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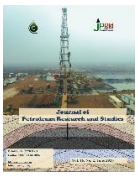

A Review on Desulfurization of Kerosene: Current Practices and Future Innovation

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Abstract

Kerosene desulfurization is one of the most pressing tasks for the petroleum sector because the amount of slfur emissions that affect air quality is more strictly controlled by legislation. This review addresses the growing scope and challenge of kerosene desulfurization technology by providing an integrative perspective on current practices and development trends. The perspectives presented in this paper aim to help improve the development of efficient and environmentally friendly solutions to meet changing social and industrial requirements. In this review, advanced desulfurization technologies are available for use in kerosene including hydrodesulfurization (HDS), oxidative desulfurization (ODS) and adsorption desulfurization methods to meet the permissible compliance level of the Global Fuel Standard (October 2023). HDS is very efficient and widely applied but there are a number of limitations to HDS such as high energy consumption and high maintenance cost as the refractory sulfur compound cannot be removed. This is because recent developments in utang technologies are of great interest as they may improve the degree of desulfurization at low environmental and economic costs. These include advanced catalyst designs, ionic liquids and bio-desulfurization techniques. The paper presents key aspects of new possibilities such as green chemistry application and hybrid setup of processes that utilize the advantages of several technologies to achieve better performance.

Keywords: Desulfurization, Oscillatory Baffled Reactor (OBR), Kerosene, Petroleum refining.

مراجعة لعمليات ازالة الكبريت من الكيروسين: الممارسات الحالية والابتكارات المستقبلية

الخلاصة:

إزالة الكبريت من الكيروسين تعد واحدة من أكثر المهام إلحاحًا في قطاع البترول، نظرًا لأن انبعاثات الكبريت التي تؤثر على جودة الهواء تخضع لرقابة أكثر صرامة من قبل التشريعات. تناقش هذه المراجعة النطاق المتزايد والتحديات المتعلقة بتقنيات إزالة الكبريت من الكيروسين من خلال تقديم منظور شامل حول الممارسات الحالية واتجاهات التطوير. تهدف الرؤى المقدمة في هذه الورقة إلى المساهمة في تحسين تطوير حلول فعّالة وصديقة للبيئة لتلبية المتطلبات الاجتماعية والصناعية المتغيرة. تستعرض هذه المراجعة تقنيات إزالة الكبريت المتقدمة المستخدمة في الكيروسين، بما في ذلك تقنية إزالة الكبريت الهيدروجينية (HDS)، وتقنية إزالة الكبريت بالأكسدة (ODS)، وطرق إزالة الكبريت بالامتصاص، وذلك لتحقيق الامتثال لمستويات الكبريت المسموح بها وفقًا للمعيار العالمي للوقود (أكتوبر 2023). تُعتبر تقنية HDS فعّالة

للغاية ومُطبّقة على نطاق واسع، إلا أن هناك عددًا من القيود المرتبطة بها، مثل استهلاك الطاقة العالي والتكاليف المرتفعة للصيانة، حيث لا يمكن إزالة مركبات الكبريت المقاومة. لهذا السبب، تحظى التطورات الحديثة في التقنيات البديلة باهتمام كبير، حيث يمكنها تحسين درجة إزالة الكبريت بتكاليف بيئية واقتصادية منخفضة. تشمل هذه التطورات تصميمات محفزات متقدمة، السوائل الأيونية، وتقنيات إزالة الكبريت الحيوية. تقدم الورقة الجوانب الرئيسية للإمكانيات الجديدة، مثل تطبيق الكيمياء الخضراء وإعداد أنظمة هجينة تجمع بين مزايا عدة تقنيات لتحقيق أداء أفضل.

1. Introduction

Kerosene is widely used as a fuel source in places where access to electrical power is difficult. In addition to being readily available, kerosene has an efficient energy content that enables it to produce a lot of energy when completely burned. This ability explains why kerosene is ideal for use in motor fuels - such as jet engines. Like other refining products obtained from oil, kerosene is sought after for its production at a boiling point range of 150 °C to 275 °C. Most of the molecules are hydrocarbon chains containing six to sixteen carbon atoms in their structure [1]. Kerosene is produced as a result of sequential or simultaneous chemical processes in nature, these processes are used to purify and modify kerosene. Some of the important reaction pathways are catalytic reforming, alkylation, catalytic cracking, and hydrotreating [2]. The type of kerosene produced contains different types of compounds including straight-chain alkanes, aromatics, alkylbenzenes, and naphthalene [3].

