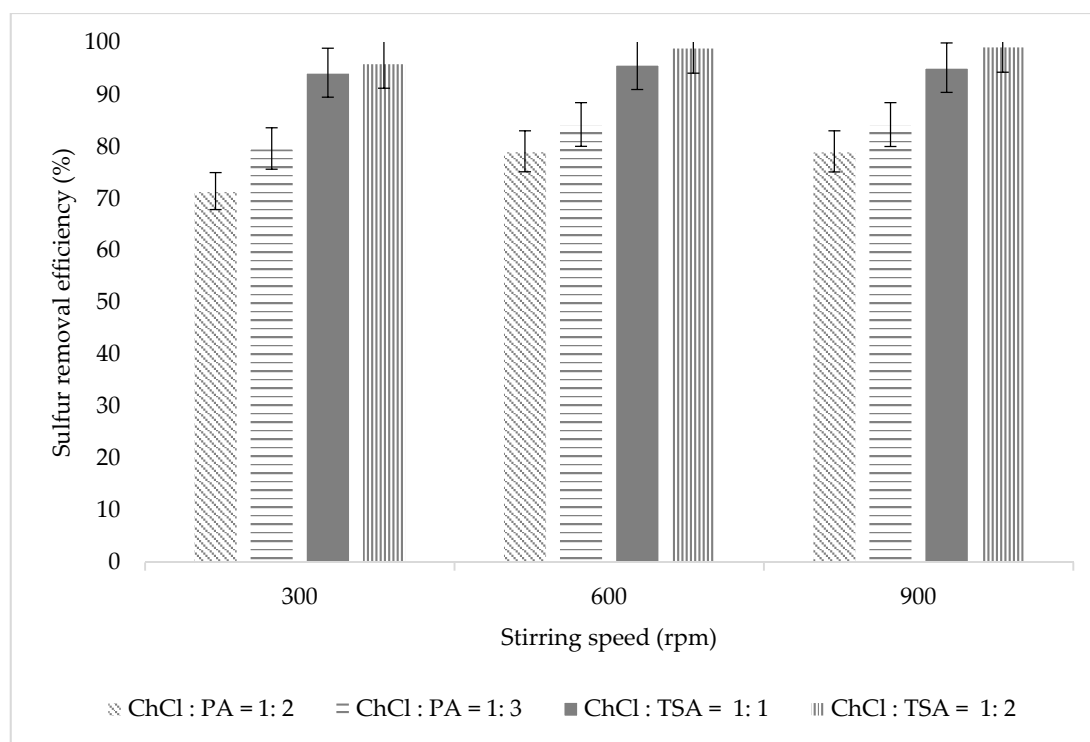


Figure 4. The effect of stirring speed on the sulfur removal efficiency (0.01 g Cu-Fe/TiO₂, H₂O₂ as oxidant with ratio to DBT of 1:2, 10 mL of 100 ppm model oil (DBT), room temperature, and EIL to model oil ratio of 1:5).

