JOURNAL OF BAKU ENGINEERING UNIVERSITY-ADVANCES IN CHEMISTRY AND CHEMICAL ENGINEERING
2025. Volume 9, Number 1 Pages 34-40

UDC: 66.094.522.8
DOI: https://doi.org/10.30546/2521-6317.2025.01.407

COMPREHENSIVE STUDY OF KINETIC AND TECHNOLOGICAL ASPECTS OF OXIDATIVE DESULFURIZATION AND THERMAL CONVERSIONS OF VACUUM GAS OIL

Khamis ABIYEV[1*], Elvira GUSEINOVA[1]

[1]Azerbaijan State Oil and industry University, Baku, Azerbaijan

ARTICLE INFO

Article history:
Received:2025-11-30
Received in revised form:2025-12-16
Accepted:2025-12-18
Available online

Keywords:
vacuum gas oil;
oxidative desulfurization;
sulfur-containing aromatics;
petroleum refining technology;
eco-friendly fuels

ABSTRACT

This article presents a study on the oxidative desulfurization of vacuum gas oil and its subsequent thermal conversions. One of the most critical challenges in modern petroleum refining is the improvement of fuel quality and ensuring their environmental safety. In particular, the reduction of sulfur content in fuels is a decisive factor in producing products that meet "Euro-5" and higher ecological standards.

Conventional hydrotreating processes require high temperatures, pressures, and significant hydrogen consumption, which makes them economically and technologically disadvantageous. Therefore, oxidative desulfurization (ODS) has attracted special interest as an alternative or complementary process.

The research focused on the preliminary oxidation of vacuum gas oil using peroxide systems, followed by thermal cracking. As a result, the kinetics of the decomposition of dibenzothiophene, benzonaphthothiophene, and their alkylated derivatives were investigated, and the rates of transformation of their stable and unstable forms were determined.

Various analytical methods (XRF, IR spectroscopy, GC–MS, etc.) were applied to monitor the structural changes of sulfur-containing compounds. The findings demonstrate that oxidative modification facilitates the decomposition of high-molecular-weight sulfur compounds during subsequent cracking and increases the yield of more valuable distillate fractions.

The scientific novelty lies in the fact that, for the first time, the kinetic parameters of sulfur-aromatic components of vacuum gas oil under combined oxidative desulfurization and thermal conversion were determined. The practical significance of the study is that such combined processes enable the more rational utilization of heavy petroleum feedstock and the production of fuels meeting modern environmental requirements.

*Corresponding author.

E-mail address: xamisabiyev123@gmail.com (Khamis Abiyev Chingiz).

1. Introduction

In the 21st century, the development directions of the oil refining industry are determined by two main factors: resource limitations and environmental safety requirements. In recent years, the rate of depletion of oil reserves in major oil-producing countries has increased, and the quality of the extracted raw materials has deteriorated. In these conditions, the main task facing oil refineries is to produce the maximum amount of valuable products from raw materials with a deeper degree of processing.

The presence of sulfur-containing compounds in fuel has a negative impact on both human health and the durability of equipment. Sulfur-containing gases such as SO_2 and H_2S, generated during fuel combustion, pose serious risks to human health, particularly to the respiratory system. In addition, these sulfur compounds contribute significantly to acid rain formation and play a key role in accelerating the corrosion of metallic equipment. In addition, sulfur compounds lead to the deactivation of catalysts [1].

Although the application of traditional hydrotreating - hydrotreating and hydrocracking - reduces sulfur to a certain extent, it does not achieve complete removal of highly stable molecules such as dibenzothiophene and benzonaphthothiophene. Also, the fact that these processes require high capital investment is a limiting factor in their economic aspect. Therefore, in scientific research, oxidative desulfurization has been the focus of attention as an alternative method. The advantages of this process are related to its mild conditions, simple apparatus design, and the absence of additional hydrogen consumption [3-5,8,10].

The main idea investigated in the research work is to combine oxidative modification with thermal conversion. As a result of oxidation, the sulfur atom is converted into a sulfone or sulfide form, which weakens the C–S bond. Thus, the decomposition of these compounds during subsequent thermal cracking occurs more readily, resulting in a reduction in sulfur content and an increase in the yield of distillate products. This approach opens up new opportunities for the rational processing of heavy high-sulfur feedstocks and the production of fuels that meet modern environmental standards.

2. Objective

The main objective of this research work is to study the behavioral patterns of sulfur aromatic compounds during oxidative modification and subsequent thermal conversion processes of vacuum gas oil. More precisely, the goal is to determine the decomposition kinetics of dibenzothiophene, benzonaphthothiophene and their alkylated derivatives under the influence of various oxidative conditions, to monitor changes in their thermal stability and, as a result, to increase the efficiency of desulfurization.