On the other hand, sulfur and sulfur-containing compounds are still present in high concentrations which can be troublesome in terms of environmental compliance and engine performance. Other petroleum products (e.g. pyrolysis oil) also contain up to 6% sulfur which exceeds the permissible limit for safe engine operation [4]. Long industrial development and application have shown that reducing the sulfur content in kerosene is the only way to improve the quality of kerosene while maintaining the performance characteristics of kerosene, and therefore controlling the kerosene content is the prerequisite for meeting more stringent environmental protection standards. To reduce sulfur in fuels and enhance combustion characteristics, advanced desulfurization processes have become essential aspects of petroleum refining operations. This work has a wide scope - aromatic sulfur compounds (benzothiophene, dibenzothiophene, and their alkylated derivatives) as well as heterocyclic compounds (thiophene, thiolane, mercaptan, and aromatic disulfide) are ubiquitous in fuels. Kerosene also contains traces of inorganic sulfur compounds, including dissolved pyrite, elemental sulfur, and carbonyl. Several desulfurization methods have been developed and applied to address these challenges, such as deep oxidative desulfurization [1], low-cost adsorbent-based desulfurization [5], extractive desulfurization [6], hydrodesulfurization or HDS, ultra-deep desulfurization [3], and oxidative desulfurization (ODS) [7]. Hydrodesulfurization is a widely used method in the petroleum industry due to its ability to remove a wide variety of sulfur compounds, although it is an energy-intensive process. Hydrodesulfurization has shown technical limitations in

some refractory sulfur species such as dibenzothiophene and its alkyl ring derivatives, emphasizing the need for advances in technology development to overcome the limitations [8]. New approaches are emerging to make the entire desulfurization process more efficient while reducing operating costs and environmental impacts. These include the development of new catalysts, the incorporation of ionic liquids, and hybrid methods that combine multiple processes. Continued development in these lines is essential for desulfurization due to evolving challenges and increasingly stringent environmental standards [9].

This review aims at providing a thorough critique and review of the existing kerosene desulfurization technologies. It intends to focus on the effectiveness, limitations and environmental impact of each of the explored methods Desulfurization methods include Hydrodesulfurization, Oxidative Desulfurization and adsorption among others. This review seeks to identify what has changed and what has been done in the area. It seeks to show how new types of catalysts, ionic liquids, and biodesulfurization can help solve the problems associated with conventional processes, especially with regard to energy requirements and cost of operation. Besides, the paper discusses the potential of combining green chemistry and hybrid process designs to improve on the existing performance of sulfur removal without compromising the global standards of fuels. The aspiration of this review is to help readers understand the major issues related to kerosene desulfurization focusing on the kerosene desulfurization technologies of today, as well as the potential developments for tomorrows. In the end, the review is skilled in understanding the potential and barriers in kerosene desulfurization from re-engineering perspective, contributing to more sustainable and cheaper options in the oil industry.

2. Typical Forms of Sulfur Compounds in Kerosene

Sulfur compounds in petroleum are classified into broad groups, namely refractory sulfur and non-refractory sulfur. Refractory sulfur compounds are characterized by molecules that remain stable; they include thiophene (T), benzothiophene (BT), dibenzotophene (DBT), and their individual alkylated derivatives. Among these compounds, dibenzotophene and its alkylated forms are particularly resistant to conventional desulfurization techniques that require more energy-intensive and advanced procedures [10, 11]. Refractory sulfur compounds are currently among the major issues being evaluated in desulfurization research due to their occurrence, resistance, and presence in heavier petroleum fractions. Non-refractory sulfur compounds, which include sulfides, disulfides, and mercaptans, are less stable and easier to remove using standard treatment processes such as

hydrodesulfurization (HDS). However, they tend to contribute significantly to the total sulfur levels of fuels and, therefore, must be treated to comply with stringent environmental regulations aimed at reducing sulfur emissions. They are usually classified according to their sulfur content as sweet or sour crude oil. Any oil with 0.5% or more sulfur by weight is sour crude while those with less sulfur are called "sweet crude". The reasons for the benefits derived from desulfurization of sour crude oil, other than emission control, are the prevention of corrosion and catalyst poisoning in downstream processing units so that the operating life of refining equipment can be extended. Therefore, it becomes very important to know the type of sulfur compounds encountered in the petroleum refining process in order to come up with suitable and effective desulfurization techniques. The typical compounds and distribution within petroleum fractions are represented in Fig. (**1**).

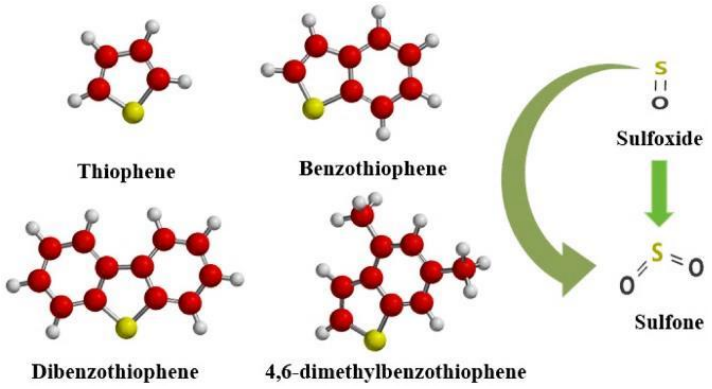

Fig. (1): Typical forms of sulfur compounds [14]

Interestingly, organosulfur compounds release toxic sulfur oxides during combustion, posing serious health and environmental problems. They are primarily responsible for air and water pollution and are the main driver of acid rain formation. Acid rain destroys ecosystems: it degrades soil, acidifies water, and harms plants, all of which affect long-term environmental stability. Furthermore, sulfur oxides also exacerbate and contribute to global warming and affect air quality, among other measures, directly affecting human health and the health of other living organisms through respiratory problems, ecosystem transformations, and reduced biodiversity.

