Oxidative Desulfurization of Diesel from the Topping Plant using 1-Butyl-3-Methylimidazolium Hydrogen Sulfate [Bmim][HSO₄] as Catalyst

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Abstract. This investigation was carried out with the purpose of reducing the sulphur content in diesel from the topping plant and avoiding air pollution, due to the presence of SOₓ in the emissions, at the same time reduced the corrosion rate in the equipment, machinery or mechanical components of the industry. An oxidative desulphurization (ODS) process was carried out with ionic liquid (1-butyl-3-methyl imidazolium hydrogen sulfate [BMIM][HSO₄]) that serves as a solvent and catalyst. H₂O₂ (30 % wt) was used as an oxidizing agent, because it is benign to the environment. A maximum of 43.14% removal was obtained at a volumetric ratio V_IL/ V_diesel (1:1), molar ratio H₂O₂/ S (5) and reaction time (2 hours). In addition, the IL was evaluated after subjecting it to a regeneration process, being able to recycle it only once until it is saturated again; also the physical-chemical properties of diesel were studied before and after of exposed it to the ODS process.

1. Introduction
Desulphurization of fuel oils is an important process in oil refining, and hydrodesulphurization (HDS) is considered the traditional process widely used in industry. However, growing environmental concerns, legal limits imposed on sulphur content in fuels, and the ineffectiveness of HDS to remove the aromatic structure of sulphur compounds have led researchers to seek alternative methods of desulphurization. Methods such as oxidation, adsorption, extraction and bioprocesses have been investigated, and oxidative desulphurization (ODS) is considered the most competitive [1].
In the ODS, the sulphur compounds, such as dibenzo thiophene (DBT) and its derivatives can be almost completely removed from diesel fuel by oxidation to their corresponding sulfones and subsequent extraction of these by some polar solvents such as: N-Methyl Pyrrolidone (NMP), N, N- dimethylformamide (DMF), Dimethyl Sulfoxide (DMSO), methanol (MeOH) and acetonitrile, in a simple process under less severe conditions, with low equipment and operating costs. Studies on ODS using IL have been reported recently in literatures. It has been observed that ODS using IL which served as both extractants and catalysts can effectively remove those HDS-immune cyclic S-compounds and reduce the S-component in fuel oils [2].

By means of the conventional oxidative desulphurization process, sulphur removal efficiency greater than 90% can be obtained by using a solution of hydrogen peroxide (H₂O₂) as an oxidant, which is combined with catalysts of the complex type of acetic acid, peroxotungsten or peroxomolibdene.
However, the use of these catalysts raises some problems such as the difficulty in separating or regenerating them, as well as in the contamination of the fuel, so alternative catalysts are investigated such as ionic liquids (IL) for use in this process [2].

Most works, were focused on the investigation of model diesel fuel. However, ODS of the real oil is rarely studied and the desulphurization efficiency is not ideal. Therefore, for this study, real diesel produced in the topping plant was used, this product content 3000 ppm S approximately. In previous work, with real diesel of 97 ppm S, 85.5 % S-removal efficiency after one stage of ODS with IL 1-butyl-3-methyl imidazolium hydrogen sulfate [BMIM][HSO₄], and other studies with IL Brønsted-Lewis acid zinc chloride N-methylpyrrolidonium ([Hnmp] Cl / (ZnCl₂), for FCC real diesel fuel, removal efficiency is less than 38% in a one stage and can reach 83 % after five stages [3].

In ODS study conducted at temperatures of 25 °C, 40 °C and 60 °C, room temperature was considered the most optimal, because a high temperature decreases the viscosity of the IL, which is favorable by allowing a complete mixture between this and the fuel, however, there is a rapid decomposition of H₂O₂. When the reaction temperature increased from 25 °C to 60 °C, the removal of sulphur from DBT decreased considerably from 99.6% to 64.6 %; therefore, the optimal reaction temperature was adjusted to room temperature [4].

2. Experimental Section

2.1. Reagents
1-Butyl-3-methyl imidazolium hydrogen sulfate, ≥ 95% purity imported and supplied by SIGMA-ALDRICH, Hydrogen Peroxide (30%), 99.7% purity Diethyl Ether.