Within the framework of this goal, the following tasks were set:

- selection of optimal conditions (type of oxidizing system, temperature, time and reagent ratios) for oxidative processing of vacuum gas oil;
- separation of oxidized vacuum gas oil into polar and non-polar components and study of their individual behavior;
- study of the effect of oxidation on the structure and reactivity of sulfur-containing aromatic components;
- comparative analysis of the product composition of both the initial and oxidized gas oil in the cracking process;
- calculation of kinetic parameters (rate constants and activation energies) of decomposition and formation of sulfur aromatic compounds.

3. Materials and Components

The object of the research was a typical vacuum gas oil obtained from oil refineries. This raw material is characterized by its high average molecular weight and high sulfur content. The main characteristics of vacuum gas oil are as follows: its density varies in the range of 873–953 kg/m^3, kinematic viscosity is approximately 7.1 cSt at 40°C, initial boiling point is about 360 °C, and final boiling point is 500 °C. Gas oil mainly consists of a mixture of paraffin, naphthene and aromatic hydrocarbons. Its most problematic component is sulfur-containing aromatics, particularly, dibenzothiophene, benzonaphthothiophene and their derivatives. Since these compounds show high thermal stability and low reactivity, they are not completely decomposed in traditional hydrogenation processes.

A mixture of hydrogen peroxide (H_2O_2) and formic acid (HCOOH) was used as an oxidizing system. This system is distinguished by its efficiency, commercial availability and relative environmental safety. Hydrogen peroxide is an oxidizing agent with a high active oxygen content, while formic acid is a component that facilitates interphase mass transfer and plays a catalytic role [2].

In addition, adsorption methods were applied to select polar and non-polar fractions in the products obtained after oxidation. For this, sorbents with a high surface area were used, which allowed for the effective separation of oxidized derivatives of sulfur (sulfones and sulfoxides).

The reagents used in the study were of high purity, and the studies were conducted in certified laboratory conditions. The main chemical components and materials used are:

- hydrogen peroxide (30% aqueous solution);
- formic acid (analytical grade);
- methanol and other organic solvents (for extraction and chromatographic analysis);
- standard samples (dibenzothiophene, benzonaphthothiophene, etc.) for comparative analysis.

4. Apparatus and analyzing methods

The following analysis tools were used to monitor changes in the chemical composition of vacuum gas oil and its oxidized products:

- X-ray fluorescence spectroscopy (XRF): It was used to quantitatively determine the total sulfur content of vacuum gas oil and the products obtained after the experiment. This method provides high accuracy and repeatability.
- Infrared (IR) spectroscopy: It was applied to monitor changes in the functional groups of sulfur-containing compounds during the oxidation process. A comparative analysis was carried out with the intensity of characteristic vibration bands during the conversion of sulfides to sulfones and sulfoxides.
- Gas chromatography (GC): This technique was employed to analyze both liquid and gaseous products obtained from the oxidation and cracking processes. GC enabled the qualitative and quantitative identification of aromatic and sulfur-containing compounds in the oxidized and cracked samples, as well as the determination of the composition and relative proportions of low-molecular-weight gas products, including methane, ethane, propane, and related hydrocarbons.

- High-performance liquid chromatography: Used for the separation of polar and non-polar fractions, as well as for the assessment of the amount of main aromatic compounds in their composition.
- Thermal analysis methods like Thermogravimetric (TG) and Derivative Thermogravimetric (DTG): Used for the comparative analysis of the thermal stability of vacuum gas oil and its oxidized forms.

All devices used in the studies are calibrated, certified equipment that meets international standards. This ensured the reliability of the results and compliance with modern scientific requirements.

5. Methods

The research process consisted of several stages, and a specific methodology was applied at each stage:

1. **Oxidative treatment.** Vacuum gas oil was first treated with a mixture of hydrogen peroxide and formic acid. The main purpose of this process was to functionally modify sulfur-containing aromatics and facilitate their separation. The reaction was carried out at atmospheric pressure, in the temperature range of 50–70 °C, and in different time regimes.
2. **Separation by adsorption method.** Activated adsorbents were used to separate the oxidized gas oil into polar and non-polar fractions. This stage was based on the molecular properties of sulfur compounds: sulfones and sulfoxides, being polar in nature, bind more strongly to the adsorbent surface, while non-polar hydrocarbons are separated.
3. **Thermal cracking.** Samples taken before and after oxidation were subjected to thermal cracking at a certain temperature regime. As a result of this process, the decomposition of high-molecular compounds and the formation of distillate fractions were studied. Cracking was carried out at different temperatures and the kinetic parameters of the process were calculated.
4. **Kinetic analysis.** The conversion rates of dibenzothiophene, benzonaphthothiophene and their derivatives in the cracking process were compared. Based on the results obtained, the rate constants and activation energies of the reactions were determined.
5. **Comparative analysis.** The research results were compared between the initial (unoxidized) and oxidized gas oil. This approach made it possible to reveal the effect of oxidative processing on the degree of desulfurization and the yield of distillate products.