3. Desulfurization Technologies

Desulfurization methods are typically classified based on several factors, including the types of sulfur compounds, the means by which they are performed, and the role of hydrogen in desulfurization. Methods also differ from each other in terms of their application (Fig. **(2)**.

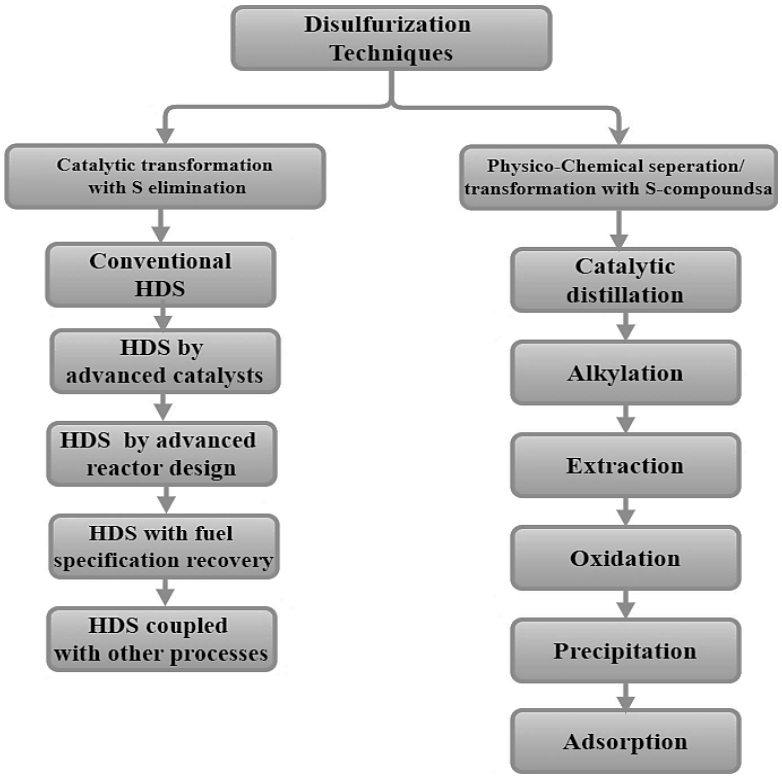

Fig. (2): Classification of desulfurization technologies

3.1. Hydrodesulphurization (HDS)

The standard is hydrodesulfurization, which is the most common and commercially viable desulfurization process practiced in refineries worldwide. This process can remove thiols, disulfides or sulfides but has very little effect on the more resistant sulfur compounds such as dibenzothiophene (DBT) and its derivatives. These compounds have proven resistant to hydrogenation due to their strong aromatic structures.

One of the main drawbacks of hydrodesulfurization is the operating conditions: typical temperatures are 300°C - 400°C and typical pressures are 3 to 6 MPa. Such harsh operating conditions increase operating costs and accelerate catalyst degradation, resulting in decreased efficiency and selectivity over time. Deactivation of the catalyst under such harsh conditions has a significant impact on the long-term sustainability of the process.

For example, Hussain et al. studied the HDS of raw kerosene with 0.364% sulfur and 16.498% aromatic components from the Durra refinery. Relatively high-metallic Ni-W/γ-Al2O3 catalysts were used in a single-stage reactor, and this study reported desulfurization efficiencies ranging from 74.9% to 95.6%, while aromatic reductions ranged from 1% to 12.8% under different operating conditions. This demonstrates the dependence of HDS performance on the feedstock composition

and reaction parameters, thus clarifying the limitations and continuous improvement of the process [6,7,18,19].

3.2. Non-Hydrodesulphurization Based (Non-HDS)

So-called non-hydrogen desulfurization technologies are those that do not rely on hydrogen for the catalytic decomposition of organosulfur compounds. These methods are promising alternatives to desulfurization because they overcome some of the major drawbacks of non-hydrogen desulfurization technologies, which consume a lot of hydrogen, require large amounts of energy, and are inefficient when processing highly resistant sulfur compounds such as thiophene and benzothiophene. A number of new methods have been invented to remove sulfur with high efficiency. One method involves changing the boiling point of sulfur-containing compounds to improve their separation from hydrocarbon mixtures. This is most often achieved by extraction desulfurization, in which the salt is selectively dissolved in a solvent to facilitate its extraction from the fuel matrix. Another very attractive method is adsorption desulfurization, which uses low-cost sorbents with very high selectivity for sulfur species. These sorbents effectively capture and remove sulfur compounds but do not require high temperatures or pressures. High standards have been set for some of the innovations developing towards high-efficiency desulfurization. One such innovation is modifying the boiling points of sulfur-containing compounds to facilitate their separation from hydrocarbon mixtures. This is often achieved by extraction desulfurization, where sulfur compounds are selectively dissolved in a solvent, making extraction very simple from the matrix fuel. Another attractive method is adsorption desulfurization, which relies on low-cost sorbents with very high selectivity for sulfur species; the sorbents efficiently capture and remove sulfur compounds without the need for high temperatures or pressures, making it energy and cost effective.

