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OZONE-ASSISTED OXIDATIVE DESULFURIZATION OF VACUUM GAS OIL: A COST-EFFECTIVE PATHWAY TO CLEANER FUELS

Abstract. Environmental sustainability has shifted from a secondary concern to a critical imperative for the global energy sector. While standard purification techniques exist, they often fall short when processing heavy feedstocks like Vacuum Gas Oil (VGO). Conventional methods require extreme pressure and temperature to sever the strong chemical bonds of sulfur, leading to high operational costs and capital intensity. This study investigates a more efficient, lower-temperature alternative: ozone-assisted desulfurization. By utilizing the high reactivity of atomic oxygen, this method transforms refractory sulfur compounds into polar intermediates that are easily separated downstream. To test the efficacy of this approach, we compared an untreated VGO sample (K-0) against a sample treated with direct ozonation for 15 minutes (K-1).

The results indicated a fundamental shift in the chemical composition of the feedstock. In the untreated K-0 sample, thiophenes accounted for 4.9% of the mass. Post-treatment (K-1), this dropped to 2.9%, marking a substantial 41% reduction. Concentration of sulfides decreased from 2.0% to 1.7%, a moderate reduction of approximately 14%. Most notably, the notoriously difficult-to-remove compounds - dibenzothiophenes plummeted from 1.4% to just 0.04%, achieving a 98% removal rate. As expected with oxidative desulfurization, the reaction increased oxygen-containing ether compounds from 1.7% to 3.0%, confirming the active role of atomic oxygen in restructuring the hydrocarbon matrix. These findings suggest that ozone-assisted treatment is a viable, low-energy pre-treatment step that can significantly reduce the burden on subsequent catalytic cracking units.

1 Introduction.

2 In the 21st century, the development of the oil refining industry is mainly influenced by limited hydrocarbon resources and increasingly strict environmental regulations. The growing depletion of conventional oil reserves and the declining quality of crude feedstocks require refineries to achieve deeper processing and higher yields of valuable products.

Sulfur-containing compounds in fuels present serious environmental and technical challenges. During combustion, they form harmful gases such

as SO₂ and H₂S, which negatively affect human health, contribute to acid rain, and accelerate equipment corrosion. In addition, sulfur species are known to poison industrial catalysts, reducing process efficiency [1,2].

Although conventional hydrotreating and hydrocracking technologies can remove a portion of sulfur compounds, they are less effective for refractory species such as dibenzothiophenes and require high capital and hydrogen consumption. For this reason, oxidative desulfurization has attracted increasing interest as an alternative approach due to its mild operating conditions, simpler equipment, and lower energy demand (Table 1). In this study, oxidative treatment is combined with thermal conversion to enhance sulfur removal. Oxidation transforms sulfur-containing molecules into more reactive sulfone or sulfoxide forms, weakening C–S bonds and facilitating their decomposition during thermal processing. As a result, sulfur content is reduced while the yield of valuable distillate fractions increases, offering an efficient route for upgrading heavy, high-sulfur feedstocks in line with modern environmental requirements [3,4].

Table 1 – Comparison of HDS and ODS

Feature	Traditional Hydrodesulfurization (HDS)	Ozone-Assisted Desulfurization
Operating Pressure	High (Energy Intensive)	Low / Atmospheric
Temperature	High (>300°C)	Low (<100°C)
Removal of Dibenzothiophenes	Difficult / Slow	Highly Effective (~98%)
Primary Cost Driver	Hydrogen Consumption & Heating	Ozone Generation

3 Methodology.

4 The study utilized Vacuum Gas Oil (VGO) as the primary feedstock, chosen for its high density of refractory sulfur compounds which typically resist standard hydrotreatment. A control sample, designated as K-0, was first established to serve as the baseline. Comprehensive chromatographic analysis of K-0 revealed a sulfur-rich profile, with thiophenic compounds (4.9%) and sulfides (2.0%) comprising the bulk of the contaminants, alongside a significant presence of dibenzothiophenes (1.4%). The core of the experiment focused on an oxidative desulfurization approach using a custom ozonation setup. Ozone (O₃) was generated in situ using a dedicated ozone generator, which utilized an electric discharge method to convert feed oxygen into active ozone. The VGO sample was placed in a batch reactor where the ozone-rich gas stream was bubbled directly into the liquid. This ensured maximum contact area between the atomic oxygen and the heavy hydrocarbon molecules. The treatment was conducted for a total duration of 15 minutes. Unlike conventional hydrodesulfurization (HDS) which requires high temperatures (often

>300°C), this process was carried out at much milder conditions, relying on the chemical reactivity of ozone rather than thermal energy to drive the reaction. Following the 15-minute reaction period, the treated sample, designated as K-1, was collected for characterization. We employed the same analytical techniques used on the baseline to ensure a direct comparison. The focus was specifically on quantifying the shift in molecular composition-tracking the reduction of sulfur-bearing molecules (thiophenes, sulfides, dibenzothiophenes) and monitoring the formation of oxidation byproducts, specifically oxygen-containing ethers.