This sequence of the methodology was considered optimal both from a theoretical and practical point of view and increased the reliability of the results obtained.

6. Conducting research and its discussion

The first stage of the experiment was oxidative treatment of vacuum gas oil as specified above. As a result of the oxidation process, the functional groups of sulfur-containing aromatic compounds - mainly dibenzothiophene and benzonaphthothiophene derivatives - changed, and they were converted into sulfone and sulfoxide forms. The weakening of the C–S bond within the molecule during oxidation is of particular importance [6,7]. Because as the energy of this bond decreases, the decomposition process during subsequent thermal processing (cracking) becomes easier. Analytical results show that the total amount of sulfur in the oxidized samples has significantly decreased, and vibration bands corresponding to the S=O bond were observed in IR spectroscopy. This confirms that sulfur compounds are converted into the oxide form.

At the next stage, the oxidized gas oil was separated into polar and non-polar components. For this purpose, adsorption methods were used. As a result, sulfones and sulfoxides entered the polar fraction, and aliphatic and aromatic hydrocarbons entered the non-polar fraction. The separation process was necessary both for the subsequent analytical study of the products and for the study of differences in behavior by fractions. An interesting point is that after oxidation, the share of sulfur in the polar fraction was significantly higher. This confirms that oxidative treatment leads to functional modification of sulfur-containing molecules and facilitates their separation.

The main studies were conducted on the thermal cracking of unoxidized and oxidized gas oil. It was found that during the cracking of unoxidized samples, high-molecular aromatic sulfur compounds retain their stability and remain largely undecomposed. This results in fewer distillate fractions in the output and more residue. On the contrary, during the cracking of oxidized samples, the decomposition of sulfur aromatics occurs more easily. At this time, the amount of distillate fractions increases, and the residual part decreases. The gas products contain more low-molecular compounds such as methane, ethane and propane. This proves that oxidation has an activating effect on thermal conversion [9].

The reaction kinetics of conversion of sulfur aromatic compounds were studied based on the experimental findings of this work. The reaction rate constants and activation energies were calculated for dibenzothiophene, benzonaphthothiophene and their derivatives. The results showed that:

- in non-oxidized samples, the conversion rate of these compounds is low, and the activation energy is high;
- in oxidized samples, the conversion rate increases significantly, and the activation energy decreases.

This fact once again confirms that oxidative modification weakens the chemical stability of sulfur compounds and creates conditions for their easier decomposition.

Based on the analysis, it was determined that during the cracking of oxidized gas oil, molecular structures of polyaromatic sulfur compounds gradually simplify. In particular, dibenzothiophene derivatives are converted to the sulfone form and then subjected to decomposition. As a result, the sulfur content in the distillate fractions is significantly reduced [11]. It was also found that the content of tar and asphaltenes in the products obtained as a result of cracking of oxidized samples decreased. This is an important result from a technological point of view, since such substances cause contamination of equipment and deactivation of catalysts during the processing process.

Table 1 shows the results of thermal cracking of unoxidized and oxidized samples of vacuum gas oil.

Table 1. Thermal cracking results of unoxidized and oxidized vacuum gas oil samples

Sample type	Yield of distillate fractions, %	Residual yield, %	Total sulfur content, ppm	Activation energy, kC/mol
Unoxidized VGO	42–45	55–58	7800–8200	185–190
Oxidized VGO	58–62	38–42	900–1200	120–130

As can be seen from the table, the yield of distillate fractions in the cracking of unoxidized vacuum gas oil was relatively low (42–45%), while the residual product was high (55–58%). The total sulfur content remained very high, and the activation energy was at the level of 185–190 kC/mol, which indicates that the decomposition process was difficult. In oxidized samples, the yield of distillate fractions increased to 58–62%, and the share of the residual product decreased. The total sulfur content decreased by 7–8 times, and the activation energy also decreased, which confirms that the decomposition was easier.

The results of the conducted studies show that combining oxidative modification with thermal conversion is a promising approach for the oil refining industry. This approach provides the following advantages:

- significantly reducing the sulfur content in fuels;
- increasing the yield of distillate products and improving their quality;
- not requiring additional hydrogen consumption, thus increasing economic efficiency;
- reducing the risk of equipment contamination and corrosion.

