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Desulfurization methods and the challenges associated with their application to heavy fuels

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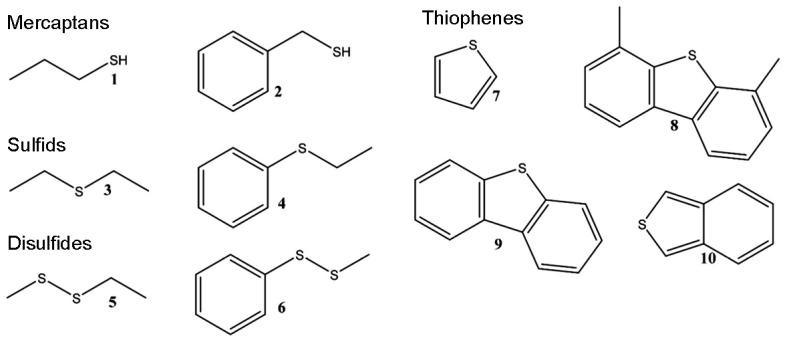
ABSTRACT: This article presents a comparative analysis of existing desulfurization methods. The evaluated techniques include hydrodesulfurization (HDS), extractive desulfurization (EDS), oxidative desulfurization (ODS), alkylation-based desulfurization, adsorptive desulfurization (ADS) and bio desulfurization (BDS). Compared to the conventional HDS method, ODS method offers two major advantages:
- The ODS process is carried out in the liquid phase under very mild operating conditions, thereby requiring lower capital investment.
- This method exhibits high reactivity and selectivity toward certain refractory sulfur compounds, such as dibenzothiophene (DBT) and its derivatives, which are difficult to remove via HDS.
The ODS process is particularly beneficial for small and medium-scale refineries and can also serve as a finishing step downstream of existing HDS units, especially for streams containing more than 1000 ppm sulfur.
Among the reviewed methods, only a few demonstrate practical potential or efficiency for the desulfurization of heavy oils. This limitation is primarily due to the inherent properties of heavy oils, including high sulfur content, high viscosity, elevated boiling point, and the refractory nature of the sulfur-containing compounds.
One promising approach for heavy oil desulfurization is autoxidation followed by thermal decomposition of the oxidized sulfur species. Combining autoxidation with other techniques, such as hydrodesulfurization, may also create synergistic effects and enables the production of a fuel with a sulfur content of less than 50 or even 10 ppm.
Furthermore, this article identifies research gaps and provides important recommendations for addressing future challenges in the field of fuel desulfurization.

Keywords: *Desulfurization, Heavy Oil, Oxidative, Solvent, challenge*

INTRODUCTION

Fuel desulfurization is an essential process for reducing air pollution, protecting human health, increasing equipment efficiency, and complying with environmental regulations. This process not only helps to improve fuel quality, but also plays an important role in sustainable development and reducing the negative effects of

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fossil fuels on the environment.

Now a days, global recommendations have been made to implement strict regulations on the sulfur content in fuels. The primary stakeholders, including refineries and end-users, must adhere to these regulations to achieve minimal or zero sulfur emissions. This can only be achieved by processing petroleum-based oils to remove sulfur compounds during the refining stage, prior to their distribution to consumers [1].

The sulfur-containing compounds found in petroleum can be classified into four main categories: mercaptans (R-SH), sulfides (R_2S), disulfides (RSSR), and thiophenes. Examples of these compounds are illustrated in Figure 1 [2].

Figure 1. Examples of S-containing compounds found in petroleum:

Mercaptans: propane-1-thiol (1), phenylmethanethiol (2)

Sulfides: diethylsulfane (3), ethyl phenyl sulfide (4)

Disulfides: (methyldisulfanyl)methane (5), methyl phenyl disulfide (6)

Thiophenes: thiophene (Th) (7), 4,6-dimethyldibenzothiophene (4,6-DMDBT) (8), dibenzothiophene (DBT) (9), and benzothiophene (10)

It has been recognized that dibenzothiophene (DBT) and its derivatives, particularly 4,6-dimethyldibenzothiophene (4,6-DMDBT), are the most challenging sulfur-containing compounds to remove due to their significant steric hindrance [3].

In general, the chemical structure of sulfur significantly influences its removal. Desulfurization of aliphatic sulfur compounds, such as thiols and sulfides, is relatively easier compared to aromatic sulfur compounds, such as thiophenes[4].

In vacuum gas oil and vacuum residue, sulfur is predominantly found in compounds belonging to the benzothiophene family and so, desulfurization of heavy oils is more complex and faces greater challenges.

Achieving low (<10 ppm) or zero content sulfur in fuel depends on a combination of factors, including desulfurization methods, fuel type, feedstock source, and associated economic consideration [5].

Desulfurization processes are generally divided into two main categories. The selection of the appropriate method should be based on fuel type, sulfur composition, cost, and safety risks. A classification of the processes is presented below:

1. Hydrodesulfurization (HDS)

2. Non-Hydrodesulfurization:

- Oxidative Desulfurization (ODS)
- Bio desulfurization (BDS)
- Adsorptive Desulfurization (ADS)
- Solvent extraction desulfurization (SEDS)
- Alkylation Desulfurization

HDS technology operates under high temperature and pressure conditions and demands a significant amount of hydrogen. Due to the requirements of elevated pressure, temperature, and a substantial quantity of catalyst, HDS is consequently an expensive option [6].

In the ADS process, sulfides are directly adsorbed onto the adsorbent and adsorbent surface plays a crucial role in the adsorption of sulfur molecules.

BDS technology can be operated under mild temperatures and pressure and selecting a proper biocatalyst seems necessary in it.

In the ODS method, organosulfur compounds are oxidized into sulfoxides and sulfones, which are subsequently separated through extraction, adsorption, or distillation.

Alkylation desulfurization involves reacting sul-

fur compounds, such as thiophenes, with alkylating agents (e.g., olefins) in the presence of a catalyst. This method offers advantages such as lower operating temperatures and pressures compared to HDS, but it requires careful selection of catalysts and alkylating agents.

Solvent extraction desulfurization (SEDS) is particularly effective for removing aromatic sulfur compounds, such as thiophenes and dibenzothiophenes, which are challenging to eliminate through conventional hydrodesulfurization. However, the process requires careful solvent selection, efficient separation, and solvent recovery to ensure economic viability and environmental sustainability.

