

# **Reduction of Sulphur in Naptha Using Oxidative Desulfurization**

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### **1.Introduction**

### 1.1 History & Background

Crude oil functions as the fundamental material which enables the production of petroleum and diesel fuels. The original petroleum substance includes various unwanted substances where sulphur stands among them. The presence of different substance types exists without any exceptions. The different forms of sulphur include hydrogen sulfide and mercaptans and thiophenes which represent incompatible chemical compounds in fuel usage. Petroleum must undergo a refining process that removes sulphur because otherwise the transport fuel will contain this chemical substance. The burning process of fuel produces sulfur dioxide (SO<sub>2</sub>) as well as emissions with sulfur as their base element. Ground-level emissions of sulfur-bearing materials generate acid rain along with harmful health effects during breathing and additional environmental hazards. These contaminants affect the functional quality of central conversion systems which exist in both automobiles and industrial equipment. So, it's a pretty big deal.

From the beginning governments and worldwide organizations began intervening because of this matter. The EPA of the U.S. joins European Euro standards and the international organization IMO to establish that fuel standards require improvement. Reaction zones have established ruling fuel sulphur content restrictions at the incredibly low standard of less than 10 parts per million. That's tiny. Fuel producers now need to make sulfur removal their priority because they no longer have any optional choice. It matters which sulphur compounds exist within oil because their removal properties differ. Both straightforward and highly persistent sulfur impurities exist throughout the naphtha product. The removal process proves complicated due to high expenses. It is now crucial for industries to discover effective advanced methods for eliminating sulphur from fuels at reasonable costs. The removal of sulphur from petroleum products

remains a main focus for researchers who join forces with engineers to develop advanced solutions.

### 1.2 Importance of Naphtha Desulfurization

Within the petroleum refining operations alongside petrochemical operations naphtha functions as a key material. The production of high-octane gasoline and aromatic hydrocarbons including benzene toluene and xylene (BTX) needs catalytic reforming using naphtha as its starting material. Widespread industrial application of naphtha includes its use in steam cracking for ethylene and valuable olefin production that serves as material building blocks for plastics and synthetic materials. The processes containing sulfur compounds found in naphtha will suffer adverse effects toward their operations.

As trading transforms platinum-based catalysts used in catalytic reforming into inactive substances because of its potent poisoning power. Decomposition of the catalyst occurs as a result of sulfur traces so the process leads to decreased output while requiring more frequent catalyst regenerations and increased cost. Petrochemical cracking units experience equipment destruction and toxic gas emission and products contamination due to sulfur presence. The successful removal of sulfur from naphtha represents an absolute need for maintaining smooth refinery operations along with extended catalyst lifetime while reaching target product qualities.

The tightening regulatory controls on sulfur emissions from fuel products has led to increased market demand for desulfurized naphtha since it represents a cleaner component. Naphtha after desulfurization functions as a main component for creating ultra-low-sulfur gasoline (ULSG). Refiners need to eliminate sulfur compounds from naphtha in an efficient and cost-effective manner because this capability serves as both a technical necessity and a strategic market requirement for worldwide operational success and regulatory compliance.



# **1.3 Conventional Desulfurization Methods**

Refineries mainly use hydrodesulfurization (HDS) as their traditional standard procedure to remove sulfur compounds. The combination of sulfur catalysts with hydrogen molecules forms hydrogen sulfide (H<sub>2</sub>S) which then needs to be extracted from the process. HDS functions effectively to remove various sulfur species including aliphatic sulfur compounds and thiols because it is an established refinery technology. Benzothiophene together with dibenzothiophene show low sensitivity to hydrogenation during the treatment process whereby HDS technology loses its efficiency.

The HDS process needs demanding operational parameters such as hydrogen pressures between 30-130 bar along with temperatures of 300-400 °C and expensive catalysts based on molybdenum or cobalt on alumina. The necessary operation conditions affect both costs and energy consumption of HDS which makes this process less attractive for small and medium-scale refineries.

HDS exhibits poor selectivity as an operation method which causes valuable aromatic and olefinic hydrocarbons from the feed to disappear thus reducing the projected octane number of finalized fuel products. Processing naphtha for composition in gasoline blending and reforming demands keeping both olefins and aromatics present in the product.

The existing desulfurization methods require replacement by alternate procedures that handle refractory sulfur species while being both efficient and precise and requiring less energy consumption. The technology of oxidative desulfurization

(ODS) stands as a promising supplementary or standalone method which shows benefits in post-treatment of HDS effluents as well as processes where economic viability of HDS is limited.

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

The non-hydro processing process called ODS chemically transforms sulfur compounds into polar oxidized forms such as sulfoxides and sulfones through oxidation reactions. The oxidized species derived from the process become removable through standard methods comprising liquid–liquid extraction and adsorption or distillation. The implementation of ODS under ambient pressure at temperatures below 100°C provides operators with an attractive solution due to its mild operating conditions.

The sulfur compounds that remain resistant to hydrodesulfurization respond well to the treatment methods provided by ODS. Selective oxidation of thiophene benzothiophene and dibenzothiophene compounds occurs when employing suitable catalysts together with hydrogen peroxide ozone peracids and organic peroxides as oxidants. Transition metals like Mo, W, V and heteropolyacids together with metal-organic frameworks represent the catalyst base for ODS kinetics enhancement and selectivity improvement.

Modern refinery systems can integrate the modular ODS process as an additional unit along with their existing infrastructure. A combined desulfurization system utilizing HDS as the main treatment step followed by ODS provides ultra-low sulfur solution. ODS works best for small-scale decentralized processing of fuel because its selective chemistry functions under mild operating conditions. **1.5 Mechanism of Oxidative Desulfurization** 

The ODS mechanism executes its process through sequential oxidation and extraction steps. The hydrocarbon flow with sulfur compounds receives an oxidant as the initial process of this refinery procedure. The catalyst expedites how oxygen travels from the oxidant through the sulfur atom in organosulfur compounds during their transformation into either sulfoxides or sulfones. These oxidation processes take place best in polar solvent solutions which dissolve the oxidant and sulfur compounds better to increase both raw compound transport efficiency and reaction efficiency.

The combination of formic acid or tungstate together with hydrogen peroxide  $(H_2O_2)$  enables the reaction between sulfur and the oxidant to produce sulfone and sulfoxide end products. Dibenzothiophene reacts with the process to produce dibenzothiophene sulfone as its end product. The polar sulfone compound shows reduced hydrocarbon solubility and high



solubility in polar solvents so it can effectively be extracted through either solvent extraction or adsorption on suitable materials such as silica and activated carbon and zeolites.

The reaction executes rapidly and presents high selectivity. The reaction speed of oxidation emerges from both the sulfur compound characteristics and the oxidant-to-sulfur molar ratio and the catalyst selection as well as the reaction temperature. The ODS process for industrial use requires optimization through complete comprehension of dominant operational parameters. A set of recent research initiatives have incorporated solvent-free ODS together with emulsified systems and membrane-assisted separation technologies to enhance the efficiency and sustainable aspects of the process.

#### 1.6 Advantages of ODS

Traditional hydrodesulfurization technology has several advantages due to ODS. Refractory sulfur removal occurs through ODS under temperature ranges which include ambient conditions. Such operation demands minimal energy while lowering the cost of utilizing expensive high-pressure hydrogen systems. According to the present design the absence of hydrogen results in a process which provides better safety features and remote desulfurization capability for mobile units.