3.2.1. Extractive Desulfurization (EDS)

The extraction desulfurization process is based on the principle that organosulfur compounds are more soluble in certain solvents than hydrocarbons. In this process, sulfur-containing compounds are selectively dissolved in a suitable solvent, effectively separating them from the fuel. As shown in Figure (3), the process begins in a mixing tank, where sulfur compounds from the fuel oil move into the solvent due to their high solubility. The solvent-fuel mixture is then directed to a separator, where the hydrocarbons are separated from the solvent. The desulfurized hydrocarbon stream can be blended directly into the final fuel product or used as a feedstock for further refining. After separation, the organosulfur compounds are separated from the solvent, typically through

distillation, allowing the solvent to be recycled and reused in the process. This recycling step not only enhances the efficiency of the process, but also contributes to its cost-effectiveness. Extractive desulfurization represents a promising alternative to hydrodesulfurization (HDS), especially for achieving deep desulfurization under milder conditions and without the need for hydrogen, making it an attractive solution from an environmental and economic perspective [17].

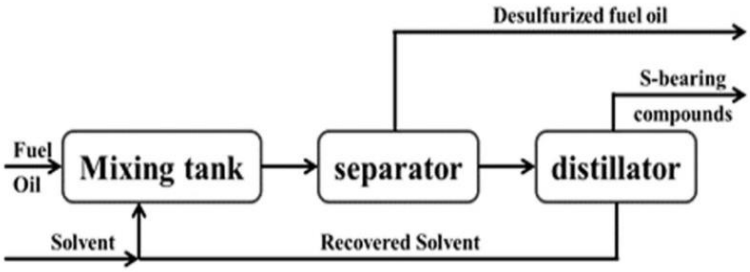

Fig. (3): General process flow of extractive desulfurization [18]

Deep extractive desulfurization (EDS) process is currently gaining scientific interest because it operates without hydrogen or catalysts at ambient temperature and pressure, while maintaining fuel quality and stability and minimal environmental impact [7]. In this process, the solubility of sulfur compounds plays an important factor in the extraction. The experiment on kerosene with sulfur content ranging from 0.206 to 1.272 w/w% demonstrated the application of hydrogen peroxide and acetic acid oxidation system combined with imidazolium-based ionic liquids for extraction desulfurization. The ionic liquids, 1-butyl-3-methylimidazolium bromide (BMIM) and 1-butyl-3-methylimidazolium hydrogen sulfate (HSO4) were synthesized and characterized using FT-IR and ^{1}H NMR, and were used as solvents in a six-cycle extraction procedure. The obtained desulfurization percentage for kerosene was 85% [19]. Jassim et al. [20] described the use of an intrinsic nanocatalyst for the removal of dibenzothiophene (DBT) from gasoline. In this paper, it was demonstrated for the first time that MnO2-MoO2 supported by tin(IV) oxide (SnO2) acts as a highly efficient catalyst in oxidative catalytic desulfurization (OEDS) in the presence of H2O2 oxidant to oxidize sulfur compounds. Under the optimum conditions (i.e., with 5% MnO2/SnO2 as catalyst, reaction temperature of 75 °C, and reaction time of 100 min), DBT was removed from kerosene fuel with an efficiency of 92.4%. The removal efficiency of other sulfur compounds was 91.2%. The extraction stage was carried out using acetonitrile as solvent at a stirring speed of 900 rpm for 30 min [19].

3.2.2. Adsorptive Desulfurization (ADS)

Adsorption desulfurization is one method by which organic sulfur compounds can be effectively removed from refinery streams using solid sorbents. Along this line of descent, the activity between

these sulfur compounds and the sorbent classifies the process into two forms: adsorption desulfurization and reactive adsorption desulfurization. The former process relies on organic sulfur compounds adsorbed on the surface of a solid sorbent. Here, the sulfur compounds are captured by means that can be considered non-covalent such as van der Waals forces or hydrogen bonding. The captured compounds are released during regeneration by washing the sorbent with an adsorbent. This concentrates the organic sulfur stream for further treatment or systematic disposal. In general, this is a simple process that requires less energy than other processes. However, the process may be limited by capacity and the need for reactivation. Reactive adsorption desulfurization involves a chemical reaction between organic sulfur compounds and an adsorbent. In this case, the sulfur chemically bonds with the adsorbent, typically resulting in the formation of stable non-sulfide compounds. This results in the separation of sulfur from the hydrocarbons released in the clean fuel streams. Spent sorbent rich in sulfur can be regenerated by various means such as hydrotreating to release sulfur as H2S or oxidizing to convert it to either elemental sulfur or sulfur oxides (SOx) depending on the process conditions used. Table (1) shows a comparison of studies conducted to demonstrate sulfur removal using different types of sorbents under their optimum conditions Table (**1**. This study facilitates comparative understanding of the performance and efficiency of several adsorbents in meeting desulfurization requirements.