Numerous reviews have been conducted on desulfurization in general, with a primary focus on sulfur removal from lighter refinery products such as naphtha, distillates, and light vacuum gas oil fractions. The aim of this review paper is to present a comprehensive overview of different desulfurization techniques and the associated catalysis and chemistry with special emphasis on the desulfurization of heavy fuels.

Classification of desulfurization techniques

Hydrodesulfurization process (HDS)

The removal of organic sulfur from fossil fuels is challenging because sulfur can only be separated from organic molecules when specific chemical bonds are broken. Breaking these bonds typically requires high temperatures and pressures. One of the current technologies for reducing sulfur content in middle distillates, such as diesel fuel, is hydrodesulfurization (HDS). In the HDS process, sulfur atoms in sulfur-containing compounds are converted into hydrogen sulfide (H_2S) and hydrocarbons using $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ catalysts in the presence of hydrogen gas (but there are many more types available). The resulting H_2S is then catalytically oxidized with air to produce elemental sulfur. The operating conditions for HDS vary depending on the type of hydrocarbon and the desired level of desulfurization, typically ranging from 200 – 425 °C and 150 –250 psi of H_2 pressure. To achieve ultra-low sulfur concentrations (below 15 mg/kg), even higher temperatures and pressures are often necessary [7]. Higher temperature in HDS process cause enhanced coke formation, possibly resulting in catalyst deactivation.

The sulfur compounds commonly found in fuels are detailed in Table 1. The ease of desulfurization in petroleum products largely depends on the chemical structure of the sulfur-containing compounds.

Acyclic sulfur compounds like disulfides and thiols

Table 1. Refinery products containing typical sulfur compounds.

Refinery Product	Boiling Point Range (°C)	Refinery Stream	Sulfur Compound
Gasoline	40 - 180	1. Straight Run Naphtha 2. Hydrocracker Naphtha 3. Fluid Catalytic Crackers' Naphtha 4. Coker Naphtha	1. Mercaptans (RSH) 2. Sulfides (R_2S) 3. Disulfides (RSSR) 4. Thiophene, and its derivatives 5. Benzothiophene
Kerosene, Jet Fuels	120 - 250	1. Heavy Naphtha 2. Middle Distillate	1. Mercaptans 2. Benzothiophene (BT), and its derivatives
Diesel	160 - 380	1. Middle Distillate 2. Hydrocracker Gas Oil 3. Fluid Catalytic Cracker's Light Cycle Oil 4. Coker Gas Oil	1. Derivatives of Benzothiophene 2. Dibenzothiophene (DBT), and its derivatives
Fuel Oil	200 - 650	1. Vacuum Distillation Residue 2. Cutter Stock 2.1. Heavy Gas Oils 2.2. A small amount of Kerosene	≥ 3-ring polycyclic sulfur-containing species: 1. Dibenzothiophene, and its derivatives 2. Benzonaphthothiophene (BNT) 3. Naphthothiophene (NT) 4. Thiophene (Th), and its derivatives

are highly reactive and can be removed under mild temperature and pressure conditions. Similarly, certain cyclic sulfur compounds, particularly those with six-membered rings, also exhibit high reactivity. In contrast, five-membered ring sulfur compounds, such as thiophene and its derivatives, are less reactive, and their reactivity decreases as the ring structure becomes more condensed (e.g., 1 ring > 2 rings > 3 rings) [8].

Sterically hindered sulfur compounds, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), exhibit reduced reactivity due to the presence of alkyl substituents that impede access of the sulfur atom to the catalyst surface, thereby limiting the effectiveness of the desulfurization reaction.

It is important to note that heavier hydrocarbon feeds may necessitate higher operating temperatures and more severe pressure conditions, which can consequently result in increased saturation of olefinic (alkene) compounds.

General equation of reaction that can be written for various sulfur compounds is as follows:

Mercaptans (R-S-H):

R-S-H + H2 → R-H + H2S

Sulfides (R1-S-R2):

R1-S-R2 + 2H2 → R1-H + R2-H + H2S

Disulfides (R1-S-S-R2):

R1-S-S-R2 + 3H2 → R1-H + R2-H + 2H2S

Thiophenes:

C4H4S + 4H2→C4H10 + H2S

Figure 2 shows a simple process diagram for Hydrotreating process. According to the figure, fuel oil and hydrogen are fed into the reactor, where a hydrodesulfurization catalyst facilitates the conversion of organic sulfur compounds into hydrogen sulfide (H_2S) by utilizing hydrogen (H_2) under conditions of high temperature and pressure in the presence of metal catalysts.

As the presence of sulfur compounds shortens the catalyst's lifespan so the selection of an appropriate catalyst is crucial in HDS process. Nickel-Molybdenum (NiMo) or Cobalt-Molybdenum (CoMo) are particularly effective for desulfurizing feedstocks containing sulfur compounds [9].

To have a clean final product, the liquid stream is sent to the H2S stripper. The reactor's effluent is cooled and then split into gas and liquid phases. Hydrogen sulfide (H_2S) is extracted from the gas stream, commonly through an amine-based absorption method. The extracted H_2S is usually transformed into elemental sulfur using the Claus process. This process entails partially oxidizing H_2S to sulfur dioxide (SO_2), followed by a reaction between SO_2 and H_2S to yield sulfur (S).

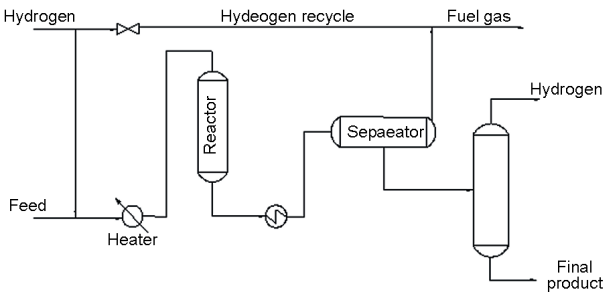


Fig. 2. Simple process diagram for Hydrotreating process.

Achieving ultra-clean fuels through conventional desulfurization processes necessitates severe operating conditions, including elevated temperatures, high hydrogen pressures, and the use of high-activity catalysts. As a result, there is an increasing and inevitable demand for alternative desulfurization techniques that are more cost-effective, energy-efficient, and operationally safer [10].