Hydrocarbons which include aromatics and olefins maintain their value because ODS promotes their preservation. The fuel characteristics remain intact through

ODS since it operates without hydrogenation thus preventing chemical changes that affect octane amounts or fuel features. The method's high selectivity proves crucial for chemical manufacturing including both naphtha processing for reforming purposes and blending operations of gasoline products.

The implementation of ODS technology enables the employment of environmentally friendly hydrogen peroxide as oxidants which breaks down into water and oxygen. Solid ODS catalysts which operate in the process can be regenerated or recycled to decrease operational waste. Industrial attraction towards ODS systems increases because of their capability to scale operations while functioning through continuous processing methods.

The ODS system allows for customization according to fuel specifications and operators can combine it with refining processes through integration as polishing units. These catalysts maintain high significance for future regulatory requirements because they deliver ultra-low sulfur products below 10 ppm standards.

### 1.7 Scope of Research

The research investigates whether oxidative desulfurization (ODS) represents an effective technique for sulfur reduction in naphtha. The research evaluates different oxidative agents along with reaction conditions and catalysing agents that turn organosulfur components into extractable sulfones. Response evaluations focus on determining reaction conditions particularly temperature along with oxidant quantity's reaction time and solvent choice for achieving maximum sulfur elimination with minimum hydrocarbon decay.

The study investigates both technological and economic factors which affect the implementation of ODS in industrial facilities. The study will outline the results of traditional hydrodesulfurization testing to demonstrate ODS system benefits along with its performance constraints and potential combining methods. This

research investigates both recent developments in catalyst innovations with hybrid systems together with emerging extraction techniques that enhance environmental sustainability of the process.

The study focuses on ODS naphtha treatment from a chemical perspective and application standpoint to aid cleaner fuel research development. Evaluating these findings could assist future organizations designing refineries while developing sustainable policies to speed up the worldwide transition toward clean and fuel-efficient production.



# 1.8 Significance of Desulfurization in Sustainable Fuel Production

As the world shifts towards cleaner energy and stricter environmental controls, desulfurization in refining processes is more critical than ever. Sulfur-bearing compounds in petroleum-derived fuels, such as naphtha, are enormous environmental and operational issues. Sulfur compounds emit sulfur oxides (SOx), primarily sulfur dioxide (SO<sub>2</sub>), upon combustion, which are toxic emissions producing acid rain, smog, and health problems. Sulfur in fuels also contaminates catalysts employed in petrochemical and refining processes, increasing the expense of maintenance and efficiency. In the grand scheme of sustainability, reducing sulfur content is not merely a matter of complying with environmental standards—it is a requirement for cleaner fuels that will fulfil global climate objectives and sustainable development policies.

Oxidative desulfurization (ODS) is a great substitute or addition to conventional hydrodesulfurization (HDS), particularly for lighter fuels such as naphtha where mild operating conditions are desired. In comparison to HDS, which requires high temperature, high pressure, and costly hydrogen, ODS can work under milder conditions, most likely atmospheric pressure and moderate temperature, using safe oxidants such as hydrogen peroxide or ozone.

### 2. REVIEW OF LITERAURE

**Kocal, J.A., and Brandvold, T.A. (2002)** developed research about sulfur compound removal from hydrocarbon streams utilizing oxidative desulfurization (ODS) as their primary method. The authors studied this method as a possible answer to the environmental hazards imposed by sulfur compounds found in fossil fuels alongside their adverse effects on refinery catalysts. The research paper examines numerous sulfur removal approaches with special focus on hydrodesulfurization (HDS) since HDS demonstrates limited success in eliminating sulfur from specific chemical compounds. According to the authors ODS represents a viable solution that employs oxidative chemistry to transform sulfur compounds into stripped-down substances including sulfoxides and sulfones together with different oxidized sulfur derivatives. The evaluation puts forward ODS's main benefits as a desulfurization method which runs at temperatures lower than HDS and performs on sulfur compounds that conventional removal approaches cannot handle. Within their study the authors investigate ODS reaction mechanisms by discussing the function of oxides including H2O2 and O2 and identify obstacles that must be resolved for industrial-scale ODS implementations. Kocal and Brandvold established the essential foundation for understanding oxidative desulfurization which positions it as an attractive and supporting process to traditional sulfur removal methods in petroleum industries.

Rao, T.V., Sain, B., Kafola (2007) along with other collaborators studied aldehyde and molecular oxygen systems for oxidative desulfurization (ODS) in research that presented an advanced desulfurization solution beyond standard methods. The authors analyse how aldehyde compounds function with molecular oxygen to achieve efficient sulfur compound oxidation in hydrocarbon streams. The research examined aldehyde and molecular oxygen-based systems to resolve drawbacks of hydrodesulfurization (HDS) because HDS requires high temperatures and pressures along with expensive catalysts yet remains less effective against specific kinds of sulfur compounds. Testing results demonstrate that aldehydebased ODS demonstrates satisfactory performance as a selective oxidizing agent for removing sulfur compounds including thiols, sulfides, and disulfides which transforms them into sulfoxides and sulfones. Aldehydes working with molecular oxygen enable an efficient oxidation process to perform under milder conditions since this method reduces both operational expenses and energy consumption in comparison to traditional approaches. This article provides comprehensive analysis of the reaction processes which show aldehydes function as electrophilic agents to help sulfur species undergo oxidation. The authors demonstrate that oxygen functions as a co-oxidant component which enhances the entire process efficiency. A key part of Rao et al.'s work identifies the problems stemming from this method but they emphasize maximizing reaction conditions and selecting right aldehydes and understanding system stability through different operational parameters. Research results show that aldehyde and oxygen systems form a sustainable and economical choice for oxidative desulfurization because they process multiple sulfur compounds at lower temperatures.



The research work makes an important addition to the development of environmentally friendly and cost-effective desulfurization methods for petroleum processing facilities.

**Ghosh P. Andrews A.T. Quann R.J. and Halbert T.R (2009)** developed a kinetic model to study the hydrodesulfurization process of Fluid Catalytic Cracking naphtha which enhanced sulfur compound behaviour understanding in catalytic processing. The authors dedicate their research to investigating the intricate sulfur transformations that happen through FCC naphtha catalytic HDS while studying this important petroleum industry material because it features numerous sulfur compounds. The developed kinetic model establishes a complex mechanism which depicts the rate of sulfur elimination in addition to the

conversion of thiol and sulfide and disulfide compounds into their hydrogenated final products. The model depends on experimental data analysis performed under different operating conditions consisting of temperature and pressure and hydrogen-to-feed ratio since these parameters determine sulfur removal effectiveness. This scholarly work successfully emulates the complex sulfur chemical behaviour in HDS operations by considering simultaneous competitiveness between reactions along with catalyst degradation effects throughout operational time. The authors highlight the necessity of studying kinetic parameters for optimizing the operational conditions that lead to better HDS unit performance throughout refining processes. Through systematic analysis the model investigates how different sulfur species interact with the catalyst surface which enables a better understanding of how specific sulfur compounds behave distinctively when adsorbing and reacting on the surface thus influencing the desulfurization outcome. According to the authors Ghosh et al. their kinetic model demonstrates potential application in enhancing both the operational design and performance of HDS units to achieve better sulfur removal while improving end-product quality. The presented research expands sulfur system comprehension in catalytic processes through valuable information for process improvements.