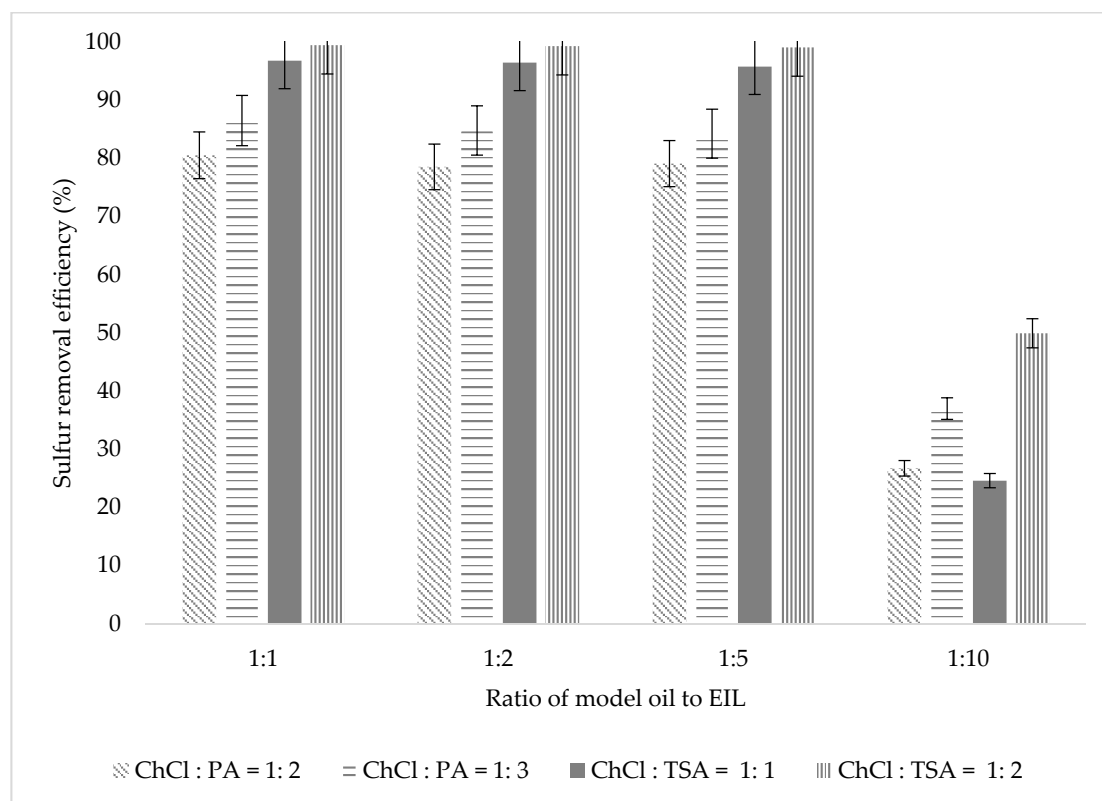


Figure 5. The effect of EIL to model oil ratio on the sulfur removal efficiency (0.01 g Cu-Fe/TiO₂, H₂O₂ as an oxidant with a ratio to DBT of 1:2, 10 mL of 100 ppm model oil (DBT), room temperature, and 600 rpm stirring speed).