Although hydrodesulfurization (HDS) is used in industry to upgrade heavy oil, its efficiency is hindered by certain characteristics of heavy oils:

(a) Elevated metal concentrations, which lead to the formation of deposits and subsequent catalyst deactivation.

(b) Tendency to form coke and fouling layers, contributing to the loss of catalyst activity.

(c) Large molecular structures, which restrict penetration into the smaller pores of the catalyst.

(d) Steric hindrance around thiophenic sulfur compounds, making their adsorption during HDS more challenging.

Adsorptive Desulfurization (ADS)

Adsorptive Desulfurization involves the adsorption of sulfur-containing compounds onto a solid adsorbent material. The adsorbent selectively captures sulfur compounds from the hydrocarbon stream. The type of adsorbent and mechanism of adsorption are the key aspects of adsorptive desulfurization. Unlike the hy-

drodesulfurization process, adsorptive desulfurization (ADS) can effectively remove refractory sulfur compounds like dibenzothiophene (DBT) and its derivatives without requiring costly and hazardous hydrogen or high-temperature and high-pressure operating conditions. Desulfurization can occur through two mechanisms:

- Physical adsorption, in which sulfur compounds are separated without a chemical reaction, and the energy required for the recovery of the adsorbed compound depends on the adsorption force.
- Chemical adsorption, which involves the reaction between sulfur-containing compounds and the surface of the solid adsorbent.

Sulfur is usually attached to the sorbent as a sulfide. A variety of porous solid materials, including various types of zeolites, activated carbon, alumina, silica, and metal-based adsorbents, can be utilized in the desulfurization process. Among these, activated carbon is regarded as more effective compared to other adsorbents such as bentonite and metal oxides. This is due to its high surface area, low cost, excellent chemical, thermal, and mechanical stability, as well as its surface morphology, which enhances its adsorption capacity for organosulfur compounds [11].

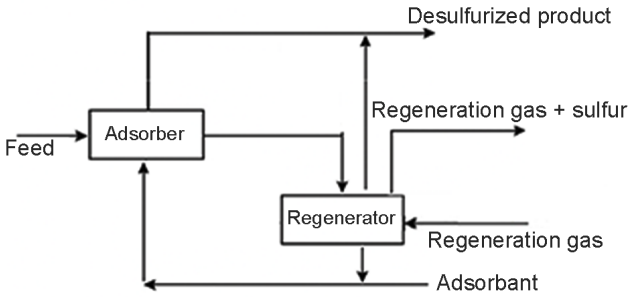


Fig. 3. The IRVAD process (Integrated Reactive Vacuum Adsorptive Desulfurization)

Figure 3 indicates an example of a process diagram for an absorptive desulfurization unit (IRVAD process), where a solid adsorbent and a hydrocarbon feed are brought into contact in a counter-current manner within an absorber. The desulfurized stream exits from the top of the absorber, while the spent adsorbent is discharged from the bottom. The outgoing adsorbent stream is then fed into a regenerator, where the saturated adsorbent is regenerated by using a heated reactivation gas and subsequently returned for reuse. In this process, alumina-based adsorbents are utilized.

In cases where ultra-low sulfur levels are required, the desulfurized product may undergo additional treatment, such as high-pressure hydrotreating, to meet stringent fuel standards.

The advantage of adsorptive desulfurization lies in its independence from hydrogen, its operation under mild temperature conditions (ranging from room temperature to approximately 100 °C), and the recyclability of the adsorbent, making it a cost-effective method for sulfur removal in diesel fuel [5]. Table 2 compiles the ADS efficiencies of various adsorbents reported in recent years. It was found that modifying adsorbents with metals, acids, or alkalis significantly boosts their adsorption performance.

Saha et al. have summarized the advantages and limitations of various adsorbents and proposed necessary modifications to advance the technology [12].

Table 2. ADS efficiencies of various adsorbents.

Sulfur compound	Adsorbent	Sulphur Removal (%)	Ref
Gas Oil	metal-impregnated activated carbon adsorbents (Cu_2O/AC, ZnO/AC and NiO/AC_2C)		[11]
DBT (500 ppm of S)	Mongolian anthracite activated carbon	99.7	[14]
DBT (31.25 mmol/L of S)	Zn/Granulated activated carbon	96.1	[15]
DBT (500 ppm of S)	Graphene nanoparticle	95.72	[16]
DBT (500 mg/ L)	Co-Acid activated Granular activated carbon	92	[16]
TH (100 mg/L of S)	Alkali treated ZSM-5	70	[17]
DBT (550 ppm of S)	mixed metal oxide (TiO_2-SiO_2)	99	[18]
DBT (1000 ppm of S)	HNO_3 / Activated carbon		[19]

In adsorptive desulfurization (ADS), the regeneration of adsorbents plays a crucial role for maintaining cost-effectiveness and sustainability. The main regeneration methods used for adsorbents in ADS processes are thermal or chemical (solvent-based).

The thermal regeneration method involves heating the adsorbent in the presence of air or an inert gas at temperatures exceeding the boiling points of the adsorbed organic sulfur compounds. However, this approach can compromise the adsorbent's structural integrity and generate toxic byproducts such as H_2S and SO_x due to sulfur combustion.

In the chemical regeneration, adsorbents are washing with organic solvents such as ethanol, methanol, toluene, or dichloromethane. Unlike thermal methods, this technique eliminates the risk of producing harmful H_2S or SO_x gases, making it an environmentally friendly alternative [13]. The role of solvent is removing oil and other contaminants from spent adsorbents. The effectiveness of this regeneration method depends on three key factors: (1) the adsorption mechanism of contaminants (how contaminants are adsorbed, physical or chemical), (2) the solvent's polarity, and (3) the potential leaching of active metals from the adsorbent during washing.

Although promising levels of desulfurization have been achieved under mild conditions in laboratory and pilot-scale studies, the efficiency of even the most advanced adsorbents remains inadequate for industrial-scale implementation. The use of this method is particularly ineffective for heavy fuels due to low accessibility of large molecules in small pores that reduces adsorption efficiency.

Bio desulfurization (BDS)

Bio desulfurization (BDS) is an environmentally friendly process that uses microorganisms to remove sulfur from hydrocarbons, particularly fossil fuels.