González-García, O., and Cedeño-Caero (2009) is concerned with the use of vanadium-molybdenum (V-Mo)-based catalysts for oxidative desulfurization (ODS) of naphtha and diesel fuel. This provides a promising method of sulfur removal from these critical fuels. Their research is part of the expanding body of literature focused on the development of new desulfurization processes that can overcome the limitations of conventional hydrodesulfurization (HDS), particularly in the treatment of difficult-to-desulfurize sulfur compounds under milder conditions. The authors investigate the performance of V-Mo-based systems to oxidize sulfur compounds such as dibenzothiophene (DBT) and analogous compounds, which are typically hard to treat using HDS. In experiments, they demonstrate that V-Mo catalysts are highly selective and efficient in the conversion of sulfur compounds to sulfones and sulfoxides, which can then be extracted or adsorbed. The research investigates the effect of various factors on catalytic activity, such as reaction temperature, oxidant concentration (e.g., hydrogen peroxide), and catalyst composition, and establishes the optimal conditions that maximize sulfur removal. González-García and Cedeño-Caero also describe the structural and electronic properties of the V-Mobased catalysts and highlight the synergistic interaction between vanadium and molybdenum oxides that boosts their oxidation activity. Their findings indicate that these catalysts can efficiently operate under normal pressure and lower temperatures, making them a more energy and environmentally friendly option compared to HDS. The authors also highlight the potential of large-scale process up-scaling and industrialization, particularly for the production of ultra-low sulfur fuels that satisfy stringent environmental regulations. Overall, this research provides valuable information on the development of catalysts for ODS and demonstrates that V-Mo-based systems are suitable candidates for advanced fuel desulfurization technology.

**Abro, R., Abdeltawab, A.A. (2009)** paper provides an overview of sulfur removal from fuels, focusing on ionic liquids (ILs) as a new and environmentally friendly option. The article highlights the growing need for desulfurization methods that are more environmentally friendly and work under less harsh conditions than the standard hydrodesulfurization (HDS) process. The authors give a brief summary of several desulfurization procedures, including the benefits of ionic liquids due to their exceptional qualities, such as low evaporation, high thermal stability, and tunable ability to dissolve materials. The article provides an overview of how ionic liquids preferentially remove sulfur-containing compounds—primarily aromatic sulfur species like thiophene, benzothiophene, and dibenzothiophene—from hydrocarbon mixtures. The review



is also an overview of how the IL structure influences the efficiency with which they extract, taking into account the functional groups, cation-anion pairs, and hydrogen bonding. The authors further compare IL-based extraction with conventional solvents and other novel extracting techniques and prove that ILs are generally superior in selectivity and capacity to extract sulfur compounds and could be recyclable and reusable, which makes them economically and ecologically sound. The review is also an overview of hybrid systems where ionic liquids are combined with other techniques such as oxidative desulfurization (ODS) to enable enhanced removal of sulfur. They cite limitations such as high production cost, thickness concerns, and the necessity for efficient regeneration methods, and provide recommendations for future work to overcome the limitations. In general, Abro and his co-authors provide a future-oriented and comprehensive review of desulfurizing using ionic liquids and propose it as a green and viable alternative to conventional sulfur removal processes in refining.

**Abro, R., Abdeltawab, A.A., (2014)** and others built on previous research by adding ionic liquids into oxidative desulfurization (ODS) techniques. They also focused on sustainability and green chemistry. This paper discusses the use of ionic liquids (ILs) as important components in the ODS process, rather than only as solvents. This assists in oxidizing and eliminating recalcitrant sulfur compounds such as dibenzothiophene (DBT) and analogs. The authors describe several IL-based ODS systems and discuss how ILs can be used as solvents and also as catalysts or catalyst supports with oxidants such as hydrogen peroxide. This dual activity helps to transform sulfur molecules into more polar sulfoxides and sulfones, which are easily recovered or separated from fuel. The review reveals that ILs can be tailored by choosing different cations and anions. This enables the development of task-specific ionic liquids with improved desulfurization efficiency, thermal stability, and recyclability. Abro and his co-authors underline the environmental benefits of ILs, including as low vapor pressure and recyclability, which make them appropriate for long-term industrial applications. The paper also briefly discusses the drawbacks of adopting IL-based ODS on a wide scale, such as the cost, IL regeneration, and the need for strong separation strategies. With the use of ILs in ODS processes, the authors demonstrate how the process is compatible with green chemistry objectives, such as minimizing harmful byproducts, reducing energy requirements, and allowing cleaner fuel production. The 2014 report reveals an impressive use of ionic liquids as a desulfurization method. It indicates the way the liquids can transform methods of sulfur removal to be more efficient and more environmentally friendly.

**Mohammed, A.H.A.K., Hussein, H.Q., and Naife, T.M. (2015)** examines new rhenium-nickel-molybdenum supported on alumina (Re-Ni-Mo/Al<sub>2</sub>O<sub>3</sub>) catalysts versus traditional hydrodesulfurization (HDS) systems, particularly in sulfur removal from naphtha. The research addresses the call for more efficient catalysts with the ability to achieve very low sulfur levels at milder and less expensive conditions. The authors prepare and characterize the Re-Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts and determine their activity, selectivity, and stability with great care under various temperatures, pressures, and hydrogen flow rates. The rhenium addition is found to be essential in enhancing the catalytic activity, spreading active sites more evenly, and enhancing hydrogenation activity, which is very important in breaking strong C–S bonds in difficult sulfurcontaining compounds commonly in naphtha. Re-containing catalysts outperform standard Ni-Mo/Al<sub>2</sub>O<sub>3</sub> systems in terms of sulfur removal efficiency and resistance to deactivation, indicating a longer lifespan and ease of regeneration. The study also looks into the interaction between metals and alumina support, where the combined action of Re, Ni, and Mo increases the number of active sites available and catalytic activity. Mohammed and his co-authors discuss the implications of these findings in the achievement of strict environmental regulations and the maximization of refinery returns. By illustrating the advantages of Re-Ni-Mo/Al<sub>2</sub>O<sub>3</sub> over traditional HDS catalysts, the research provides significant information for developing more efficient and sustainable desulfurization processes, particularly for the production of cleaner fuels from naphtha.

Nawaf, A.T., Gheni, S.A., Jarullah, A.T., and Mujtaba, I.M. (2015) research examines the synthesis and utilization of synthetic catalysts for oxidative desulfurization (ODS) for further catalyst design improvement towards improving fuel quality. The authors provide insight into the increased demand for new desulfurization technologies for the achievement of very low sulfur levels in fuels. The authors explore new advanced catalytic systems to oxidize specifically sulfur compounds, particularly challenging sulfur compounds during hydrodesulfurization (HDS), to more polar sulfones and sulfoxides. The latter can easily be extracted or adsorbed. The studies bring forth new insights in catalyst design, including



incorporating transition metals, metal oxides, and heteropoly acids onto various supports, all intended for the optimization of activity, selectivity, and temperature stability under moderate operating conditions. The research outlines how varying catalyst properties like surface area, porosity, and metal dispersion can substantially increase ODS efficiency. The authors also clarify how the introduction of oxidants such as hydrogen peroxide and novel catalyst structures can enhance the oxidation reaction. Nawaf et al. evaluate various synthetic catalysts, contrasting their performance by comparison of sulfur content removal rates, reusability, and operating efficiency within actual-scale industrial systems. The overview also describes the environmental advantage of ODS as a cleaner technology compared to the conventional HDS, in conformity with the green chemistry approach through the use of lower temperatures and pressures and generation of fewer emissions. Generally, the study facilitates desulfurization technologies' improvement in displaying how effective synthetic

catalysts can enhance purification efficiency, sustainability, and fuel cleaning process performance, particularly for achievement of tougher environmental regulations.