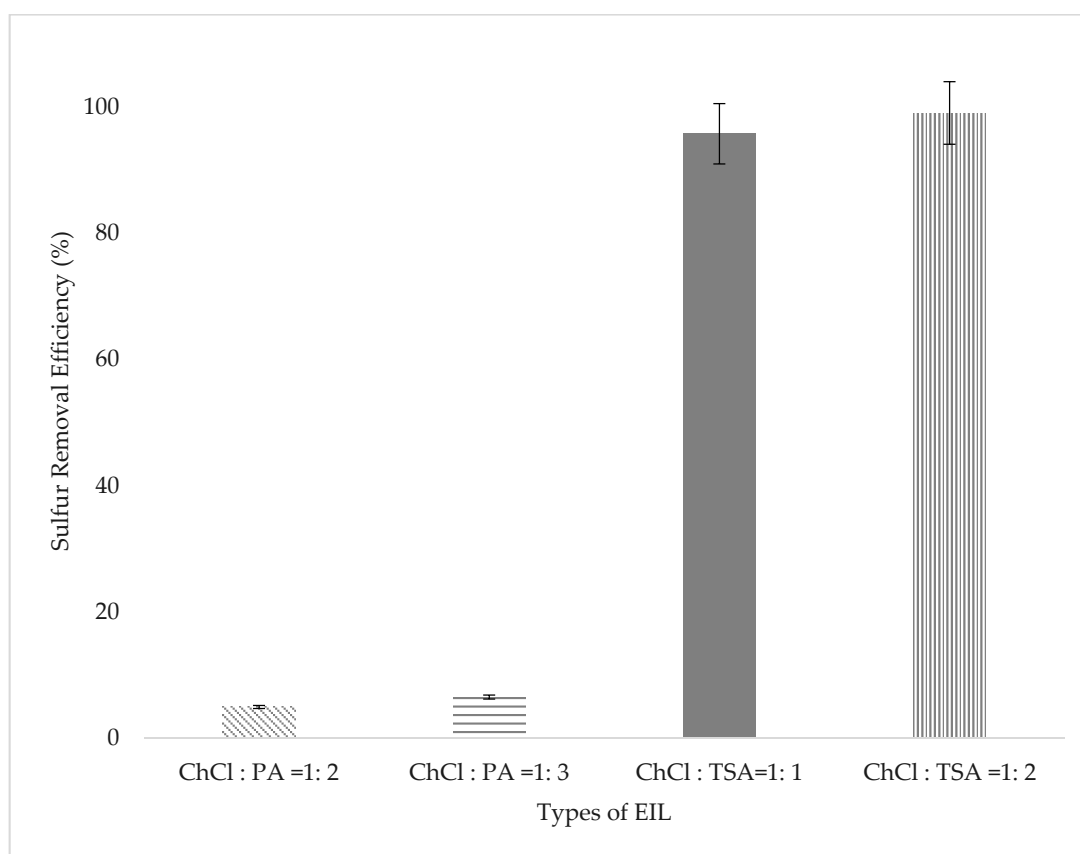


Figure 6. The effect of different types of EILs on the sulfur removal efficiency (0.01 g Cu-Fe/TiO₂, H₂O₂ as an oxidant with a ratio to DBT of 1:2, 10 mL of 100 ppm model oil (DBT), room temperature, EIL to model oil ratio of 1:5, and 600 rpm stirring speed).

3.2.6. Effect of Concentration of Sulfur Species

Usually, it is more common to assume that a higher initial concentration of fuel would result in a higher extraction efficiency by the solvent based on the principle of effect of concentration gradient on mass transfer. Figure 7 shows the effect of different concentrations of DBT in the model oil (100 and 1000 ppm) in the desulfurization efficiency. As can be seen in Figure 7, the desulfurization efficiency decreases with the increase in concentration of sulfur species in the model oil for all the different types of EILs. At 100 ppm, with solvent ChCl:TSA = 1:2, the sulfur removal efficiency achieved was 99.06% compared to 51.80% that was achieved when the 1000 ppm model oil was used. Previous researchers have reported similar findings, when the concentration of DBT increases, the removal efficiency of sulfur compounds decreases [13,21]. In addition, the HDS process that is already in the market is known to be very effective in terms of removing sulfur compounds from fuel oil when the concentration is more than 300 ppm. Thus, it was important to study the effect of low concentration of sulfur compounds in order to introduce a supplementary process for the conventional HDS process [21].

3.2.7. Effect of Different Sulfur Species

To study the effect of different sulfur species on removal efficiency, desulfurization was performed with 4,6-DMDBT under the same condition using ChCl:TSA = 1:2 as the EIL. This study is important to demonstrate that the EIL can be used for different refractory sulfur compounds. The reason for using this EIL is due to the fact that it gave the highest removal efficiency when DBT was used as the sulfur species. As can be seen in Figure 8, the removal of DBT and 4,6-DMDBT were 99.06% and 41.23%, respectively. The difference in the sulfur removal efficiency for the two different types of sulfur species is due to its steric

hindrance of the methyl group on the sulfur atom and the electron density [17,19,22–24]. Previous researchers have stated the electron density of DBT and 4,6-DMDBT as 5.758 and 5.760, respectively [22,24]. The electron density of DBT and 4,6-DMDBT is approximative. Thus, due to steric hindrance of the two methyl groups, the removal efficiency of 4,6-DMDBT is lower than of DBT [24]. The presence of methyl group at 4- and 6- position on 4,6-DMDBT greatly exacerbated the steric hindrance which was the main obstacle for bond formation between the sulfur atom and hydrogen in the EIL, causing the removal efficiency to be low [17,19].

