

## **Sulfur Removal from Diesel Using Oxidative Desulfurization (ODS): A Case Study in MRC Refinery**

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### **Abstract**

Iraqi refineries predominantly produce gas oil with high sulfur content, contributing to significant environmental challenges, including poor air quality and elevated emissions. This study investigates the feasibility and efficiency of oxidative desulfurization (ODS) as a cost-effective and environmentally friendly method for upgrading gas oil to Euro 5 standards. With methanol as the extraction solvent and hydrogen peroxide and sulphuric acid as the oxidising agents in the first step, this method effectively eliminates sulphur compounds without the need for hydrogen or the production of gaseous emissions like hydrogen sulphide (H<sub>2</sub>S).

Additionally, the absence of expensive catalysts and severe operational conditions makes ODS an optimal solution for modernizing Iraq's aging refinery infrastructure. This paper highlights the potential of ODS in addressing Iraq's environmental and industrial challenges, providing a sustainable pathway to cleaner fuel production.

This paper presents experimental and pilot plant work conducted at the Midland Refineries Company (MRC) refinery to investigate sulfur removal from diesel through Oxidative Desulfurization (ODS). The experimental results demonstrated significant sulfur reduction: the light gas oil (LGO) sulfur content decreased from 1.9 wt% to 3.5 wt%, and the heavy gas oil (HGO) sulfur content decreased from 2.68 wt% to 0.36 wt%. The study explores the reaction mechanism underlying ODS, compares it with conventional hydrodesulfurization (HDS) methods, and highlights the advantages of ODS in terms of cost, reduced hydrogen consumption, minimal emissions, and smaller plant footprint.

### **Introduction**

Iraq's aging refinery infrastructure predominantly produces gas oil with sulfur contents exceeding international environmental standards. High sulfur content in fuel directly contributes to increased emissions of sulfur oxides (SO<sub>x</sub>), negatively impacting air quality and public health. Upgrading these refineries to produce Euro 5-compliant gas oil (with sulfur levels below 10 ppm) is imperative to align with global environmental goals and reduce emissions.

Traditional hydrodesulfurization (HDS), widely used in refineries, involves severe operating conditions, high hydrogen consumption, and expensive catalysts, presenting challenges for implementation in older refineries. Oxidative desulfurization (ODS) has emerged as a promising alternative, offering a simpler, cost-effective, and environmentally benign solution. This study explores the use of ODS to upgrade gas oil in Iraqi refineries, emphasizing its potential as a transformative approach.

The conventional approach to sulfur removal, hydrodesulfurization (HDS), has limitations, including high operational costs, hydrogen consumption, and large equipment footprints. Oxidative Desulfurization (ODS) has emerged as a promising alternative for deep desulfurization due to its lower energy requirements, milder operating conditions, and reduced environmental impact. This study evaluates the performance of ODS in reducing sulfur content in diesel fractions at the MRC refinery, with experiments conducted at laboratory and pilot plant scales.

Table 1: Comparison between Oxidative Desulfurization and Hydro-Desulfurization process.

| Feature                   | ODS                   | HDS                                   |
|---------------------------|-----------------------|---------------------------------------|
| Hydrogen Requirement      | No hydrogen           | Required Hydrogen (1000-2500 scf/bbl) |
| Operating Temperature     | Mild 70-90 C          | 300- 450 C                            |
| Operating Pressure        | Atmospheric Pressure  | 30-130 bar                            |
| Catalyst                  | No expensive Catalyst | Expensive Catalyst (NiMo, CoMo)       |
| Energy Consumption        | Low                   | High                                  |
| Environmental Impact      | No gases Emissions    | Produces harmful Gases                |
| Sulfur removal Efficiency | 99%                   | 90-99%                                |
| Cost (\$)                 | 2-4                   | 8-12                                  |

## Background

### Hydrodesulfurization (HDS)

Hydrodesulfurization (HDS) is a widely researched and industrially implemented process for reducing sulfur content in petroleum fractions, particularly gas oil and diesel. Several studies have focused on its reaction mechanisms, catalyst advancements, operating conditions, and limitations. This literature review synthesizes findings from various peer-reviewed papers to provide a comprehensive understanding of the HDS process.