Table (1): Sulfur reduction by adsorption under optimum conditions

Technique	Sample	Adsorbent	Sulfur Content (ppm)	Temp. (℃)	Result	Reference
Batch reactor	DBT	Zn-MMT	1000	25	76% Desulfurization	[5]
Batch reactor	DBT	bentonite material	1000	25 - 45	95.83% sulphur removal	[21]
Packed Bed	DBT	activated carbon	430	35	97.6 % sulphur removal	[22]
Batch reactor	DBT	Zn and Mn loaded on AC	200	30	92% DBT from kerosene	[23]
Batch reactor	Thiophenes	Cu_2O/AC	500	-	87.4 % sulfur removal	[24]

3.2.3. Photo-catalytic Desulfurization (PCDS)

Photocatalytic desulfurization has recently started to become one of the research stars. For example, using a photoreactor with continuous injection of O2, Mohamed and Ismail discovered the oxidative photodesulfurization of thiophene. The researchers fabricated a heterogeneous structure of D-Ag2O/ZrO2 by a simple sol-gel technique when using visible light at room temperature. The results demonstrated the increased photocatalytic activity due to light scattering, synergistic effect and rapid formation of radicals that added their reactivity upon their assembly. This method may efficiently

remove ultra-rare sulfur contents from fuels. Other studies include the photooxidation and desulfurization of dibenzothiophene (DBT) using H2O2 (30%) and Ag/ALa4Ti4O15 (where A = Ca, Sr and Ba) as photocatalysts. The effects of reaction time, temperature and amount of hydrogen peroxide on the improvement of the reaction were investigated. A possible removal mechanism from photooxidation was also reported. Very high selective desulfurization activity was found with Ag(2 wt%/CaLa4Ti4O15) and Ag(1 wt%/BaLa4Ti4O15) under desulfurization tests with DBT conversions of 99.0% and 98.0%, respectively [26]. Further evidence of the potential of photocatalytic desulfurization as a method to reduce sulfur levels within fuels is due to the implications for combating the environmental pollution effects of these sulfur emissions (Fig. **(4)** [27].

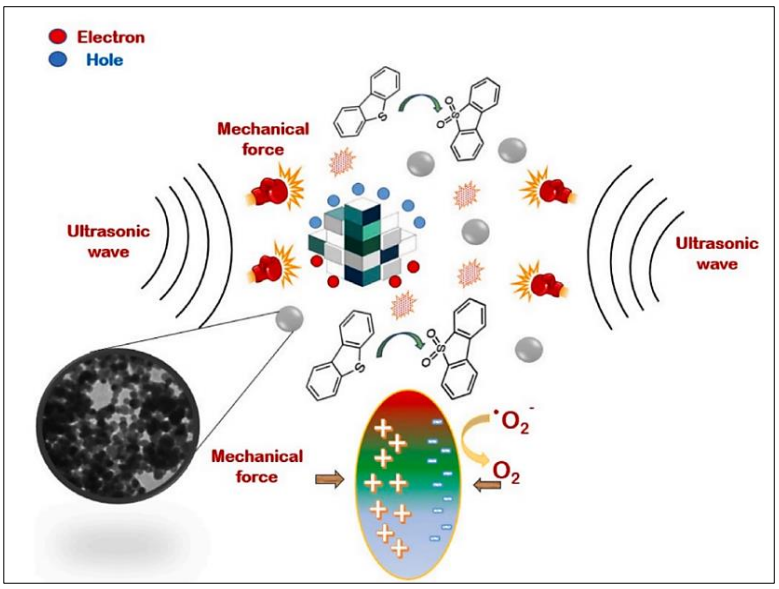

Fig. (4): Supposable piezo-desulfurization mechanism under external mechanical force provided by ultrasonic vibration by prepared CexOx/SrO Nano-composite [27]

3.2.4. Bio-sulfur desulfurization (BDS)

In general, hydrogen desulfurization (HDS) and oxidative desulfurization (ODS) methods work on all sulfur compounds. However, one of the most important organosulfur compounds, dibenzothiophene, and its derivatives have shown high resistance to many conventional desulfurization methods. Therefore, specific and precise methods must be used to selectively remove these compounds. Enzymatic degradation pathways used in biodesulfurization constitute an emerging alternative route in this regard. The proposed mechanism states that the reaction proceeds through protonation, electrophilic aromatic substitution, formation of thiols, and liberation of sulfur in the form of HSO_3^- [29]. However, it is generally accepted that the main mechanism of

desulfurization by these enzymes involves electrophilic aromatic substitution [30]. In fact, laboratory results have proven to be very encouraging for biodesulfurization; however, the practical implementation of this technology has not yet been achieved due to a number of serious obstacles such as enzyme contamination, rather slow reaction kinetics, and expensive processes. Enzymes such as 2'-hydroxybiphenyl-2-sulfinate desulfinase [31] and other enzymes derived from Rhodococcus erythropolis strain perform remarkably well in desulfurization applications but have not yet been optimized for real-world use [32, 33].

3.2.5. Oxidative Desulfurization (ODS)

Oxidative desulfurization is a method that has proven to be one of the most promising desulfurization technologies because it is efficient and has relatively mild operating conditions. Thus, the sulfoxides and sulfonates formed in this way are blocked in their extraction or adsorption techniques. A common oxidant can also carry out these reactions under mild process conditions in order to maintain the catalyst activity and prevent the breakdown products, so that the recovery of the resulting high-quality fuel is better. The by-products, sulfoxides and sulfonates, will then be separated from the solvent matrix through liquid-liquid extraction or adsorption. Polar solvents are often used for such selective extraction of these sulfur-containing compounds. Various oxidants such as potassium peroxide monosulfate ($K2FeO_4$), nitrogen dioxide (NO_2), hydrogen peroxide ($H2O_2$), oxygen (O2), ozone (O_3), and other organic peroxides can be used to carry out the oxidation reaction. In addition to ionic liquids (ILs), which can be utilized with a very wide range of catalysts without compromising product yield or quality, many advanced ODS processes can be performed with a vast array of catalysts. However, in a similar vein, the high viscosity of ionic liquids presents long-standing challenges with their promising desulfurization efficiency. High viscosity can reduce mass transfer rates, thus prolonging reaction times and impacting the economic viability of the process. This will be an important task to facilitate the success of IL-based ODS processes in terms of scalability and costs.