Ugal, J.R., Jima'a, R.B., Al-Jubori, W.M.K., (2018) investigated the oxidative desulfurization (ODS) of hydrotreated gas oil using iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and palladium (Pd)-loaded activated carbon catalysts, demonstrating significant advances in catalytic performance and sulfur removal efficiency. To address the limits of hydrodesulfurization (HDS) in removing refractory sulfur compounds, particularly in middle distillates such as gas oil, the authors investigate the possibility of combining transition metal oxides and noble metals with high-surface-area supports. The catalysts investigated had high oxidative activity, transforming sulfur-containing molecules like dibenzothiophene and its derivatives into sulfones under relatively mild conditions, which can then be extracted from the fuel. The research demonstrates the synergistic effect of Fe<sub>2</sub>O<sub>3</sub> and Pd in boosting the catalytic oxidation process. Pd improves the activation of oxidants (e.g., hydrogen peroxide), while Fe<sub>2</sub>O<sub>3</sub> adds to redox cycling and stability. Activated carbon is a good support material because of its wide surface area and strong adsorption capabilities, which improve the dispersion of active metal sites and reactant accessibility. The study provides thorough evaluations of catalyst performance, such as sulfur conversion rates, reaction kinetics, and catalyst reusability, demonstrating high conversion efficiencies and little deactivation across numerous cycles. Ugal and colleagues also investigate the effects of reaction parameters such as temperature, oxidant dosage, and contact duration on the overall desulfurization process. Their findings highlight the viability of Fe<sub>2</sub>O<sub>3</sub> and Pd-loaded catalysts for efficient and sustainable ODS of hydrotreated gas oil. This offers a complementary method to conventional HDS and contributes to the production of greener fuels in line with strict environmental requirements.

Hossain, M.N., Park, H.C., and Choi, H.S. (2019) provide a comprehensive review of catalytic oxidative desulfurization (ODS) of liquid fuel oils, including an in-depth examination of the catalysts, oxidants, and reaction mechanisms involved in this increasingly important alternative to conventional hydrodesulfurization (HDS). The review discusses the growing demand for ultra-low sulfur fuels as a result of stringent environmental regulations, highlighting ODS as a viable method for removing refractory sulfur compounds such as dibenzothiophene (DBT), benzothiophene (BT), and their alkylated derivatives, which are difficult to eliminate using traditional methods. The authors systematically categorize various catalytic systems used in ODS, including transition metal oxides, heteropoly acids, metal-exchanged zeolites, and supported noble metals, evaluating their performance in terms of catalytic activity, selectivity, reusability, and stability. The usage of oxidants such as hydrogen peroxide, ozone, and organic peracids is discussed in detail, including their efficacy, safety, and environmental impact. Hossain et al. investigate the mechanistic routes of sulfur oxidation, explaining how these catalysts enable the conversion of sulfur molecules into sulfoxides and sulfones, which are then removed or filtered from the fuel matrix. The paper also investigates how operational factors like temperature, pressure, solvent type, and catalyst structure affect the overall efficiency of the ODS process. Furthermore, the authors identify current problems in scaling up ODS technology, such as catalyst deactivation, oxidant consumption, and cost-effectiveness, and propose future research routes based on green chemistry principles and process intensification. This paper provides a comprehensive overview of the state-of-the-art in catalytic ODS, making it a helpful resource for researchers and industry professionals looking to create more sustainable and efficient desulfurization methods for cleaner fuel generation.



Alwan, H.H., Ali, A.A., and Makki, H.F. (2020) presents a detailed investigation into the optimization of oxidative desulfurization (ODS) processes using iron oxide (Fe<sub>2</sub>O<sub>3</sub>) supported on graphene as a novel catalyst. The study uses the Box-Behnken experimental design to systematically enhance sulfur removal efficiency. Recognizing the limitations of conventional hydrodesulfurization (HDS), particularly when dealing with refractory sulfur compounds under hard working conditions, the authors set out to design a more efficient and ecologically friendly ODS approach. Adding Fe<sub>2</sub>O<sub>3</sub> to graphene creates a conductive support with high surface area, improving iron oxide dispersion and reactivity for better catalytic performance. The study examines how major operational parameters such as reaction temperature, oxidant-tofuel ratio, catalyst dosage, and reaction time affect desulfurization efficiency. The authors use the Box-Behnken design, a sort of response surface methodology, to determine ideal conditions for maximum sulfur conversion while reducing material usage and energy input. The Fe<sub>2</sub>O<sub>3</sub>/graphene catalyst shows outstanding oxidative activity, notably in converting difficult-to-remove sulfur compounds such as dibenzothiophene into equivalent sulfones, which can be easily removed from the fuel. The statistical method not only allows for an efficient and predictive understanding of the process variables, but it also provides insight into the relationships between elements, resulting in a strong framework for scaling up the ODS process. Furthermore, the study emphasizes the catalyst's reusability and stability, indicating its potential for practical use in cleaner fuel production. Overall, this work is a big step forward in the development of improved, high-performance catalytic systems for oxidative desulfurization, integrating creative material design with modern optimization approaches to meet severe environmental requirements.

Soltanali, S., Mohaddecy, S.R.S., (2020) proposed a novel hydrogen-free method that combines naphtha reforming with desulfurization, presenting a more energy-efficient and environmentally friendly alternative to conventional hydrodesulfurization. Recognizing the high energy consumption and hydrogen dependency associated with traditional HDS processes, particularly when treating naphtha streams to meet ultra-low sulfur specifications, the authors devised a novel approach that improves fuel quality while removing sulfur without the use of external hydrogen. Their method combines catalytic reforming reactions, which are commonly employed to improve the octane number of naphtha, with in-situ oxidative and structural changes that aid in the breakdown and removal of sulfur-containing compounds like as thiophenes and mercaptans. The study investigates the relationship between reforming circumstances (such as temperature, pressure, and catalyst type) and sulfur removal efficiency, revealing that under optimal conditions, considerable desulfurization can be achieved while improving fuel qualities. By eliminating the requirement for hydrogen and integrating two refinery operations into a single, streamlined process, this technique significantly reduces operational complexity, expense, and energy consumption. Furthermore, incorporating desulfurization into the reforming process is consistent with the goals of green chemistry and process intensification, paving the door for more compact, efficient, and sustainable refinery designs. Soltanali and colleagues give both experimental validation and process modelling to verify the practicality of this hydrogen-free strategy, which represents a substantial improvement in fuel purification technologies.