2.2. Equipment
To measure the sulphur content, an X-ray fluorescence spectrophotometer, HORIBA brand, model: SLFA-20 / SLFA-2100 / SLFA-2800 was used, and to measure the other properties of diesel, the equipment of the Refinery Laboratory was used of Block 56 / Petroamazonas EP.

2.3. Oxidative Desulphurization
The ODS reaction was carried out in a 50 ml round bottom flask, IL and 30 wt % H₂O₂ solution were put into bottom, the diesel fuel was added in the required proportion and the mix were magnetically stirred at some temperature( 25 °C) for a certain time (1, 2 or 3 hours). After a certain time of oxidation, the mixture was laid aside for 3 hours for phase separation. The diesel phase was analyzed by X-ray fluorescence spectrophotometer.

2.4. Regeneration of IL
The regeneration of IL is of vital importance for the industrial application, in this case, the process to regenerate the IL was carried out as follows, the IL phase was treated with rotary evaporation to remove impurities and regenerate the IL to reuse it in ODS.

Distilled water was first added in the same volume proportion, as the extract phase obtained. The mixture was produced stirred for 10 minutes at 1000 rpm, at temperature of 25 °C. Thereafter, the mixture was treated at 105 °C using a rotary evaporator at a vacuum of 420 mbar for three hours to remove the water. The regenerated IL, was washed three times with diethyl ether with a volume equal to that of the extract obtained, to later perform the separation in a rotary evaporator and recover the IL for recycling [5]. A summary scheme of what was done in the laboratory can be seen in figure 1.
3. Results and Discussion

3.1. Effect of the volumetric ratio $V_{IL}/V_{diesel}$

The effect of volumetric ratio $IL$ / fuel of 1/3, 1/2 and 1/1 were evaluated, as can be seen in figure 2, the volumetric ratio that has the highest proportion is the one with the best performance, either that work with a molar ratio of 3, 4 or 5. The highest S-removal efficiency of 43.14% is obtained when the volumetric ratio of $IL$ / fuel was 1/1.

![Figure 2. Effect of the volumetric ratio $V_{IL}/V_{diesel}$.](image)

3.2. Effect of molar ratio $nO/nS$

According to the stoichiometric reaction, to oxidize the sulphur-containing compounds to their corresponding sulfones using hydrogen peroxide, 2 mol of hydrogen peroxide is consumed per 1 mol of sulphur-containing compound. As show in figure 3, the sulphur removal was 7.51% for the molar ratio of 2, this can be attributed to the fact that there is not enough $H_2O_2$ to completely oxidize the sulphur
compounds. The removal efficiency increased to 28.85 % when nO/nS was 5. This effect is assigned to the increase in the concentration of H$_2$O$_2$ resulting in a greater possibility of oxidizing sulphur compounds. However, when working with nO / nS equal to 8 and 10, the efficiency decreased, it was considered that at molar ratios greater than 5, there is no longer a significant effect of the oxidant, an excess of H$_2$O$_2$ introduces water into the reaction environment and dilutes the IL, so it negatively influences the ODS process [6].

![Figure 3](image3.png)

**Figure 3.** Effect of the oxidant on the removal efficiency of S (Cond: T (25° C), stirring for 2 hours, $V_{IL}$ / $V_{diesel} = 1: 3$).

3.3. **Effect of reaction time**

The effect of the reaction time (30 min, 1 h, 2 h, 3 h and 5 h) were evaluated at the conditions: volumetric ratio $V_{IL}$ / $V_{diesel}$ (1: 3), molar ratio nO / nS (5), temperature (25 °C) and 900 rpm stirring. According to figure 4 here are approximately equal removal values between 1, 2 and 3 hours. However, at 30 min and greater than 5 hours the removal efficiency decreases, in the latter case, the increase in the contact time of the phases generated an increase in the solubility of the IL in the fuel, which was verified with the sulphur content result equal to 3535.9 ppm.