4. Reactivity of Sulfur Compounds

In the context of oxidative desulfurization (ODS) process, the initial step in the oxidation of organosulfur compounds (OSCs) is the loss of electrons. With the high electron density of these sulfates within OSCs, it is their nature that makes them susceptible to oxidation [36]. The electron density increases in the presence of electron donor groups; hence, their influence is important in determining the reaction rate of the oxidation process. Besides, the tendency of OSCs to oxidize is

inhibited by steric hindrances that can prevent oxidizing agents from approaching [37, 38]. Hence, both the electron density above the sulfur atom and the steric background surrounding the sulfur compounds are very important in determining the reactivity of OSCs during the oxidation process [39]. The orientation and length of the alkyl groups attached to sulfur-containing compounds continue to further modify the electron density in compounds such as dibenzothiophene (DBT). In general, the reactivity towards oxidation follows the following order: mercaptans > sulfides > thiophenes. This trend demonstrates the combined effects of electron density and steric agents [40]. A great deal of research has been done on measuring activity rates among different stem cells, and indeed the work indicates a so-called specificity or dependence of the system for any particular combination of stimulant and oxidant used, as summarized in Table (2).

Table (2): Summary of the reactivity of OSCs

Catalyst/oxidant system	Reactivity	Reference
Formic acid / H_2O_2	thiols > sulfides > DBT > BT	[44]
Ti-Beta / H_2O_2	thiophene < DBT < BT	[45]
Formic acid / H_2O_2	thiols > sulfides > DBT > BT	[46]
Phosphotungstic acid / H_2O_2	DBT > 4-methyl, 6-ethyl DBT > BT	[47]
(16 wt % MoO_3/Al_2O_3) / t-BuOOH	DBT >> 4,6-DMDBT > C3-DBT	[48]
green carboxylate-anion-based protic ionic liquid (PIL) / H_2O_2	DBT > 4,6-DMDBT > BT	[49]

5. Other Emerging Technologies

Old methods of desulfurization were effective, but have been superseded by new age methods, which are believed to be more efficient, have faster desulfurization rates, and operate under very favorable conditions. One such promising method is oxidative desulfurization (ODS) in oscillating reactors [46]. The oscillating reactor is designed to give maximum mixing efficiency of the reactants, accelerate mass transfer, and improve the conversion of the chemical reaction, thus providing many advantages in various processes. Several types of oscillating reactors have been investigated for oxidative desulfurization. One such development is the ultrasound-assisted oscillating reactors which have shown improvements in process performance. However, oscillating stirred reactors and pulsed bed reactors, which are widely used in a variety of chemical processes, have not yet been fully utilized for oxidative desulfurization in kerosene. Table (3) provides a summary of various oscillating reactors and their applications in different chemical processes.

Table (3): Some of the oscillating reactors with some of its applications

Type of reactor	Application	References
Ultrasound	ODS process using tetraoctyclammonium bromide and Phosphotungstic acid as catalyst / H_2O_2 as oxidant	[47]
	ODS process using formic acid as catalyst / H_2O_2 as oxidant	[48]
	ODS process using activated carbon-supported Phosphotungstic acid as catalyst / H_2O_2 as oxidant	[49]
Pulsed Trickle Beds	α-methyl-styrene hydrogenation	[50]
	The effect of the superficial gas velocity on liquid velocity and liquid holdup	[51]
		[52]
	Hydrogenation of phenylacetylene	[53]

5.1. Oscillatory Baffled Reactor (OBR)

A homogeneous and completely unchanged mixing can lead to a constant product quality from continuous reactors. This is what happens, and can be achieved using a series of shaker tanks or by a tubular reactor in turbulent operation. The main problem with a series of shaker tanks is that they incur very high capital costs due to the different control systems for each shaker tank. Oscillating baffle reactors serve as another option with which a wide range of chemical transformations can be optimized, even in terms of the behavior of the shaker flow at Reynolds numbers that work well within a laminar flow regime [54, 55]. Oscillating baffle reactors are thus a new type of shaker flow reactor, in which a tube or column built on an orifice plate baffle is separated into several mixed volumes within which extended time reactions take place before they are lost in a continuous processing batch. In terms of the impractically high length-to-diameter ratios of conventional baffle flow reactors, they always incur other penalties, e.g., high capital and pumping costs and control issues [54, 56]. Thus, OBRs present a unique situation where baffle systems synergistically interact with the oscillatory motion of the fluid in a way that produces somewhat approximate peristaltic flow conditions around them in an attempt to induce uniform mixing and enhanced mass transfer [57]. A distinctive feature of OBRs is their construction of a periodic geometry, primarily with sharp baffle edges, as shown in Fig. (**5**), and periodically reversing flow within the tube or column, enabling efficient and continuous processing.