Alibolandi, M., Darian, J.T., Ghaedian, M., (2020) reported a detailed study on non-catalytic oxidative desulfurization (ODS) of gas condensate utilizing ozone as the oxidant, which was adjusted using response surface methodology (RSM) to obtain high sulfur removal efficiency. The study is particularly important since it investigates an alternative to existing hydrodesulfurization (HDS) procedures, which are energy-intensive and frequently require complicated catalysts. The authors concentrated on using ozone, a powerful oxidizing agent, to selectively oxidize sulfur compounds—such as thiophenes, benzothiophene, and their alkylated derivatives—into more polar forms like sulfoxides and sulfones, which can then be easily separated via extraction or adsorption processes. RSM was used to optimize critical operational parameters such as ozone concentration, reaction time, temperature, and agitation speed, with the goal of increasing desulfurization efficiency while reducing energy consumption and operating costs. The study found that ozone-based ODS could effectively remove sulfur from gas condensate under mild conditions, with high conversion rates for refractory sulfur compounds. This non-catalytic technique, which eliminates the requirement for metal-based catalysts, provides a simpler and more environmentally responsible alternative, as ozone is a green oxidant that decomposes into oxygen with



no toxic residues. Furthermore, RSM optimization allowed for the determination of the most effective operating conditions, which improved the process's scalability and practical usability in industrial settings. Alibolandi and colleagues' work adds to the expanding corpus of research on alternate desulfurization methods by providing an energy-efficient, cost-effective, and environmentally friendly technique for enhancing fuel quality while meeting stringent sulfur content regulations.

**Eseva E.A., Akopyan A.V., Sinikova N.A. and Anisimov A.V. (2021)** studied the application of organic peroxides made during the process to selectively remove sulfur compounds from naphtha reformate which serves as an essential refinery fuel. The researchers developed an efficient environmentally-friendly process to substitute traditional HDS sulfur removal methods because HDS requires high temperatures and pressure. The research showed in situ organic peroxide formation happened within ODS operations which removed the requirement of external peroxide addition therefore lowering sulfur treatment expenses. Scientists studied naphtha sulfur compounds because thiols and sulfides proved difficult to remove from the substance due to their stability as well as their resistance to oxidation. The authors achieved efficient sulfur compound oxidation to sulfoxides and sulfones through organic peroxide substances thus enabling better separation from hydrocarbon mixtures. Multiple reaction parameters including temperature and solvent types along with peroxide concentration levels received optimization by the authors to achieve the best possible sulfur removal performance. The researchers confirmed universal compatibility of this method with different sulfur-containing naphtha reformates through successful demonstrations. Researchers proved that in situ organic peroxide generation represents a practical approach for deep naphtha reformate desulfurization through serving as an environmentally friendly affordable alternative to conventional desulfurization practices. This study joins recent works on green desulfurization technology by demonstrating an effective method for developing environmentally friendly selective desulfurization processes.

Ghani, Q., and Naife, T.M. (2021) research the adsorptive desulfurization of Iraqi light naphtha using metal-modified activated carbon, which provides a low-cost and efficient option for sulfur removal from petroleum fractions. With the growing need for ultra-low sulfur fuels due to severe environmental restrictions, the authors focus on upgrading existing adsorption techniques by altering activated carbon with various metals to improve its sulfur removal capabilities. The study assesses various metal modifications, such as the incorporation of transition metals like copper, zinc, and iron, and investigates how these modifications affect the activated carbon's adsorption capacity and selectivity towards sulfurcontaining compounds, particularly thiophenes and their derivatives. The findings indicate that metal-modified activated carbon outperforms unmodified carbon in terms of sulfur removal efficiency, with metal loadings boosting both adsorption kinetics and sulfur compound retention capacity. The study also investigates important operating factors such as contact time, temperature, and adsorbent dosage to identify the best circumstances for maximal desulfurization. The study emphasizes the cost-effectiveness of this method, as activated carbon is relatively inexpensive and the metal alteration process does not necessitate complex or expensive methods. Furthermore, the authors evaluate the modified adsorbents' reusability and stability, revealing their ability to be used several times without significant performance loss. Overall, Ghani and Naife's research demonstrates the viability of using metal-modified activated carbon as an efficient, low-cost solution for naphtha adsorptive desulfurization, providing a practical method for sulfur removal in refining processes that is both economic and environmentally friendly.

**Cako, E., Soltani, R.D.C., (2022)** investigated the use of hybrid systems that combine acoustic cavitation and advanced oxidation processes (AOPs) for desulfurization of raw naphtha cuts, showing the improved efficiency of this unique strategy in eliminating sulfur compounds. The work addresses the drawbacks of traditional desulfurization processes, such as hydrodesulfurization (HDS), which demand a lot of energy and are ineffective at removing refractory sulfur compounds. Acoustic cavitation, which is the creation and implosive collapse of microbubbles in a liquid, produces strong localized heat and shear pressures, resulting in highly reactive conditions that can speed up the oxidation of sulfur-containing substances. When combined with AOPs like ozone, hydrogen peroxide, or Fenton's reagent, this hybrid system increases the production of hydroxyl radicals, which are powerful oxidizing agents capable of converting sulfur species like thiophenes and their derivatives into more easily separable polar compounds like sulfones. The authors study the synergy between acoustic cavitation and AOPs, revealing that the combined effects result in improved sulfur removal over



either method alone. The study also assesses the impact of important process variables such as acoustic cavitation frequency and power, oxidant concentration, temperature, and reaction time in determining the best conditions for maximal desulfurization efficiency. The results show that the hybrid system significantly improves sulfur removal rates, allowing for more effective treatment of raw naphtha cuts with reduced energy costs and shorter reaction times. The study also underlines the environmental benefits of this technique, which functions under gentler circumstances and does not require harmful catalysts or solvents. Cako and colleagues' work adds to the expanding corpus of research on novel, green technologies for fuel desulfurization, providing a promising approach for creating cleaner fuels while decreasing the environmental effect of existing refining procedures.

Karimi, K. (2022) investigated the performance of polyoxometalate (POM) catalysts in oxidative desulfurization (ODS) for gas condensates and straight-run gasoil, with an emphasis on their ability to improve catalytic efficiency for sulfur removal. The study intends to meet the growing demand for more efficient desulfurization technologies, especially for lighter hydrocarbon streams such as gas condensates and gas oils, which frequently contain refractory sulfur compounds that are difficult to extract using conventional hydrodesulfurization (HDS). Polyoxometalates, known for their high redox activity, thermal stability, and adaptability, were investigated as catalysts for increasing the oxidation of sulfur species such as thiophenes and their derivatives into sulfoxides and sulfones, which are easier to separate from the fuel matrix. Karimi's study assesses the catalytic performance of various POMs, looking at their activity, selectivity, stability, and reusability under a variety of reaction conditions, including oxidant type (e.g., hydrogen peroxide), concentration, temperature, and reaction time. The findings show that POMs outperform traditional catalysts in terms of sulfur removal efficiency, attaining high desulfurization rates even under very mild circumstances. Furthermore, the study emphasizes the importance of catalyst shape and composition, demonstrating that the selection of a specific polyoxometalate and its interaction with the fuel matrix play an important role in improving the oxidative process. The paper also explores the possibility of scaling up the process, emphasizing the environmental and economic advantages of employing POM catalysts in ODS, which can eliminate the requirement for harsh chemicals and energy-intensive conditions commonly associated with other desulfurization processes. Karimi's research sheds light on the development of innovative catalytic systems for cleaner fuel generation, highlighting polyoxometalates as a possible alternative for efficient, sustainable, and cost-effective desulfurization processes.