Sulfur constitutes approximately 0.5–1% of the dry weight of bacterial cells and is essential for the growth and biological functions of microorganisms. It is commonly found in the structure of enzyme cofactors (e.g., Coenzyme A, Thiamine, and Biotin), amino acids (e.g., Cysteine and Methionine), and proteins. Depending on their enzymatic and metabolic capabilities, microorganisms can obtain the sulfur they need from various sources. Certain microorganisms are capable of utilizing sulfur from thiophenic compounds, such as dibenzothiophene (DBT), thereby reducing the sulfur content in fuels. Microbial desulfurization occurs under mild temperature and pressure conditions, making it an energy-efficient process. Furthermore, since this process relies on biocatalysts (enzymes), it is highly selective.

Using free microbial cells (immobilized) in bio desulfurization (BDS) can result in microbial contamination of fuels, whereas immobilized microbes provide advantages like easier separation, avoidance of microbial pollution, and recyclability of the [12].

Various studies have been conducted on the BDS process, but key challenges remain before it can be scaled up for industrial use. Issues such as managing and storing live microbes in industrial environments, expensive culture media for microbial cultivation, and the difficult separation of oil and biomass need to be resolved. Overcoming these problems is crucial for the practical application of this technology.

Alkylation Desulfurization

Among the various desulfurization strategies under investigation, alkylation desulfurization has emerged as a promising alternative aimed at enhancing the reactivity of refractory sulfur compounds, particularly dibenzothiophene (DBT) and its alkylated derivatives. This method is based on the concept of modifying the molecular structure of sulfur-containing species through alkylation reactions, which introduce alkyl substituents at specific positions on the aromatic ring. Such modifications can significantly alter the electronic distribution and steric hindrance around the sulfur atom, making the compounds more susceptible to subsequent oxidative or extractive removal.

In recent research, alkylation has been shown to activate otherwise unreactive DBT molecules, thus facilitating their conversion into more polar or less stable forms that can be effectively separated from the hydrocarbon matrix. This approach can act as a pre-treatment step, especially valuable in processes where conventional hydrodesulfurization (HDS) fails to achieve ultra-low sulfur targets due to the strong stability of certain sulfur species like 4,6-dimethyldibenzothiophene (4,6-DMDBT).

Despite its potential, alkylation desulfurization faces several challenges that must be addressed before industrial deployment.

These include:

- Selective alkylation at reactive positions without forming unwanted byproducts
- Integration with downstream processes (e.g., ODS or EDS)
- Catalyst development for efficient and cost-effective alkylation
- Economic viability compared to well-established methods like ODS or HDS

Nevertheless, the method holds promise for complementing existing desulfurization technologies, especially in contexts where fuel quality regulations are becoming increasingly stringent.

Extractive desulfurization

Extractive desulfurization is a liquid–liquid extraction process. One of the advantages of this method is that it does not require Hydrogen gas and operates under mild conditions. Figure 4 indicates a simple flow diagram for Extractive desulfurization process. According to the figure, In the mixing tank, the feedstock is combined with the solvent, allowing the organosulfur compounds to dissolve into the solvent due to their greater solubility. Next, in the separation stage, the hydrocarbon is separated from the solvent. After this separation, the treated hydrocarbon, which has a reduced sulfur content, can undergo further processing. During distillation, the organosulfur compounds are removed from the solvent, and the recovered solvent is then recycled back to the mixing tank.

To enhance mixing and extraction, the viscosities of both the oil and the solvent should be kept as low as possible. This factor poses a challenge with heavy oil, as it necessitates higher temperatures during extraction to lower its viscosity. Additionally, this requirement limits the volatility of the solvent, potentially making it necessary to carry out the extraction process under pressure.

The solvent needs to have a boiling point distinct from that of the sulfur compounds extracted from the oil. Since the solvent is used in much larger volumes compared to the sulfur compounds, it is generally preferable to use a solvent with a higher boiling point than the sulfur compounds. However, in the case of heavy oil extraction, using a high-boiling solvent is not feasible, and a lower-boiling solvent must be employed instead, leading to significantly higher solvent recovery costs.

The recovered solvent may still contain certain compounds extracted from the oil that cannot be effectively separated through distillation. As the solvent is recycled, these compounds can accumulate, making it necessary to purge a portion of the solvent. Additionally, the requirement to use a light solvent and the possibility of solvent loss due to its dissolution in the complex composition of heavy oil reduce the economic viability of solvent-based desulfurization methods for heavy oil.

Traditionally, dimethylformamide (DMF), acetonitrile (AcN), pyrrolidones, and dimethyl sulfoxide (DMSO) have been the primary solvents utilized in extractive desulfurization processes. In recent years extractive desulfurization of fuels such as diesel using ionic liquids (ILs), compared to conventional organic solvents, is considered as an attractive and alternative approach for achieving ultra-clean fuels.

Although ionic liquids possess unique properties such as low solubility in hydrocarbon phases, low viscosity and High rate of phase separation after mixing and extraction, their application in heavy fuels faces several challenges, which are outlined below:

- Although ionic liquids exhibit high distribution coefficients for model sulfur compounds like dibenzothiophene in simplified model mixtures, their performance significantly declines when applied to real straight-run distillates. In other words, ionic liquids are not optimal solvents for the extractive desulfurization of actual straight-run fuels and this limitation becomes even more pronounced when dealing with heavy oils.
- Ionic liquids have high boiling points, making the separation and recovery of the extracted sulfur compounds more difficult compared to conventional organic solvents. In a study conducted by Javadli et al. (2012), several strategies were reported to overcome this limitation [4].

The effectiveness of an extraction process using ionic liquids improves when the organosulfur compounds are first oxidized to their corresponding sulfoxides and sulfones, as these oxidized sulfur compounds exhibit

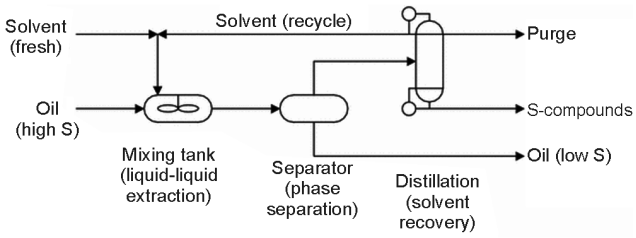


Fig. 4. Simple flow diagram for Extractive desulfurization process.

significantly higher distribution coefficients [20]. Currently, desulfurization of heavy oil through ionic liquid extraction is not considered a practical approach.