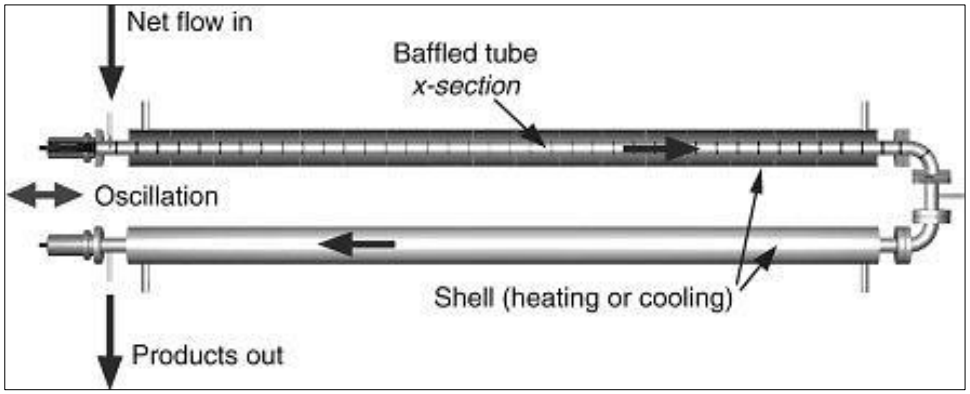

Fig. (5): Typical oscillatory baffled reactor [59]

In relation to a continuous stirred tank reactor or CSTR, which incorporates one or more stirring mechanisms or turbulent flow conditions for mixing – another method of mixing is the oscillatory method. The oscillatory stirred reactor is a unique reaction vessel in which, unlike a normal tubular reactor, stirring or turbulent flow is used with oscillations, creating vortices. These vortices form at regular intervals along the length of the reactor and then cause each section between the baffles to behave like a continuous stirred tank reactor, making the OBR appear as a series of CSTRs connected in series to achieve a time-space distribution of the flow. While both tubular reactors and OBRs are capable of mixing, the intensity of mixing within an OBR is controllable whereas the cavitation defined by a tubular reactor is not. The intensity of mixing in an OBR can be controlled by changing several geometric and operational parameters such as baffle diameter, baffle spacing, oscillation frequency, and amplitude. Factors affecting vortex size and formation frequency OBR is able to give a very wide range of directional mixing without changing the volume flow rate [61].

5.2. Ultrasound Assisted Oxidative Desulfurization (UAOD)

The advantages associated with the enhanced features of ultrasound-assisted desulfurization in the base include improved catalyst activity, better mass transfer, and increased radical ion production. The most recent studies apart from other works on ultrasound-assisted oxidative desulfurization (UAODS) from Arabian extra light crude oil reported a desulfurization efficiency of about 55.1% [62]. Characterization of the sulfur compounds at the molecular level included a variety of species, S1, S2, O4S2, and O2S1, with O2S1 being found to be the most prominent. Most of these compounds were characterized by carbon chain lengths between 11–20 and 20–40 carbon atoms. Kinetics study indicated that the UAODS process followed pseudo-first-order reaction pathways and that accelerating the reaction temperature significantly increased the reaction rate. The critical benefits of ultrasound-assisted desulfurization include improved catalytic activity, enhanced mass transfer, and increased radical ion production. Recent studies on ultrasound-assisted oxidative desulfurization

(UAODS) of Arabian extra light oil have reported desulfurization efficiencies of up to 55.1% [62]. Molecular characterization of sulfur compounds identified a wide range of sulfur species such as S1, S2, O4S2, and O2S1, the latter being the most abundant. Most of these properties were attributed to carbon chains with lengths ranging from 11–20 and 20–40 carbon atoms. Kinetic study indicates a pseudo-first-order reaction for UAODS and was found to increase the reaction rate significantly with increasing temperature.

There are advantages such as superior catalytic activity, better mass transfer, and enhanced radical ion production in the ultrasound-assisted desulfurization process. Recent work on ultrasound-assisted oxidative desulfurization (UAODS) from Arabian extra-light crude oil has shown a desulfurization efficiency of 55.1% [62]. Molecular characterization of sulfur compounds identified different types of species such as S1, S2, O4S2, and O2S1, among which O2S1 is the most abundant. Most of these compounds were characterized by carbon chains with a length of 11–20 and 20–40 carbon atoms. Kinetic study indicated a pseudo-first-order reaction pathway for the UAODS process and that increasing the reaction temperature significantly accelerates the reaction rate. Ultrasound-assisted desulfurization has given several benefits in terms of increased catalytic performance, enhanced mass transfer, and increased radical ion production. Recent work on ultrasound-assisted oxidative desulfurization (UAODS) from Arabian extra-light crude oil has shown a desulfurization efficiency of 55.1% [62].

6. Comparison of Desulfurization Methods

Studies were further extended to compare the results of HDS with other desulfurization techniques, such as EDS, ADS, PCDS, and ODS , BDS as shown in Table (4).