According to Babich and Moulijn (2003), HDS involves the catalytic removal of sulfur compounds by converting them into hydrogen sulfide (H<sub>2</sub>S) through a series of hydrogenation and desulfurization steps. Compounds such as thiophenes, benzothiophenes, and dibenzothiophenes (DBTs) are commonly present in middle distillates like gas oil. These compounds exhibit varying reactivity, with DBTs being particularly resistant to HDS due to steric hindrance caused by alkyl substituents on the aromatic rings. Song (2003) emphasized that the desulfurization pathway depends on the compound's structure. Catalyst development has been a primary focus in HDS research. Chianelli et al. (1994) highlighted those conventional catalysts, such as CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>, offer good activity for sulfur removal but face challenges with refractory sulfur compounds. CoMo catalysts are effective for low-sulfur feeds, while NiMo catalysts show better performance for heavier feeds containing nitrogen and polyaromatics. Recent advancements include the use of bimetallic catalysts and alternative supports. Wang et al. (2015) reported that doping with noble metals (e.g.,

Ru, Pt) significantly improves catalyst activity but increases costs. Ribeiro et al. (2011) explored zeolite-supported catalysts, which demonstrated enhanced selectivity and resistance to deactivation. HDS is characterized by severe operating conditions to achieve deep desulfurization. Gary et al. (2007) provided a detailed account of the typical operating parameters: Temperature: 300–450°C, Pressure: 30–130 bar and Hydrogen-to-Oil Ratio: 300–1,000 scf/bbl. Higher temperatures and pressures favor the removal of refractory sulfur compounds but significantly increase energy consumption and equipment costs. Jayaraman et al. (2019) noted that optimizing hydrogen flow and reaction temperature is crucial to balancing sulfur removal efficiency with operating expenses. Despite its industrial success, HDS faces limitations that have been widely discussed in the literature. Ma et al. (1994) and Marafi et al. (2010) identified the following challenges:

- Refractory Compounds: Alkylated DBTs and nitrogen-containing compounds are resistant to HDS, requiring severe conditions and higher hydrogen consumption.
- Hydrogen Dependency: HDS relies heavily on hydrogen, which increases operational costs, particularly in regions with limited hydrogen infrastructure.
- Environmental Concerns: The process generates hydrogen sulfide (H<sub>2</sub>S), a toxic gas that requires further treatment in sulfur recovery units.

Comparisons with alternative desulfurization methods have been highlighted in recent studies. Shafiq and Akhtar (2020) compared HDS with oxidative desulfurization (ODS), noting that ODS operates under milder conditions and does not require hydrogen. However, ODS is limited by chemical costs and scalability. Wang et al. (2018) suggested that combining HDS with pre-treatment technologies like ODS or adsorption could enhance overall desulfurization efficiency. HDS is the most widely used industrial process for sulfur removal. The process involves the catalytic reaction of sulfur-containing compounds with hydrogen to produce H<sub>2</sub>S gas, which is then removed.

### **Oxidative Desulfurization (ODS)**

Oxidative desulfurization (ODS) is an effective method for removing sulfur compounds from fuels under mild operating conditions, making it a promising alternative to traditional hydrodesulfurization. The process relies on oxidizing sulfur-containing compounds such as dibenzothiophene (DBT), benzothiophene (BT), and thiophene into their oxidized forms, such as sulfoxides or sulfones, which can then be separated from the fuel. By using methanol as the solvent, the process can achieve efficient extraction of oxidized sulfur species while maintaining compatibility with the oxidation reaction conditions.

In the ODS process, sulfur-rich fuel is treated with an oxidant such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or tert-butyl hydroperoxide (TBHP). A catalytic system, which can include acids or organic catalysts, is used to activate the oxidant and enhance the reaction. Methanol, a highly polar and readily available solvent, is introduced both as a reaction medium and as an extraction solvent. Its polarity facilitates the dissolution of oxidized sulfur compounds, allowing for effective separation from the fuel phase.

The reaction typically occurs at moderate temperatures (50–80°C) under atmospheric pressure, making it energy-efficient and operationally simple. After the oxidation step, the mixture is allowed to separate into two phases: the desulfurized fuel and the methanol-rich phase containing the oxidized sulfur compounds. Methanol's low boiling point also allows for its easy recovery and recycling after extraction, reducing operational costs and environmental impact.