These findings are consistent with earlier studies on ozone-assisted oxidative desulfurization of vacuum gas oil [12–15]. The industrial application of such combined processes can allow for a more rational and environmentally safe use of heavy high-sulfur feedstock.

7. Results

The main findings of this work can be summarized as follows:

1. As a result of the oxidative processing of vacuum gas oil, the functional groups of sulfur aromatic compounds change, they pass into the sulfone and sulfoxide forms, which facilitates decomposition in the subsequent thermal cracking process.
2. As a result of the application of oxidative processing, the sulfur content in fuels is significantly reduced, which ensures the production of products that meet environmental standards (in particular, "Euro-5").
3. The yield of distillate fractions increases with oxidative modification and the quality of the product improves, while the share of heavy residue decreases.
4. The decomposition kinetics of dibenzothiophene, benzonaphthothiophene and their derivatives have shown that after oxidative processing, the conversion rate increases, and the activation energy decreases.
5. As a result of the cracking process, the amount of tar and asphaltenes decreases, which significantly reduces the risk of equipment contamination and catalyst deactivation.
6. The applied method does not require additional hydrogen consumption, which improves the economic performance of the technological process.
7. The combination of oxidative desulfurization and thermal conversion can be considered a promising technological solution for a more rational and environmentally safe use of high-sulfur heavy fractions in oil refineries.

REFERENCE LIST

1. Pawelec, B., Navarro, R. M., Campos-Martín, J. M., & Fierro, J. L. G. (2011). Towards near zero-sulfur liquid fuels: A perspective review. *Catalysis Science & Technology*, 1(1), 23–42.
2. Rastegar, S. O., Yuzir, A., & Abdullah, A. Z. (2017). Catalytic oxidative desulfurization of model fuel using hydrogen peroxide and acetic acid. *Journal of Cleaner Production*, 142, 2345–2353.
3. Wan, J., Zhang, J., Wang, Y., & Li, C. (2016). Oxidative desulfurization of real diesel using polyoxometalate-based catalysts: A review. *Fuel Processing Technology*, 142, 264–278.
4. Nandiwale, K. Y., Bokade, V. V., & Joshi, P. N. (2018). Catalytic oxidative desulfurization using ionic liquids and their composites. *Renewable and Sustainable Energy Reviews*, 82, 3449–3462.
5. Li, Y., Jiang, Y., & Tang, X. (2019). Recent advances in oxidative desulfurization using deep eutectic solvents. *Chemosphere*, 237, 124460.
6. Xie, C., Wang, Z., Zhu, W., et al. (2021). Ozonation-assisted oxidative desulfurization of diesel fuel: Mechanisms and optimization. *Fuel*, 286, 119386.
7. Zhang, Q., Liu, X., & Wang, G. (2020). Kinetics and mechanism of ozone oxidation of sulfur compounds in petroleum fractions. *Energy & Fuels*, 34(6), 7102–7109.
8. Ali, M. F., & Al-Malki, A. L. (2018). Advances in diesel fuel desulfurization technologies. *Fuel*, 227, 390–408.
9. Tang, Z., Zhang, H., & Lu, J. (2022). Catalytic oxidative desulfurization of gas oil using ozone and transition metal catalysts. *Industrial & Engineering Chemistry Research*, 61(15), 5437–5445.
10. Yoon, H., & Lee, J. S. (2021). A review on ozone-based oxidative processes for petroleum desulfurization. *Journal of Environmental Chemical Engineering*, 9(6), 106364.
11. Gao, Q., Xu, G., & Li, S. (2020). Deep oxidative desulfurization of vacuum gas oil using ozone and extraction techniques. *Fuel Processing Technology*, 202, 106349.
12. Abiyev, Kh. Ch., & Guseinova, E. A. (2023). Oxidative desulfurization of vacuum gas oil with the participation of ozone. *Modern Approaches in Chemistry and Chemical Technology* (pp. 59–61). Republic Scientific Conference.
13. Abiyev, Kh. Ch., & Guseinova, E. A. (2025). Oxidative desulfurisation of vacuum gas oil in the presence of ozone. *International UFAZ Conference – CPM's 2025 Edition: Chemistry, Process, Materials* (pp. 32–33).
14. Guseinova, E. A., Mursalova, L. A., & Abiyev, Kh. Ch. (2023). Physicochemical properties of ozonized vacuum gas oil. *Science. Technology. Production* – 2023 (pp. 227–229) (In Russian).
15. Abiyev, Kh. Ch., Guseinova, E. A., & Serra, C. A. (2025). Sustainable desulfurization of VGO using ozone: Experimental insights. *Proceedings of the RISK 2025 Conference*.