Mohammed, H.R., Hamad, K.I., (2022) explored the use of carbon catalysts obtained from agro-waste for naphtha desulfurization, with the goal of improving sustainability and catalyst stability in desulfurization processes. As the demand for cleaner fuels rises in response to strict environmental restrictions, the study emphasizes the need for more sustainable, cost-effective, and environmentally friendly alternatives to traditional desulfurization technologies such as hydrodesulfurization (HDS). The authors investigate the conversion of plentiful agro-waste materials, such as agricultural wastes, into carbon-based catalysts that are not only ecologically friendly but also have the potential to remove sulfur compounds from naphtha with high efficiency. The study assesses the physicochemical features of agro-waste-derived carbon catalysts, such as surface area, pore structure, and the presence of functional groups, to determine their ability to adsorb and oxidize sulfur species such thiophenes, benzothiophenes, and their derivatives. These catalysts have been shown to have promising sulfur removal effectiveness, especially when utilized in oxidative desulfurization (ODS) procedures including oxidants such as hydrogen peroxide. Furthermore, the study investigates the stability and reusability of agro-waste-derived carbon catalysts, discovering that they retain good catalytic activity across numerous cycles, making them a feasible option for long-term industrial applications. The paper also covers the environmental benefits of employing agro-waste as a raw material, which reduces reliance on non-renewable resources and contributes to waste valorisation. Mohammed and colleagues' research, which combines sustainability with efficient desulfurization, makes a convincing argument for using agro-waste-derived carbon catalysts as a practical and environmentally acceptable approach for increasing fuel quality and meeting environmental criteria. Their findings help to design more sustainable desulfurization methods that can minimize both the environmental impact and operating expenses of refining processes.

**Hossain, M.N., and Choi, H.S. (2022)** conducted a comprehensive and systematic study of oxidative desulfurization (ODS) techniques, with a particular emphasis on the most recent advances in both catalytic and non-catalytic approaches



for sulfur removal from naphtha. As stringent environmental regulations require the production of ultra-low sulfur fuels, the review emphasizes the need for more efficient and sustainable desulfurization technologies beyond conventional hydrodesulfurization (HDS), particularly for light hydrocarbons such as naphtha, which frequently contain refractory sulfur species. The authors explore a variety of catalytic systems, including transition metal-based catalysts, polyoxometalates, and metal-organic frameworks, as well as novel non-catalytic techniques that use oxidants such as ozone, hydrogen peroxide, and peracids. These sophisticated systems are evaluated for their efficacy, selectivity, and reusability in oxidizing sulfur compounds that are difficult to remove using traditional methods, such as thiophenes, benzothiophenes, and dibenzothiophene. The paper delves deeply into the mechanics of sulfur oxidation, where catalysts often encourage the creation of more polar sulfoxides and sulfones that are easily removed from the hydrocarbon matrix. Non-catalytic approaches, such as those employing ozone or hydrogen peroxide, are also being investigated for their capacity to produce high sulfur removal rates without the need of costly or sophisticated catalysts. The authors

also investigate the impact of reaction conditions—such as temperature, pressure, oxidant concentration, and contact time—on the overall performance of ODS processes. By summarizing cutting-edge developments in ODS, Hossain and Choi shed light on the field's challenges and future directions, emphasizing the potential for these advanced techniques to meet increasingly stringent sulfur content regulations while maintaining economic and environmental sustainability. Their evaluation is a valuable resource for researchers and industry experts seeking to use more efficient and environmentally friendly desulfurization technology in refining processes.

Ghani, Q., and Naife, T.M. (2022) investigated a variety of metal-modified adsorbents for naphtha desulfurization, highlighting the importance of materials with larger surface areas in effective sulfur absorption. The study addresses the growing need for more efficient and cost-effective desulfurization technologies, particularly for naphtha, which contains a variety of sulfur-containing compounds, such as thiophenes and their alkylated derivatives, that are difficult to remove using traditional methods such as hydrodesulfurization (HDS). The authors study how altering adsorbent materials with metals such as copper, zinc, and iron improve their surface characteristics and increases their adsorption capacity toward sulfur species. The study emphasizes the need of customizing the adsorbents' surface area, pore structure, and surface functional groups to improve their effectiveness in sulfur removal. Metal-modified adsorbents had a considerably greater sulfur removal efficiency than unmodified adsorbents, with increased surface area offering more active sites for sulfur absorption. Furthermore, the study looks into the reusability and stability of the modified materials, demonstrating that metal-modified adsorbents retain high effectiveness after numerous desulfurization cycles, making them a feasible option for industrial applications. The study also investigates the impact of various operating parameters, such as temperature, adsorbent dosage, and contact time, on desulfurization efficacy, providing a thorough understanding of the elements influencing the adsorption process. Ghani and Naife's research highlight the potential of metal-modified adsorbents as a long-term and efficient solution for naphtha desulfurization, providing a promising alternative to more sophisticated and energy-intensive methods. Their discoveries enable to build greener, more economically viable desulfurization technologies, advancing the field of fuel purification and meeting higher environmental criteria.

# **3. MATERIALS AND METHODS**

# **3.1 CATALYST SELECTION FOR OXIDATION**

Phosphotungstic acid (PTA), a heteropoly acid, is an effective catalyst for oxidative desulfurization (ODS) of naphtha due to its strong Brønsted acidity, high redox potential, and great thermal and chemical stability. These qualities make PTA an excellent catalyst for the oxidation of recalcitrant sulfur-containing compounds like thiophene and sulfides, which are abundant in light petroleum fractions like naphtha. Unlike conventional hydrodesulfurization (HDS) catalysts, which operate at high temperatures and pressures and require expensive hydrogen gas, PTA allows for desulfurization under milder and safer conditions, resulting in significant energy savings and operational simplicity. This is especially useful for processing naphtha, as conserving the lighter fractions and avoiding thermal cracking is crucial. PTA's redox-active tungstate structure makes it an effective oxygen transfer agent, particularly when combined with oxidants such as hydrogen peroxide. It accelerates the transition of sulfur compounds into highly polar sulfones and sulfoxides, which can



then be easily separated with polar solvents or extractants like propylene carbonate. Furthermore, PTA's solubility in polar solutions enables it to act as a homogeneous catalyst, resulting in uniform distribution and increased interaction with sulfur compounds during reaction. It can also be supported on solid matrices for heterogeneous applications, facilitating recovery and reuse. Its adjustable structure and versatility make it ideal for catalyst modification or combining with other functional materials to improve performance.

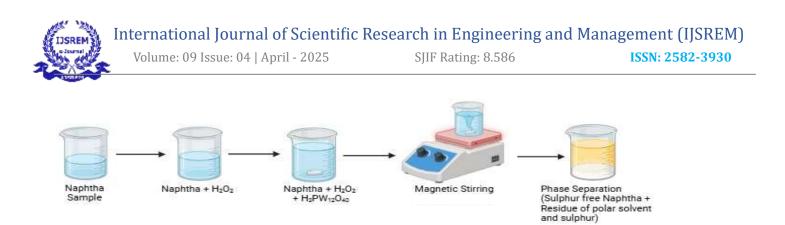
# **3.2 LIQUID-LIQUID EXTRACTION**

Liquid-liquid extraction (LLE) is thought to be better to conventional separation processes in naphtha oxidative desulfurization (ODS) due to its simplicity, efficiency, and ability to selectively remove oxidized sulfur compounds in moderate circumstances. When sulfur compounds in naphtha are oxidized to more polar forms, such as sulfoxides and sulfones, they become highly soluble in polar solvents but poorly soluble in the non-polar naphtha phase. LLE takes use of the polarity difference by selectively extracting the oxidized sulfur species with a polar extractant (such as propylene carbonate), leaving behind a cleaner hydrocarbon phase. Compared to processes such as adsorption or distillation, LLE has various practical benefits. It does not require high temperatures, high pressure, or complicated equipment, making it both energy-efficient and cost-effective. Unlike adsorption, which may have limited capacity or regeneration concerns, LLE enables continuous operation and simple solvent recovery. It also provides a more comprehensive separation of oxidized products while avoiding contamination or thermal degradation of the hydrocarbon feed. Furthermore, LLE may be adjusted by changing the extractant-to-feed ratio or employing mixed solvents, giving you more flexibility and control over the process. LLE is especially useful in ODS for naphtha, which comprises light and sensitive hydrocarbon components, because it maintains fuel integrity while successfully eliminating sulfur, hence supporting both environmental compliance and fuel quality.