Oxidative desulfurization (ODS)

Oxidative desulfurization (ODS) process is considered to be one of the most promising methods for desulfurization. The process consists of two key steps. The organic sulfur compounds in petroleum are first oxidized (using a catalyst and oxidant) into polar sulfoxides/ sulfones. In the presence of excess oxidizing agent, sulfones are obtained and no sulfoxide detected. After converting sulfur-containing compounds into their corresponding sulfones, separation processes such as solvent extraction or adsorption are performed on them. The oxidation of thiophene derivatives into sulfones increases their polarity and molecular weight, facilitating their separation through abovementioned separation processes.

Unlike HDS, which requires high temperatures and pressures as well as large amounts of hydrogen, ODS operates efficiently in the liquid phase under mild temperature and pressure conditions, making it more energy-efficient and operationally simpler. Moreover, ODS has shown high efficiency in removing refractory sulfur-containing compounds, such as dibenzothiophene (DBT) and its alkylated derivatives, which are typically resistant to HDS treatment. Another notable benefit is that ODS does not consume hydrogen, making it particularly advantageous in situations where hydrogen supply is limited [21].

Various types of oxidants and catalysts may be used in the oxidation step, and of course various types of solvents or adsorbents in the separation step (separation of the oxidized sulfur compounds). The selection of oxidant, catalyst, solvent, and appropriate operating conditions are the fundamental pillars of the ODS method.

The steps of the ODS process can be briefly classified in the following order:
involves the following steps:

1. Feed Preparation: The hydrocarbon feedstock is pre-treated to remove particulates and water, ensuring optimal reaction conditions.
2. Oxidation Reactor: The pre-treated feed is introduced into an oxidation reactor where it is mixed with an oxidizing agent (commonly hydrogen peroxide or molecular oxygen) in the presence of a catalyst. This step converts sulfur compounds into their corresponding sulfoxides or sulfones.
3. Extraction Unit: The oxidized sulfur compounds, being more polar, are extracted from the hydrocarbon phase using a polar solvent such as acetonitrile or methanol.
4. Separation Unit: The mixture is then sent to a separator where the desulfurized hydrocarbon phase is separated from the solvent containing the extracted sulfur compounds.
5. Solvent Recovery: The solvent is recovered from the sulfur-rich phase through distillation or other separation techniques and recycled back into the extraction unit.

The abovementioned stages are summarized for Diesel fuel and schematic diagram of ODS process are indicated in figure 5 and figure 6 respectively.

Oxidants used in ODS process

Selecting a suitable oxidant is a critical step, as it directly affects the reaction kinetics, process safety and overall economics of the system. Sometimes, a non-selective oxidation can lead to unwanted byproducts.

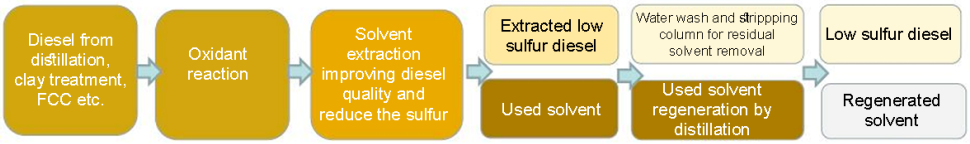


Fig. 5. Stages of ODS process for a fuel.

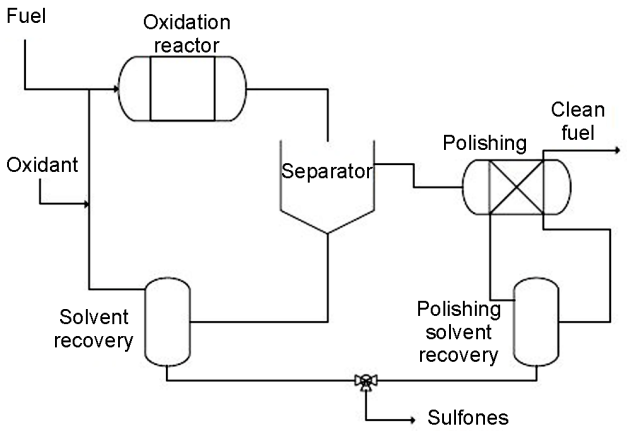


Fig. 6. Schematic diagram of ODS process [21].

Oxidation Strength, selectivity, availability and cost and stoichiometric efficiency are key factors in the selection of the appropriate oxidant.

A low oxygen-to-sulfur (O:S) molar ratio is desirable to reduce the required dosage of oxidant and limit excess waste generation. However, in many systems, molar ratios greater than 2:1 are often necessary, which can increase costs and impact process feasibility [22]. The oxidants can be divided into two categories:

- Autoxidation: Oxidation with air or oxygen
- Chemical oxidation: Hydrogen Peroxide (H_2O_2), Ozone (O_3), Peracids (e.g., Peracetic Acid), Nitric acid (HNO_3), TBHP (tert-butyl hydroperoxide) and … are included in this category.

Hydrogen peroxide (H_2O_2) is commonly used in ODS process but it may decompose under reaction conditions. This chemical substance is not present in a refinery, and its price is relatively high. For this reason, some approaches take into account possible integration of a hydrogen peroxide synthesis in the process.

Among various oxidants, O_2 stands out as a promising candidate for the oxidation of sulfur-containing

Table 3. Various types of catalysts are used in the ODS process

Type of catalyst	Examples	Reference
Homogeneous Catalysts	Polyoxometalates (POMs) CoMo polyoxometalate polyoxometalate FeMo polyoxometalate CrMo	[24]
	Organic acids (formic acid, acetic acid)	[25]
Heterogeneous Catalysts	Metal oxides (TiO_2, MoO_3, WO_3, V_2O_5, CuO, …)	[23, 26]
	Supported catalysts (Mo/Al_2O_3, MoO_3/SiO_2, CuO/Al_2O_3, Co_3O_4/Al_2O_3, MnO_2/Al_2O_3)	
	Zeolites & Mesoporous materials (e.g., TS-1, Ti-HMS)	
Carbon-based catalysts) (Carbon hybrid materials	activated carbon	[27, 28]
	(GO), graphene oxide	
	carbon nanotubes (CNTs)	
	reduced GO (rGO)	
	graphitic carbon nitride	
Nano catalysts	WO_3> Fe_2O_3 > CoMo> MnO_2> MoO_3	[29]
	Nanocomposites (nanocomposites of heterogeneous phosphor tungstic acid over natural zeolites), nanostructure of graphitic carbon nitride ($g\text{-}C_3N_4$)	[30]
Ionic Liquids (ILs)	Acidic ILs ([BMIM]Cl/$AlCl_3$)	[31]
	Polyoxometalate-based ILs	

compounds due to its natural abundance and environmentally friendly nature.