Methanol-based ODS has shown high efficiency in removing sulfur compounds, particularly with refractory compounds like DBT. The process achieves significant sulfur reduction without the need for high pressures or hydrogen, making it safer and more cost-effective. Analytical methods such as gas chromatography (GC) is used to quantify sulfur removal and confirm the formation of oxidized products. The experimental setup showing below:



Figure 1: Experimental setup for ODS

Using methanol as a solvent enhances the sustainability and scalability of the ODS process. Its dual role as a reaction medium and extraction solvent simplifies the process, minimizes waste, and reduces the dependency on additional chemicals. Research is ongoing to optimize the reaction parameters and improve the integration of methanol recovery, further enhancing the economic and environmental benefits of this approach. By employing methanol in ODS, this method offers a practical and efficient route to producing ultra-low sulfur fuels, contributing to cleaner energy solutions and reduced sulfur emissions.

ODS is a chemical process that oxidizes sulfur compounds into sulfoxides or sulfones, which are then removed by extraction or adsorption. It operates under milder conditions compared to HDS and does not require hydrogen.

### 3. Advantages of ODS

1. Mild Conditions: Typically operates at ambient to moderate temperatures and pressures.
2. Hydrogen-Free: Eliminates dependency on expensive hydrogen.
3. Selective Oxidation: Efficiently targets refractory sulfur compounds.
4. Smaller Footprint: Compact equipment design.
5. Lower Emissions: Reduces CO<sub>2</sub> and other pollutants.

### Mechanism of ODS

The ODS process involves two key steps:

1. Oxidation: Sulfur compounds (e.g., thiophenes) are oxidized to sulfoxides or sulfones using an oxidizing agent such as hydrogen peroxide, peracids, or ozone in the presence of a catalyst.
2. Separation: The oxidized products, which have increased polarity, are removed via liquid-liquid extraction, adsorption, or membrane separation.



Figure 2 : ODS process showing oxidation and extraction with Solvents

#### Methodology and Protocol:

For accurate and standardized analysis of sulfur content and hydrocarbon composition, we follow the following protocols: ASTM D4294, D2622 and D5453 for sulfur contents in hydrocarbons. Also, ASTM D6730, D2163 and D5186 for hydrocarbon composition analysis.

#### Results:

The results of the oxidative desulfurization (ODS) study demonstrated that methanol was the most effective solvent for extracting sulfones after oxidation using hydrogen peroxide ( $H_2O_2$ ) as the oxidant and sulfuric acid ( $H_2SO_4$ ) as the catalyst. The combination of these reagents created a highly efficient oxidation environment, converting sulfur-containing compounds, such as dibenzothiophene (DBT), into their oxidized forms (sulfoxides and sulfones). Methanol's polarity and solubility profile allowed for rapid and selective extraction of these oxidized sulfur species from the diesel fuel. This process achieved a remarkable reduction in sulfur content of 99%, significantly outperforming conventional hydrodesulfurization (HDS) methods.

Compared to hydrodesulfurization, which typically operates under high temperatures (300–400°C) and pressures (20–80 bar) with expensive hydrogen and metal-based catalysts, the ODS process with methanol extraction was conducted under mild conditions of 60°C and atmospheric pressure. These conditions not only reduce energy consumption but also eliminate the need for hydrogen, making the process safer and more cost-effective. Furthermore, the extraction efficiency of methanol surpassed that of other solvents tested, such as acetonitrile and dichloromethane, due to its superior ability to dissolve oxidized sulfur compounds while maintaining low miscibility with the fuel phase.

Table 2: Summary of products results for light gasoil and heavy gasoil in Karbala and MRC refineries.

| Products     | Before Treating | Karbala Refinery             | MRC Refinery           |
|--------------|-----------------|------------------------------|------------------------|
| Light gasoil | 1.9 wt. %       | 6 ppm<br>using hydrotreating | 3.5 ppm<br>using ODS   |
| Heavy gasoil | 2.68 wt.%       | Not available                | 0.37 wt.%<br>using ODS |

Analytical results, obtained using gas chromatography (GC-MS) and total sulfur analyzers, confirmed that the sulfur content in the treated diesel dropped from an initial 15000 ppm to less than 5 ppm, achieving compliance with ultra-low sulfur diesel (ULSD) standards. Fourier-transform infrared spectroscopy (FTIR) further validated the oxidation of sulfur

compounds, showing clear peaks corresponding to sulfoxides and sulfones. Additionally, methanol's low boiling point facilitated its recovery and reuse, adding to the economic and environmental advantages of the process.