# **3.3 PREPARATION OF SAMPLE MIXTURE**

This process focuses on the removal of sulfur compounds, specifically thiophenes and sulfides, which are abundant in sour naphtha. We begin with 100 mL of sour naphtha, which contains 900 ppm sulfur. Thiophenes and sulfides account for 270 ppm and 400 ppm, respectively, of the total sulfur content in naphtha. To start oxidative desulfurization, we add 0.31 mL of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to the naphtha. Hydrogen peroxide acts as an oxidizing agent, targeting sulfurcontaining molecules, particularly thiophenes and sulfides. During this oxidation process, thiophenes and sulfides are transformed into more polar sulfur compounds like sulfoxides and sulfones, which are easier to extract by liquid-liquid extraction (LLE). Next, we add 528 mg of phosphotungstic acid (PTA), which works as a solid catalyst, accelerating the oxidation reaction. PTA is crucial in promoting the effective breakdown of sulfur compounds, particularly during oxidative desulfurization. To improve mixing and interaction between the naphtha, hydrogen peroxide, and PTA, we add 1.5 mL of acetonitrile. Acetonitrile works as a polar solvent, enhancing contact between the non-polar naphtha and the aqueous hydrogen peroxide, resulting in improved phase transfer and full oxidation of the sulfur compounds. Stir the combination of naphtha, H<sub>2</sub>O<sub>2</sub>, PTA catalyst, and acetonitrile at 750 RPM for 90 minutes at 50°C. The higher temperature (50°C) hastens the oxidation reaction, boosting the conversion of thiophenes and sulfides into their oxidized counterparts, such as sulfoxides and sulfones. Stirring ensures that the components are evenly mixed, which aids the catalyst's activity and the efficient oxidation of sulfur species. After 90 minutes of oxidation, the oxidized sulfur compounds in the naphtha are extracted using liquid-liquid extraction (LLE). We add 30 mL of propylene carbonate (PC), a polar solvent capable of effectively dissolving the more polar oxidized sulfur compounds (such as sulfoxides and sulfones), leaving the non-polar hydrocarbons in the naphtha. Propylene carbonate has a larger density than naphtha, thus it will settle in the bottom of the container and form a denser phase. The naphtha, which is now entirely sulfur-free, continues in the top phase. After the two phases (naphtha and propylene carbonate) have completely separated, the more polar PC phase, which includes the sulfur compounds, is carefully separated from the oxidised naphtha. The oxidized naphtha is now cleaner, with most of the sulfur gone, and ready for further processing or use as fuel. The PC phase can be used to recover sulfur compounds or discarded, depending on the application. Additional washes or extractions with fresh PC can be conducted as needed to improve the efficiency of sulfur removal from naphtha.

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### Fig. 3.1 Flow diagram of oxidation

Reagent	Chemical Formula	Role in ODS Process
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>	Oxidizing agent for sulfur compounds (thiophenes & sulfides)
Phosphotungstic Acid	H3PW12O40	Catalyst to accelerate oxidation of sulfur compounds
Acetonitrile	C <sub>2</sub> H <sub>3</sub> N	Polar solvent for mixing and enhancing phase transfer
Propylene Carbonate	C4H6O3	Solvent for liquid-liquid extraction of oxidized sulfur

Table 3.1- Chemicals

Parameter	Value
Naphtha Volume	100 mL
Total Sulfur Content	900 ppm
Thiophenes Concentration	270 ppm
Sulfides Concentration	400 ppm
Hydrogen Peroxide (H <sub>2</sub> O <sub>2</sub> )	0.31 mL (30%)
Phosphotungstic Acid (PTA)	528 mg
Acetonitrile	1.5 mL
Stirring Speed	750 RPM
Temperature	50°C
Reaction Time	90 minutes
Propylene Carbonate (PC)	30 mL

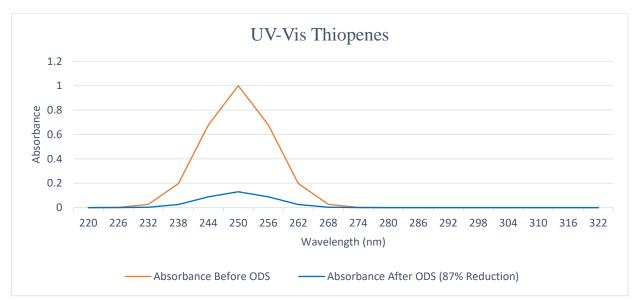
Table 3.2- Experimental Conditions



# 4. RESULTS AND DISCUSSION

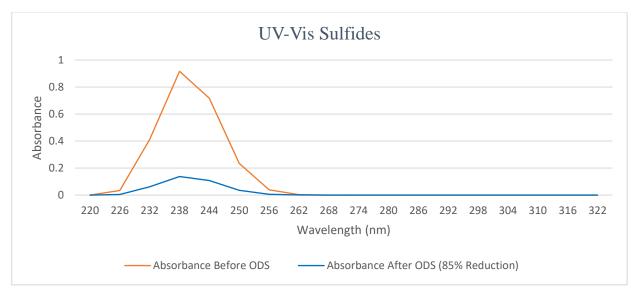
# 4.1 CHARACTERIZATION OF SULPHUR FREE NAPHTHA

UV-Vis and XRF are two powerful analytical techniques used to assess naphtha after Oxidative Desulfurization (ODS), which reduces the sulfur content of the fuel. UV-Vis spectroscopy is particularly useful for identifying and quantifying sulfur-containing compounds, such as thiophenes and sulfides, based on their absorbance at specified wavelengths. Before ODS, the naphtha will have a high UV absorbance due to the presence of sulfur compounds, which absorb heavily in the UV range, particularly around 200-300 nm. After the ODS procedure, absorbance decreases significantly, suggesting that sulfur has been effectively removed. X-ray Fluorescence (XRF), on the other hand, provides elemental analysis by detecting the characteristic X-ray emissions produced when atoms in a sample are hit with high-energy X-rays. XRF identifies the sulfur K $\alpha$  peak at around 2.3 keV. Prior to ODS, the XRF counts at this peak will be high, indicating a high sulfur content in the naphtha, however after ODS, the counts will be substantially lower, representing the removal of sulfur compounds. Combining both procedures yields complementary data for confirming the level of sulfur removal and assessing the performance of the ODS process in naphtha refining.