According to the studies the ideal stoichiometric molar ratio of Oxidant Sulfur (O:S) is 2:1. Due to inefficiencies, side reactions, and decomposition of oxidants (especially H_2O_2), a higher O:S molar ratio

Table 4. Comparison of the ODS method with other desulfurization techniques.

Process	Advantages	Disadvantages
Oxidative Desulfurization	- Effective for removal of all sulfur-containing compounds - Mild operating conditions Low time, technique, and energy costs - - Can be integrated with HDS process for deep desulfurization	- Sulfur-containing extracts as waste - Selection of suitable solvent and Oxidants is crucial
Adsorptive Desulfurization	- Low gas volume - Easy to operate and maintain	- Limited adsorption capacity - Need for frequent adsorbent regeneration - High selectivity required for adsorbents - Effective for light sulfur compounds
Hydrodesulfurization	acyclic sulfur-containing - Effective for removal of aliphatic and compounds - Sulfur is a potential product from waste (Converts sulfur into H_2S, easily removable) - High reliability and well-known technology	- Requires hard operating conditions - High hydrogen consumption concentration to 10-50 ppm - High operating costs to decrease sulfur - Problems for removal of polyaromatic sulfur-containing molecules
Bio desulfurization	- Mild operating conditions - Environmentally friendly - Does not require the use of hydrogen gas	- Low desulfurization rate - Sensitivity of microorganisms to environmental conditions - High time costs
Extractive Desulfurization	- Does not require the use of hydrogen gas - Mild operating conditions	- co-extraction of aromatic hydrocarbons along with organosulfur compounds - Choice of suitable solvent is Oxidants crucial - Solvent regeneration

Table 5. Different types of oxidants and catalysts used in the ODS method.

Fuel	Oxidant	Catalyst	Separation method	Notes	Ref.
Dibenzothiophene	H_2O_2	MoO_3–SiO_2 aerogel	Adsorption of DBT Sulfones on Catalyst		[32]
Mineral lubricant base oil	H_2O_2	Formic acid, Acetic Acid (comparison)	Extraction with Equal volume of DMF (Dimethylformamide)	Formic acid indicated higher oxidative capability than acetic acid, and the optimization of reaction conditions was carried out using formic acid as the solvent.	[25]
Non-hydrotreated Kerosene	H_2O_2	Acetic acid	Extraction with propanol-water (volume ratio: 50%)		[33]
Gasoline and kerosene	H_2O_2	Acetic, benzoic, butanoic, formic acid (Best: Acetic acid)	Extraction with 80% Acetonitrile solution		[1]
Vacuum Gas Oil	H_2O_2	Formic acid	Extraction with Dimethylformamide (DMF)	Efficiency of Dimethylformamide (DMF), acetonitrile (ACN), methanol was compared. The most effective solvent for removal of sulfur compounds was DMF	[34]
DBT	Air	BCN-20 (boron nitride incorporating with carbon atoms)		Total sulfur removal can be achieved at 100 °C and atmospheric pressure.	[35]
Diesel type Oil	H_2O_2 / Ozone	solid catalyst vanadium/tungsten/TiO_2 supported on cordierite	Extraction with Ethanol at a wt. ratio of 2:1		[36]
Diesel Fuels	Molecular Oxygen	oxygen-cobalt & cobalt salt -aldehyde (comparison)	1- Adsorption on Alumina and Silica 2- Extraction with Acetonitrile	2 stage desulphurization	[37]
DBT	Ozone	TiO2/MCM-41	Extraction with ionic liquid	IL [BMIM] Ac	[31]
DBT	Ozone	Co_3O_4/γ-Al_2O_3		IL [BMIM]Ac	[38]
Jet and Diesel Fuels	Ultrahigh purity (UHP) air	Unsupported CuO and CuO/ $Al2O_3$	Adsorption on Beta Zeolite		[26]

Table 5. Different types of oxidants and catalysts used in the ODS method.

Heavy fuel oil	solution of 30 wt.% H2O2	Formic acid, Acetic Acid (comparison)	Extraction with Equal volume of Acetonitrile: Fuel oil	Formic acid is an effective catalyst, but as the reaction progresses, it leads to the formation of sticky byproducts. Therefore, acetic acid was used in this study instead. However, if the issue is resolved, formic acid can perform more efficiently than acetic acid.	[39]
DBT	O_2	polyoxometalate catalysts		- Polyoxometalate catalysts have high activity in the presence of oxygen or air - Regeneration of catalyst was done by washing with Aceton	[24]
Model Diesel	tert-butyl peroxide (TBHP)	monometallic and bimetallic oxide catalysts	Acetonitrile, Dimethylformamide (DMF) and 1-methyl-2pyrrolidone were compared	DMF was the most selective low-boiling solvent for diesel treatment in middle distillate fractions. Meanwhile, less efficiency of acetonitrile was ascribed to low polarity and its density is similar to diesel [18].	[23]
Commercial Diesel	Oxidant = TBHP	Ce-Fe-AC	DMF		[40]
Gas Oil	H_2O_2	Fe_2O_3-GO	Acetonitrile		[41]
Real Gasoline	H_2O_2	$C_3N_2H_5@H_3PMO_{12}O_{40}@CS$ (amphiphilic carbon-based materials)	Extraction with Acetonitrile		[42]
DBT	Air	Co-Mo-O (bimetallic oxide catalyst)		At Co/Mo ratio, 2:1 the best performance was obtained	[43]
Natural Diesel	O_2	Ce-Mo-O (bimetallic oxide catalyst)			[44]

is usually required. Approximately 50 percent excess oxidant has been used to ensure proper results [23].

Catalysts used in ODS process

Determining the molar ratio of oxidant, reaction time, type and amount of catalyst is very important in this process. Catalysts can deactivate over time, and their recycling and recovering should be taken in to account. Choosing the right catalyst requires testing during the feasibility stage. Various types of catalysts are used in the ODS process. Their general classification is discussed below:

Table 4 shows a comparison between different desulfurization methods, and Table 5 summarizes the different types of oxidants and catalysts used in the ODS method.