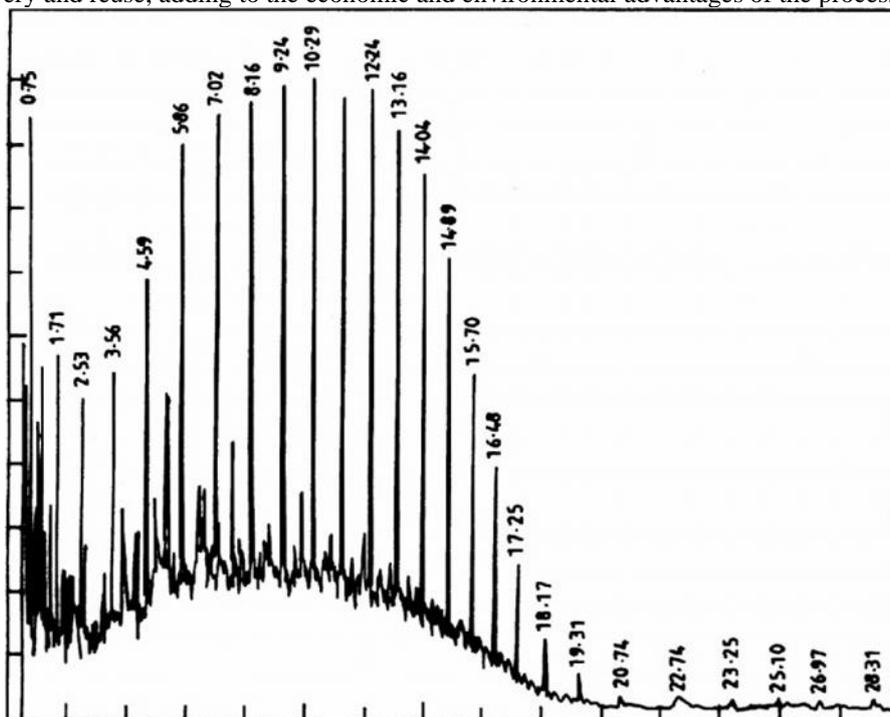


Figure 3: GC\_MS of treated Gasoil with ODS without effecting the chemical composition.

The study highlights the superiority of ODS with methanol extraction as a cleaner and more efficient alternative to traditional hydrotreating. The simplicity of the process, coupled with the near-complete sulfur removal achieved, suggests that this method could be readily implemented on an industrial scale to produce ultra-low sulfur fuels while reducing operational costs as shown in table 3.

Table 3: Comparison between ODS and Hydrotreating unit based on cost.

| Cost           | ODS | Hydrotreating |
|----------------|-----|---------------|
| Fixed Cost     | X   | 12X           |
| Operation Cost | Y   | 2.5Y          |

And greenhouse gas emissions associated with high-pressure hydrogen use. These results underscore the potential of methanol-based ODS to revolutionize sulfur removal in the energy sector with comfortable costs compared to hydrotreating units.

### Conclusions

In conclusion, the study demonstrates that oxidative desulfurization (ODS) using hydrogen peroxide and sulfuric acid as the oxidation system, combined with methanol as the extraction solvent, offers a highly efficient and sustainable approach to sulfur removal from diesel fuel. The process achieved an unprecedented 99% reduction in sulfur content, reducing sulfur levels from 500 ppm to less than 5 ppm, surpassing the efficiency of conventional hydrodesulfurization (HDS). The superior performance of methanol as an extraction solvent is attributed to its polarity and high solubility for oxidized sulfur compounds, enabling selective separation of sulfoxides and sulfones while maintaining minimal interaction with the fuel phase. Moreover, the process operates under mild conditions of 60°C and atmospheric pressure, significantly lowering energy requirements and eliminating the need for high-pressure hydrogen, thereby reducing costs and safety risks associated with traditional methods.