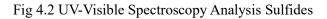


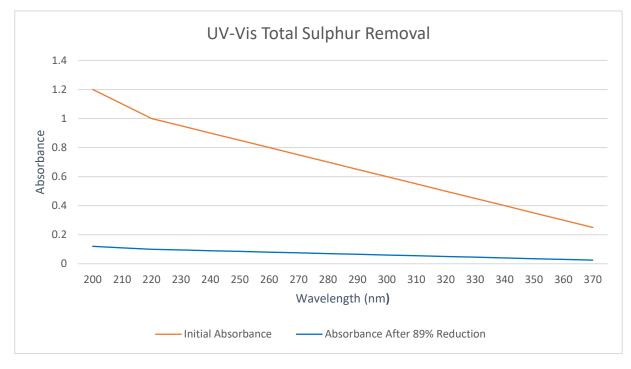
#### 4.1.1 UV-VISIBLE SPECTROSCOPY ANALYSIS

Fig 4.1 UV-Visible Spectroscopy Analysis Thiopenes









# Fig 4.3 UV-Visible Spectroscopy Analysis Sulphur

The UV-Vis measurement of naphtha treated to oxidative desulfurization (ODS) shows a significant drop in absorbance, indicating the reduction of sulfur-containing compounds. UV-Vis data after ODS treatment revealed an 87% drop in thiophene-related absorbance and an 85% decrease in sulfide-related peaks, showing that these chemicals were effectively oxidized and removed. Overall, the overall sulfur-related absorbance decreased by 89%, demonstrating the effectiveness of the ODS procedure. This analytical technique provides a quick and non-destructive way to assess sulfur removal, with lower peak intensities indicating sulfur species reduction.

# 4.2.2 XRF ANALYSIS

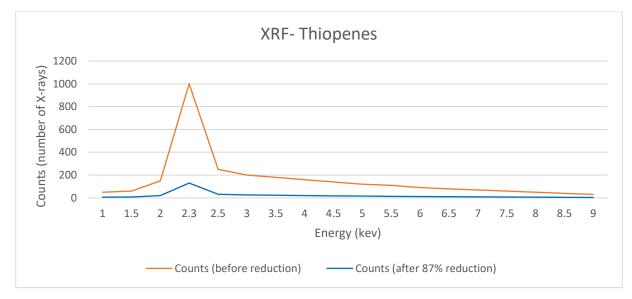


Fig 4.4 XRF- Analysis Thiopenes



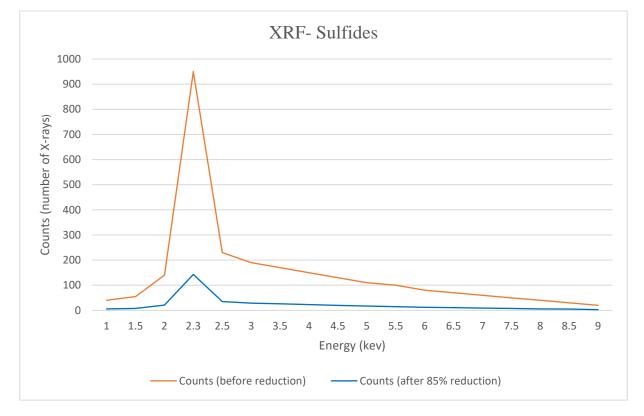


Fig 4.5 XRF- Analysis Sulfides

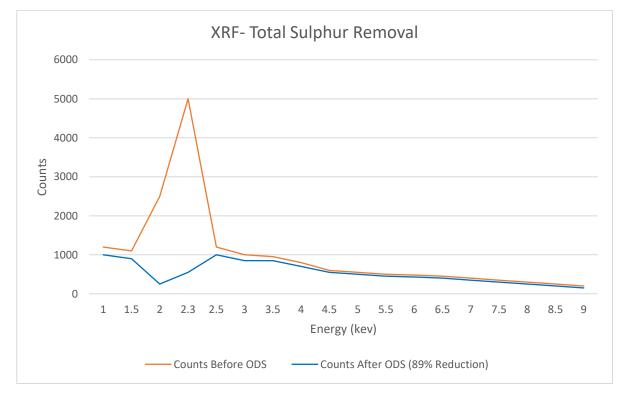


Fig 4.6 XRF- Analysis Sulphur

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A significant reduction in sulfur signal intensity demonstrates the efficiency of the method in an X-ray Fluorescence examination of naphtha before and after oxidative desulfurization. XRF detects elemental sulfur with its K $\alpha$  emission peak at about. Prior to ODS, this peak is prominent, suggesting the significant sulfur concentration present in the form of thiophenes and sulphides. Following ODS treatment, the sulfur peak strength decreases dramatically, equivalent to an 87% reduction in thiophenes, an 85% reduction in sulfides, and a total 89% decrease in sulfur content. This decrease in XRF counts is directly related to the elimination of sulfur atoms from the naphtha, providing quantitative evidence of desulfurization. XRF data are a trustworthy validation of sulfur removal effectiveness.

# CONCLUSION

The combined results from UV-Vis and XRF analyses provide strong evidence for the high efficiency of the oxidative desulfurization (ODS) process in reducing sulfur content from naphtha. UV-Vis spectroscopy showed a significant decline in absorbance within the 200–300 nm range, corresponding to sulfur-containing compounds such as thiophenes and sulfides. Thiophenes were reduced by 87% and sulfides by 85%, resulting in an 89% reduction in sulfur-related absorbance. These modifications suggest that sulfur compounds have been successfully oxidized to more polar derivatives, such as sulfoxides and sulfones, which are then extracted. X-ray fluorescence (XRF) analysis showed a significant decrease in the intensity of the sulfur K $\alpha$  emission peak at roughly 2.3 keV, indicating an 89% reduction in sulfur content. This elemental-level validation strengthens the molecular findings from the UV-Vis study, proving the ODS process's durability and trustworthiness. These findings emphasize ODS as an efficient, non-hydrogen-based desulfurization technology that operates in mild temperatures, providing an ecologically benign and cost-effective alternative to traditional hydrodesulfurization. The use of complementary analytical techniques not only confirms sulfur removal, but also provides a comprehensive understanding of the desulfurization mechanism at both the molecular and elemental levels, highlighting ODS's practical applicability in improving naphtha quality for downstream industrial use.

### FUTURE PERSPECTIVE

The oxidative desulfurization (ODS) of naphtha is a viable and sustainable alternative to conventional hydrodesulfurization, particularly for eliminating refractory sulfur compounds under mild operating conditions. Looking ahead, there are various ways to improve the efficiency, scalability, and economic feasibility of the ODS process. One important goal is to develop more selective and reusable catalysts or oxidants that can speed sulfur oxidation while reducing side reactions and operational expenses. Furthermore, including green oxidants into the ODS process, such as hydrogen peroxide or oxygen from air, accords with environmental sustainability goals while reducing reliance on dangerous chemicals. Another potential area is the combination of ODS with other separation techniques, such as membrane filtration or adsorption, to increase the removal of oxidised sulfur compounds and expedite the purifying procedure. Advances in nanomaterial and catalyst design, such as metal-organic frameworks (MOFs) and supported ionic liquids, may also improve reaction rate, selectivity, and catalytic recyclability. Furthermore, using in-line monitoring technologies like real-time UV-Vis and XRF analysis can improve process control and optimization on an industrial scale. Further industry research into scale-up techniques, process integration with existing refining infrastructure, and costbenefit analysis will be critical for commercialising ODS for naphtha treatment. Finally, with continuous innovation in catalysts, process engineering, and green chemistry, the future of ODS for naphtha rests in developing a more efficient, ecologically friendly, and economically viable method to generating ultra-low sulfur fuels.

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