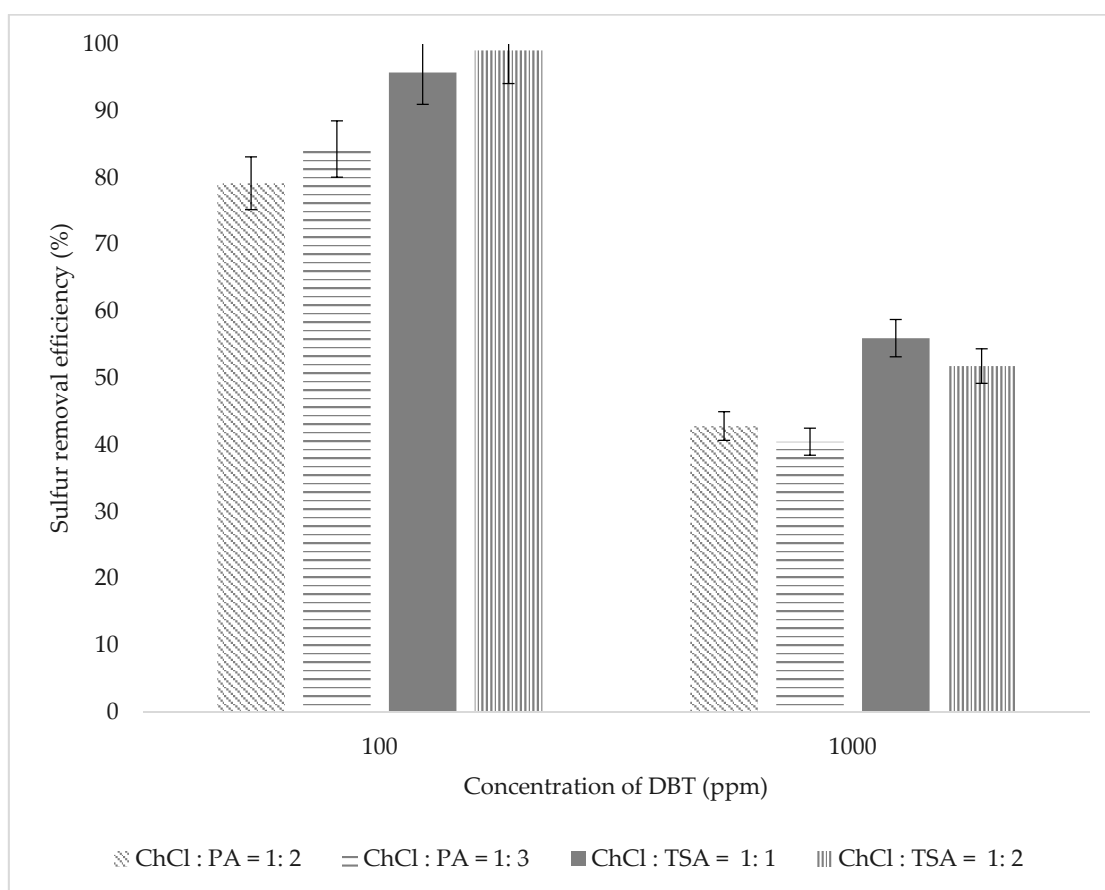


Figure 7. The effect of different concentrations of DBT in the model oil on the sulfur removal efficiency (0.01 g Cu-Fe/TiO₂, H₂O₂ as an oxidant with a ratio to DBT of 1:2, room temperature, EIL (ChCl:TSA = 1:2) to model oil ratio of 1:5, and 600 rpm stirring speed).