Methods used for the separation of sulfones in ODS process

In the oxidative desulfurization process, the removal of sulfones and by-products such as carboxylic acids, which are generated during the oxidation step, is essential. As previously discussed, the polar sulfur oxidation products generated during oxidative desulfurization can be effectively removed from the predominantly non-polar hydrocarbon fuel matrix using methods such as solvent extraction or adsorption.

When solvent extraction is employed for the separation of sulfones from fuel, an appropriate polar solvent such as dimethylformamide (DMF) can be used for extraction of the produced sulfones. After extraction of the sulfones, the solvent should be recovered by distillation of the sulfone-rich solvent. The products of this distillation are the recovered solvent, which can be recycled to the extraction section, and a high boiling product, which is the sulfone-rich waste (Raffinate).

Extraction solvent can be added simultaneously with the oxidizing agent into the fuel or after the sulfur compounds have been oxidized. After extraction, the desulfurized fuel can be obtained [45].

Researchers have reported many solvents for sulfones extraction, including Dimethyl formamide (DMF), Acetonitrile, Dimethyl sulfoxide (DMSO), Formic acid, Methanol, and etc.

Babkar et al. (2012) conducted a comparative study on the performance of various polar solvents namely acetonitrile, dimethylformamide (DMF), and 1-methyl-2-pyrrolidone, for the extraction of oxidized sulfur species during the oxidative desulfurization of diesel fuel [23]. Their findings indicated that DMF exhibited the highest selectivity and efficiency as a low boiling point solvent, particularly in the treatment of middle distillate fuel fractions. In contrast, Acetonitrile demonstrated inferior performance which was attributed to its lower polarity and a density closely matching that of diesel, leading to insufficient phase separation and reduced extraction efficiency.

In case of using adsorption technique for the separation of sulfones from the fuel, a suitable adsorbent like silica gel, alumina, or zeolites can be used. In this case, the regeneration of the spent adsorbent should be carried out by thermal treatment or solvent washing to eliminate surface-bound sulfones. The recovery of the used solvent by distillation results in the generation of the sulfone-rich waste stream (Raffinate) again that must be managed through appropriate waste management practices.

In summary, separation methods can be categorized as follows:

• Solvent Extraction: This involves using a polar solvent (e.g., acetonitrile, methanol, or DMF) to selectively extract the sulfones from the fuel, followed by separation of the solvent and oxidized compounds through distillation.

• Adsorption: Adsorption techniques, using materials like activated carbon, can be used to remove the sulfur compounds from the aqueous solution.

• Membrane Separation: Membrane separation processes, such as reverse osmosis, can be used to separate the sulfones and other byproducts from the waste stream.

Challenges of Oxidative Desulfurization (ODS) in Heavy Fuel oils

Despite the advantages of oxidative desulfurization (ODS) over conventional hydrodesulfurization (HDS), its application to heavy fuel fractions such as vacuum gas oil, atmospheric residue, and heavy diesel remains limited due to several operational and chemical challenges. One of the primary obstacles is the high viscosity of heavy fuels, which severely restricts

mass transfer and mixing efficiency between the oxidant and the sulfur-containing species, thereby lowering the overall reaction rate [46]. Furthermore, the presence of polar compounds, resins, and asphaltenes can lead to catalyst deactivation and the formation of stable emulsions, complicating the downstream separation of oxidized products. The heavy fractions also contain refractory sulfur compounds, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), which are inherently less reactive and require more active catalytic systems for efficient oxidation. Additionally, the extraction and removal of oxidation products like sulfoxides and sulfones from such complex matrices is less efficient compared to lighter fuels, often requiring the use of advanced solvents or multiple washing steps. These limitations collectively raise the operational cost and complexity of ODS when applied to heavy fuel streams.

Oxidative desulphurization (ODS) of heavy fuel oil (HFO) faces some problems such as gum formation and a high level of waste hydrocarbons. By considering dibenzothiophene (DBT) as a typical representative of sulfur-containing compounds in the fuel fraction, it has been estimated that approximately 20% of hydrocarbons are lost during the extraction stage of the process [47].

The waste management of sulphone compounds at the end of the process is one of the important challenges of this method.

The main components of by product-Raffinate oil by solvent-obtained are polycyclic aromatic hydrocarbons (PAHs), sulfur content, gums, asphaltenes and sulfur compounds.

Experimental observations indicate that the oxidative desulfurization (ODS) of 1,000 tons per day of hydrocarbon feed containing 500 $mg.kg^{-1}$ sulfur results in the generation of approximately 1 ton of sulfone-rich waste, a quantity that is considered significant [6]. This volume of waste is non-negligible and highlights a critical challenge associated with the industrial implementation of ODS technology.

Various strategies have been proposed for the management of sulfone-rich waste streams. These include [48]:

- Feeding it into the coking process
- Introducing it into gasification units to produce Syn-thesis gas.
- Recovering the hydrocarbon portion from the sulfone molecules (i.e., hydrocarbon recovery (
- Incineration of Waste (Thermal Incineration):

In this method, the waste is incinerated at temperatures above 850 °C in specialized furnaces. Due to the presence of sulfur in the structure of sulfones, SOx gases may be released if no gas treatment system is in place. The use of adsorbents such as lime (CaO) or wet scrubber systems is essential to control emissions.

- According to some sources, raffinate oil can be used in some applications, including the production of modified asphalt, as rubber processing oil, or as a component in ink solvent formulations.

Recently, the incorporation of sulfone waste into bitumen has been explored as a novel approach for sulfone waste management. Addition of the sulfone waste to bituminous mixtures can act as a softener, to reduce waste volume and costs and enhance the performance and improve the functional properties of asphalt mixtures.

Important aspects highlighted in patents on oxidative desulfurization of heavy fuels.

(a) Oxidation is carried out in an acidic environment, often using hydrogen peroxide along with short-chain carboxylic acids such as formic or acetic acid. The process is typically performed at low temperatures, around 50 °C, over a duration of approximately 6 hours. Oxidation can be followed by a thermal aftertreatment step at a temperature range of 350 to 450 °C, aimed at breaking the C–S bonds that have been weakened during the oxidation stage. The temperature for this step is selected in such a way that thermal degradation of hydrocarbons is minimized [4].