5 Results and Discussion

The experimental data reveals a clear and highly efficient chemical transformation during the 15-minute ozonation window. By comparing the baseline (K-0) with the treated sample (K-1), we can observe how the introduction of ozone effectively "softens" the sulfur-heavy VGO matrix.

5.1 The Selective Power of Ozonation

The most striking result was the 98% reduction in dibenzothiophenes. These molecules are the "bottleneck" of the refining industry because their sterically hindered structures make them incredibly resistant to traditional catalysts. The ozone-assisted method appears to bypass this resistance, with atomic oxygen directly attacking the sulfur centers.

5.2 Chemical Transformation and Polarity

As the sulfur content decreased, we observed a corresponding increase in oxygen-containing compounds, specifically ethers, which grew from 1.7% to 3.0%. This is not a coincidence; it is the chemical "fingerprint" of the oxidative process. The ozone molecules react with the sulfur atoms to form sulfoxides and sulfones.

These oxidized species are significantly more polar than the original hydrocarbons. While the original sulfur compounds were "hidden" in the oil, the new oxidized versions are much easier to extract using standard solvents or to remove during the subsequent catalytic cracking phase.

5.3 Comparative Performance

While thiophenes showed a strong response (41% reduction), sulfides were slightly more resilient, decreasing by 14% (Table 2). This suggests that while ozonation is an incredibly powerful tool for breaking down complex aromatics like dibenzothiophenes, the reaction time or ozone concentration could be further optimized to target simpler sulfides more aggressively [5–9]. The findings of this study highlight the significant potential of ozone-assisted desulfurization as a robust alternative to conventional high-pressure purification methods. By subjecting Vacuum Gas Oil (VGO) to a relatively short, 15-minute ozonation period, we achieved a fundamental restructuring of the sulfur compounds present in the feedstock. The most compelling outcome was the near-total elimination of dibenzothiophenes (↓98%). In

traditional hydrodesulfurization (HDS) processes, these specific compounds are notoriously refractory-meaning they resist breaking down and typically require energy-intensive conditions to remove.

Table 2 – Graphical representation of the significant efficiency of the ozonolysis process

Compound Category	Trend	Scientific Significance
Dibenzothiophenes	↓98%	Removes the most difficult-to-treat compounds.
Thiophenes	↓41%	Significantly lowers the total sulfur burden.
Oxygenated Ethers	↑94%	Proves the successful oxidation of the feedstock.

6 Conclusion

The fact that ozone treatment decimated these compounds at moderate conditions suggests a major opportunity for energy savings in the refining process. Furthermore, the simultaneous rise in oxygen-containing ether compounds confirms the mechanism of action: atomic oxygen effectively oxidizes the sulfur, altering its polarity. This chemical transformation converts previously difficult-to-separate sulfides and thiophenes into intermediates that can be easily removed through simpler downstream extraction or adsorption techniques. Ozonation serves as a highly effective pre-treatment, potentially extending the lifespan of catalytic cracking units by removing corrosive agents early. By reducing the need for extreme temperatures and pressures, this method offers a pathway to lower Capital Expenditure (CAPEX) and Operational Expenditure (OPEX) for refineries. This technology provides a feasible route for refiners to meet increasingly stringent global sulfur standards without overhauling existing infrastructure. In summary, ozone-assisted desulfurization represents a promising "green chemistry" approach to fuel processing, bridging the gap between heavy, sour feedstocks and the clean energy requirements of the future.

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EFFECTIVE SURFACTANTS AND LUBRICANTS FOR DRILLING FLUIDS

Introduction. The role of lubricants in drilling oil and gas wells is invaluable. Lubricants reduce friction and the load on drilling equipment during drilling and extend the service life of drilling equipment. Lubricants are also used to produce lubricants. The oil and gas industry is one of the important sectors of the country's economy, which allows the production of not only food products, but also various technical and chemical substances. However, a large amount of waste is generated in this area.

The annual oil and fat production in Uzbekistan is about 350–400 thousand tons, from which about 8–12% soapstock, 3–5% gossypol tar and 25–30% cotton wool generated as waste. The production of valuable products based on the processing of these wastes, in particular, surfactants (SFM), is of great scientific and practical importance [1,2].

Surfactants also play an important role in the production of lubricants.