![Figure 4](image4.png)

**Figure 4.** Effect of reaction time on the removal efficiency.
3.4. Effect of regenerated IL
To study the extracting effect of the regenerated IL [BMIM] [HSO₄], was worked to the best conditions of the factorial design, at volumetric ratio $V_{IL}/V_{diesel}$ equal to 1:1, molar ratio $nO/nS$ equal to 5, time of stirring for 2 hours, temperature of 25 °C in a single stage and with the same load of feeding. Three regeneration cycles were performed, considering that each cycle corresponds to a stage of extraction and regeneration. The results of the efficiencies for the three cycles are shown in table 1.

| Cycle | Extraction efficiency |
|-------|-----------------------|
| 0     | 43.13                 |
| 1     | 34.51                 |
| 2     | 19.67                 |
| 3     | 5.70                  |

According to the results in table 1, there is no positive effect when performing this process, since in the first regeneration cycle a drop of almost 9% in sulphur removal efficiency is observed. For the second and third regeneration cycle there are minor efficiencies, that is, the IL is very saturated. These results indicate that the IL [BMIM] [HSO₄] can be regenerated only once so that there is no appreciable loss in the percentage of removal obtained.

3.5. Partition coefficients (Kd)
These values are provided to specify the capacity for extracting the IL. The partition coefficient is a key parameter to determine the solvent extraction capacity in an industrial extraction process. The higher the partition coefficient, the better the desulphurization performance of an IL [7]. In figure 5 this trend is observed, at a lower Kd there is a lower percentage of sulphur removal. Regardless of the time and amount of oxidant that has been used in the test, this tendency is observed for each of the volumetric ratios tested.

![Sulfur removal, % vs Partition coefficient](image)

Figure 5. S removal efficiency and partition coefficient, Kd (Cond: $V_{IL}/V_{diesel} = 1:3$).

3.6. Diesel properties before and after process ODS
After the diesel is subjected to an ODS process with IL, it is expected that its quality will not be affected, as showed in table 2; however, there are certain variations, for example, the flash point increased to 72.42 °C. The viscosity had a minimal change; however, the result is favorable in terms of having a better-quality fuel. The sulphur content that this fuel has, decreased by almost 1500 ppm when using the ODS process described in the present investigation.
Properties such as copper sheet corrosion are not modified because the diesel fuel itself is not corrosive to copper or its alloys. And the Cetane Index Calculated did not suffer a negative change after the ODS process with IL. In general, most of the properties analyzed for this study were not seen affected after the fuel was in contact with the IL in the ODS process, indicating that the product refined with IL does not suffer alterations in its physical-chemical properties [8].

Table 2. Properties of diesel before and after of exposed it to the ODS process.

| Parameter                        | Diesel before ODS | Diesel after ODS |
|----------------------------------|-------------------|------------------|
| °API at 15°C                     | 35.04             | 35.54            |
| Density at 15 °C (g mL⁻¹)        | 0.8494            | 0.8471           |
| Flash point (°C)                 | 66.33             | 72.42            |
| Distillation temperature (90%) (°C) | 344.3           | 343.5            |
| Kinematic Viscosity at 37.8 °C (cSt) | 3.311            | 3.28             |
| Sulphur (%wt)                    | 0.3031            | 0.1346           |
| Corrosion to copper foil         | No. 1             | No. 1            |
| Cetane Index Calculated          | 49.6              | 51.3             |

4. Conclusion

The ODS process of diesel fuel with an initial sulphur content of 0.3031% wt with IL was worked at room temperature (25 °C), at the volumetric ratio of $V_{IL}$ / $V_{diesel}$ to 1: 1, at $H_2O_2$ oxidant ($nO / nS$ to 5) and at a reaction time of 2 hours to reach 43.14% sulphur removal. All the physicochemical properties of diesel evaluated in the present investigation, among them the calculated cetane index and viscosity, were not significantly modified after the ODS process with IL, so the quality of the same improves due to the decrease in sulphur compounds. The regeneration of the IL [BMIM] [HSO₄] saturated with sulphur compounds were not possible, since during the first reuse cycle the removal percentage decreased by 9 %, that is, the IL did not fully recover its catalytic activity and solvent, these is the principle reason by the ODS with IL must be a complementary and subsequent process to conventional HDS. The cost of reagents used in desulphurize diesel fuel of 0.3% to 0.1% wt, without pretreatment of HDS was 100 USD per gram of sulphur removed, at the laboratory conditions described in this study, however is necessary a total economic analysis considered energy consumption, greenhouse gas emissions and operational costs.

5. References

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