(b) Oxidation is carried out using an oxidizing agent, such as air, at temperatures between 80 and 180°C. This process can optionally take place in the presence of a non-acidic catalyst enhanced with metals from Group 5A (for example, vanadium) and Group 8 (such as nickel, palladium, or platinum). After oxidation, the material can undergo a thermal treatment at temperatures above 200°C, preferably within the range of 300 to 400°C, to release sulfur mainly in the form of SO2.

(c) Oxidation is performed using an oxidizing agent such as hydrogen peroxide, together with an acid like acetic acid and a solid catalyst. The reaction typically

occurs at approximately 50°C, though temperatures between 20 and 90°C have also been reported. Afterwards, the solvent and the products are separated through distillation and extraction.

Using Oxygen in the ODS Process

In recent years, molecular oxygen present in ambient air has been considered a promising oxidant for oxidative desulfurization (ODS) owing to its abundance, low toxicity, and cost-effectiveness. Nevertheless, achieving effective activation of molecular oxygen under mild reaction conditions remains a significant challenge. The benefits of using oxygen can be categorized as follows:

Oxygen can be produced on-site or easily generated within petrochemical facilities, lowering transportation and storage costs compared to H_2O_2 and other oxidants.

In case of using oxygen as oxidant, the following catalysts are suggested:

- Porous materials and their composites have garnered considerable interest owing to their large surface area, well-defined pore structure, and inherent stability. These properties facilitate rapid oxygen diffusion and enhance the exposure of active sites, making them highly suitable for aerobic oxidation processes.
- Porous mixed metal oxides catalysts are desirable due to their tunable electronic structure, which could facilitate the activation of molecular oxygen.
- Porous graphene-based catalysts are promising catalysts due to their excellent mechanical stability, functional groups, and high surface area [49].

Hydrogen peroxide used as an oxidizing agent during oxidative desulfurization forms water as the only byproduct of the reaction, but its main disadvantage is associated with high explosion hazard and its high cost in some countries. Although molecular oxygen is an environmentally benign and economically favorable oxidizing agent, its practical application is hindered by a pronounced induction period, during which it exhibits limited reactivity. To overcome this limitation, oxidation reactions are typically performed under elevated temperatures, using either pure oxygen or ambient air, to enhance the activation and reactivity of molecular oxygen .[50] The oxidation step is typically carried out at temperatures ranging from 80 to 180°C, depending on the type of feedstock, oxidizing agent, and catalyst used. The amount of oxygen needed usually corresponds to 1 to 6 active oxygen atoms in the oxidant for every sulfur atom present in the feedstock. Combining autoxidation with other techniques, such as hydrodesulfurization, may also create synergistic effects that enhance the overall efficiency of the process.

The catalyst's efficiency can be significantly influenced by its electronic characteristics and surface functional groups. Wang et al. demonstrated that graphite oxide co-doped with nitrogen and boron showed outstanding electrocatalytic activity toward the oxygen reduction reaction. This enhanced performance was attributed to modifications in charge and spin density resulting from heteroatom incorporation. These findings confirm that heteroatom doping plays a crucial role in significantly enhancing the catalytic efficiency [51]. Iqrash Shafiq et al. (2021) Summarized ODS performance results for different gaseous oxidants systems [8].

Heavy oil and bitumen extracted from oil sands have been examined under different conditions to study the physical and chemical changes following autoxidation. It was determined that 150°C is a critical temperature threshold influencing the oxidative desulfurization (ODS) of bitumen. At this temperature, the reaction order changes: below 150°C, autoxidation follows a high-rate first-order reaction, while above 150°C, at low levels of oxidation, the process shifts to a second-order autoxidation regime [52].

A major challenge in using autoxidation for the oxidative desulfurization (ODS) of heavy oil is preventing free radical addition reactions. These reactions lead to a substantial rise in viscosity, making transportation and subsequent upgrading processes more difficult.

In general, high viscosity and boiling point, the refractory nature of sulfur-containing compounds, the formation of sulfone-rich waste streams, gum (sticky material) formation, catalyst deactivation, and the loss of a portion of valuable hydrocarbons during the extraction process are considered among the main challenges of this method when applied to heavy fuels.

Strategies such as combining oxidative desulfurization with thermal processes or hydrodesulfurization,

as well as utilizing sulfone-rich waste streams in secondary applications (such as bitumen modifiers), have been reported as the most effective approaches for the oxidative desulfurization of feedstocks with high sulfur content.

In summary, for fuels with sulfur contents lower than 1000 ppm, the oxidative desulfurization process alone is generally sufficient. However, for feedstocks containing more than 1000 ppm sulfur, supplementary methods such as hydrodesulfurization or thermal processes are currently required [53]. Although oxidative desulfurization is technically feasible and environmentally favorable for upgrading heavy oils, further research is necessary to optimize catalysts, reduce operating costs, and develop sustainable solutions for waste management.

CONCLUSION

Oxidative desulfurization (ODS) has emerged as a promising complementary or alternative approach to traditional hydrodesulfurization (HDS) for the removal of refractory sulfur compounds, especially from heavy oils. Unlike HDS, which operates under severe temperature and pressure conditions and requires significant hydrogen consumption, ODS offers the advantage of milder operating conditions, high selectivity toward difficult-to-remove sulfur species (e.g., 4,6-DMDBT), and no dependence on hydrogen.

However, the application of ODS to heavy fuel fractions faces some challenges. These include the high viscosity and complex composition of heavy oils, which limit mass transfer and phase separation, the formation of sulfone-rich waste, gum formation, deactivation of catalysts and loss of valuable hydrocarbons during extraction. Furthermore, waste management, particularly the handling of sulfone-rich byproducts, and the lack of a fully commercialized, scalable ODS unit remain key limitations.

Integrated solutions such as combining ODS with thermal processing and hydrodesulfurization or utilizing sulfone waste in secondary applications (e.g., bitumen modifiers) are reported as the most effective ideas for ODS of feeds with high sulfur content.

In conclusion, for fuels with a sulfur content of less than 1000 ppm, the ODS process alone is sufficient but for feedstocks with sulfur content exceeding 1000 ppm, the use of complementary methods such as hydrodesulfurization (HDS) or thermal processes is currently necessary

while ODS presents a technically feasible and environmentally favorable option for upgrading heavy oils, further research is needed to optimize catalysts, reduce operational costs, and develop sustainable waste management solutions.

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