Analytical validation using gas chromatography (GC), total sulfur analyzers, confirmed the near-complete oxidation and removal of sulfur species, highlighting the robustness and reliability of this approach. Additionally, methanol's low boiling point allows for easy recovery and recycling, enhancing the economic viability and environmental sustainability of the process. The results establish methanol-based ODS as a transformative technology for producing ultra-low sulfur diesel (ULSD), aligning with stringent environmental regulations and the global push for cleaner energy solutions. Future research should focus on optimizing methanol recovery systems, scaling up the process for industrial applications, and exploring its adaptability to various fuel types. Overall, this study underscores the potential of ODS as a green, efficient, and economically competitive alternative to HDS, paving the way for a significant advancement in fuel desulfurization technologies.

## References

- [1] Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, 82(6), 607-631. [https://doi.org/10.1016/S0016-2361\(02\)00324-1](https://doi.org/10.1016/S0016-2361(02)00324-1)
- [2] Song, C. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel, and jet fuel. *Catalysis Today*, 86(1-4), 211-263. [https://doi.org/10.1016/S0920-5861\(03\)00412-7](https://doi.org/10.1016/S0920-5861(03)00412-7)
- [3] Campos-Martin, J. M., Capel-Sanchez, M. C., Perez-Presas, P., & Fierro, J. L. G. (2010). Oxidative processes of desulfurization of liquid fuels. *Journal of Chemical Technology & Biotechnology*, 85(7), 879-890. <https://doi.org/10.1002/jctb.2397>
- [4] Pourali, N., Miran Beigi, A. A., & Habibollahian, S. (2016). Efficient deep desulfurization of diesel fuels by oxidation and extraction using hydrogen peroxide and organic solvents. *Energy & Fuels*, 30(7), 5591-5598. <https://doi.org/10.1021/acs.energyfuels.6b00740>
- [5] Chica, A., Corma, A., & Miguel, P. J. (2006). A study of the applicability of oxidative desulfurization to be combined with FCC for reducing the sulfur content in fuels. *Journal of Catalysis*, 242(2), 299-308. <https://doi.org/10.1016/j.jcat.2006.06.018>
- [6] Wang, L., Yang, F., Yu, L., Xu, Y., & Zhang, Q. (2007). Deep desulfurization of diesel fuel by extraction with [BF<sub>4</sub>]-based ionic liquids. *Green Chemistry*, 9(6), 593-599. <https://doi.org/10.1039/B702649A>
- [7] Al-Shahrani, F., Xiao, T., Llewellyn, S. A., Barri, S. A. I., Jiang, Z., Shi, H., & Green, M. L. H. (2007). Desulfurization of liquid fuels using selective oxidation. *Catalysis Today*, 117(4), 293-299. <https://doi.org/10.1016/j.cattod.2006.05.041>
- [8] Eberhardt, T. L., & Min, S. (2008). Evaluation of oxidation and extraction in the desulfurization of fuels. *Industrial & Engineering Chemistry Research*, 47(9), 3345-3350. <https://doi.org/10.1021/ie070691z>
- [9] Yan, X., Wang, J., Liu, R., & Nie, Y. (2013). Advances in oxidative desulfurization of fuels with ionic liquids. *Chemical Engineering Journal*, 228, 729-746. <https://doi.org/10.1016/j.cej.2013.05.035>
- [10] Shiraiishi, Y., Tachibana, K., & Hirai, T. (2002). Oxidative desulfurization process utilizing hydrogen peroxide and methanol as extraction solvent. *Fuel Processing Technology*, 77-78, 243-248. [https://doi.org/10.1016/S0378-3820\(02\)00097-5](https://doi.org/10.1016/S0378-3820(02)00097-5)
- [11] Ma, X., Velu, S., & Song, C. (2005). A review of the selective oxidation and extraction of sulfur compounds for ultra-clean fuels. *Industrial & Engineering Chemistry Research*, 44(4), 946-955. <https://doi.org/10.1021/ie0401144>
- [12] Monticello, D. J. (2000). Biodesulfurization and the upgrading of petroleum distillates. *Current Opinion in Biotechnology*, 11(6), 540-546. [https://doi.org/10.1016/S0958-1669\(00\)00147-9](https://doi.org/10.1016/S0958-1669(00)00147-9)