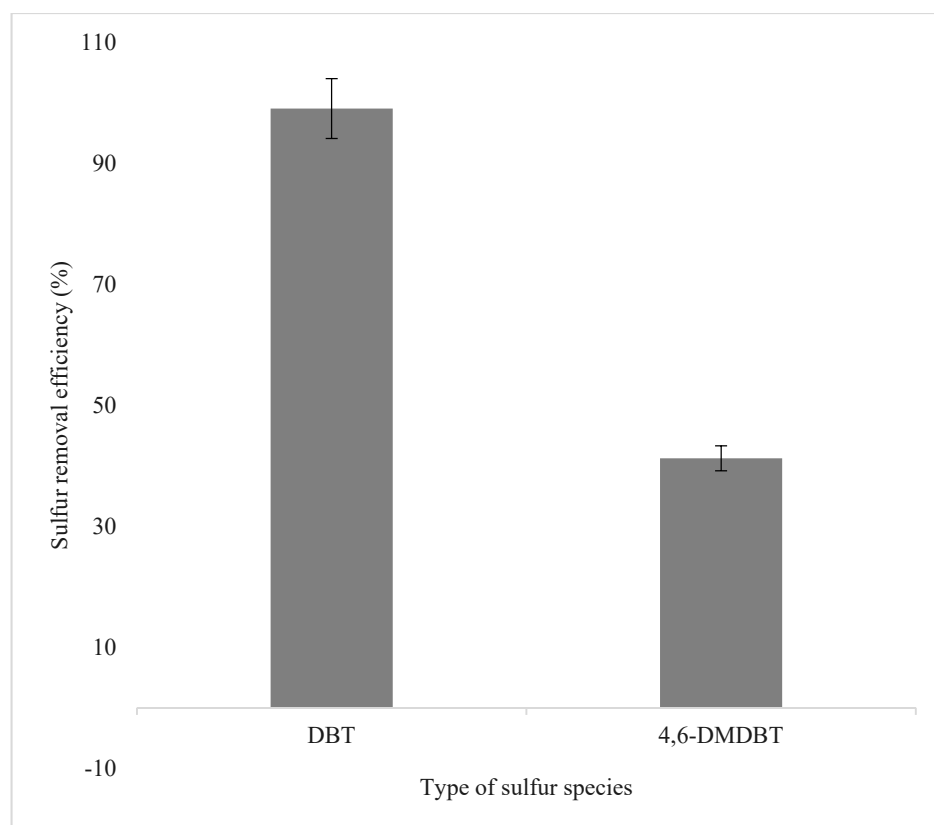


Figure 8. The effect of different types of sulfur species in the model oil on the sulfur removal efficiency (0.01 g Cu-Fe/TiO₂, H₂O₂ as an oxidant with a ratio to DBT of 1:2, 10 mL of 100 ppm concentration model oil, room temperature, EIL to model oil ratio of 1:5 and 600 rpm stirring speed).

4. Conclusions

As a conclusion, the fuel oil containing sulfur compounds is a major challenge for most oil refinery industries these days. Based on the studies and research emphasized in the present literature review, it is feasible to use the oxidative extractive desulfurization (OEDS) method to remove the sulfur compounds from fuel oil using the oxidant, photocatalyst, Cu-Fe/TiO₂, and acidic eutectic-based ionic liquid (EIL). The acidic EILs were synthesized and characterized to determine the best EIL among all the acidic EILs that were synthesized in the application of desulfurization. All the EILs synthesized have a lower melting point than its pure constituent as resulted from the DSC analysis. ChCl (1): PA (3), one of the acidic EILs that was synthesized is found to have good thermal stability compared to the other EILs. Upon conducting the experiment on the application of the synthesized acidic EILs on desulfurization, the optimum amount ratio of H₂O₂ to DBT and catalyst for the reaction to take place is found to be 2 and 0.010 g, respectively. As for the types of EILs, the best EIL is ChCl (1): TSA (2). The ratio of 1:2 was obtained for the best ratio of model oil to EIL with 600 rpm as the optimum stirring speed with the highest removal efficiency. Thus, with the best parameters obtained, the highest removal efficiency of sulfur compounds from the model oil is 99.07%. ChCl (1): TSA (2) was then also tested with model oil containing a concentration of sulfur species at 1000 ppm, which resulted in a removal efficiency of 51.8%. In addition, research was further conducted on a different sulfur species, 4,6-DMDBT, which is also one of the refractory sulfur compounds found in fuel oil. The desulfurization efficiency obtained was 41.23%. Thus, it can be concluded that, EILs synthesized with salt and organic acid can be a good medium to help with desulfurization, depending on the type of organic acid used.

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