Table (4): Deep Desulfurization of Kerosene Achieved

Methods	Treatment	S before treatment (wt %)	S after treatment (wt %)	Desulfurization	Reference
EDS	DBT	1.272	1.0812	85 %	[19]
ADS	DBT	0.105	10.248	97.6 %	[22]
PCDS	DBT	0.450	0.432	96 %	[28]
BDS	DBT	0.048	0.0137	28.26 %	[34]
HDS	non-aromatic	0.364	0.2726- 0.347	74.9 – 95.6 %	[63]

Table (5) summarizes the various currently known desulfurization technologies – from conventional ones such as hydrogen desulfurization (HDS) to emerging ones such as plasma desulfurization and photocatalytic desulfurization. Conventional methods are suitable for large-scale desulfurization,

while advanced technologies can solve more difficult challenges – such as the treatment of refractory sulfur compounds and operational sustainability improvements. This comparison illustrates the trade-offs between efficiency, cost, volume and environment, providing useful insights into the most appropriate selection of desulfurization technology according to application requirements.

Table (5): Comparison of desulfurization techniques: strengths and weaknesses

Technology	Strengths	Weaknesses
Hydrodesulfurization (HDS)	- High sulfur removal efficiency. - Widely used in industry. - Compatible with existing refineries.	- Requires high temperature and pressure. - Expensive hydrogen usage. - Less effective for sterically hindered compounds.
Adsorptive Desulfurization	- Selective sulfur removal. - Operates under mild conditions. - Reusable adsorbents possible.	- Limited capacity of adsorbents. - Adsorbent regeneration required. - High operational costs for large-scale use.
Oxidative Desulfurization (ODS)	- Effective for refractory sulfur compounds. - Operates at low temperature and pressure. - Environmentally friendly oxidants can be used.	- Requires additional separation processes. - Oxidant consumption can be high. - Complex catalyst recovery.
Biodesulfurization (BDS)	- Eco-friendly and low energy requirements. - Effective at mild operating conditions. - Selective removal of sulfur without hydrogen.	- Slow reaction rates. - Difficulty in scaling up. - Limited to specific sulfur compounds.
Extractive Desulfurization	- Operates under ambient conditions. - Suitable for fuels with low sulfur content. - High selectivity with appropriate solvents.	- Solvent recovery is energy-intensive. - High solvent costs. - Limited capacity per cycle.
Photocatalytic Desulfurization	- Utilizes renewable energy (light). - Environmentally friendly. - Effective for specific sulfur compounds.	- Requires high catalyst surface area. - Limited efficiency in non-laboratory settings. - High cost of catalyst development.
Plasma Desulfurization	- Operates at ambient temperature and pressure. - No need for chemical oxidants or hydrogen. - Emerging as innovative technology.	- High energy consumption. - Limited commercial applications. - Catalyst deactivation over time.
Ultrasound-Assisted Desulfurization	- Enhances reaction rates. - Improves efficiency of ODS and extractive processes. - Low-temperature operation possible.	- High equipment costs. - Requires careful tuning of ultrasonic parameters. - Limited scalability.

Combining hydrogen desulfurization with other technologies would greatly improve the economy of low-sulfur fuel production. A major hurdle in developing adsorption desulfurization will be the synthesis of low-cost selective sorbents for sulfur compounds with large surface areas and large porosities. However, it is preferable to adsorption desulfurization because of its milder operating conditions and does not use expensive hydrogen. Oxidative desulfurization has matured significantly over the past few years, making it one of the most promising technologies for removing refractory sulfur impurities. When ionic liquids and ultrasonic treatment are used in conjunction with ozone-depleting agents, it can successfully reduce sulfur in fuels. However, it is still economically

expensive due to the additional steps required to remove oxidized sulfur compounds and poses environmental challenges during the disposal of these by-products. Bio-desulfurization (BDS) is a very attractive method for deep desulfurization of liquid fuels, as it operates under relatively low operating conditions and requires much lower capital and operating costs than HDS. However, the low activity of currently available biocatalysts hinders their immediate and widespread use in industry, making mass implementation unlikely in the near future.

7. Challenges and Future Directions

- Extraction-based desulfurization research has greatly developed in the past decade using organic solvents and ionic liquids as extraction media. However, the high expense on the solvent, and the still unclear toxicity of the solvent, has prompted researchers to consider deep eutectic solvents (DES), another solvent option. DES is easy to produce compared to conventional solvents, low-cost and environmentally friendly [64].
- A comprehensive understanding of the metabolism of heterocyclic sulfur rings by microorganisms may require extensive experimental studies of the desulfurization process. From this review, there are several aspects that should be considered in the development of a novel desulfurization process:

1. All microbial pathways that play a role in desulfurization should be carefully investigated as preludes to process optimization and scale-up studies.

2. Studies exploring the combination of BDS with existing methods could provide a synergistic effect towards greater reduction of sulfur-containing compounds in petroleum distillates.

3. Meanwhile, developing new strains or modifying sulfur-degrading strains through recombinant DNA technology or genetic engineering may prove to be essential to improve the degradation performance of existing bacteria.

- For adsorption desulfurization (ADS) in the future, more attention should be paid to the regeneration and recycling of adsorbents to reduce waste generation and achieve sustainable resource utilization. In fact, developing cost-effective adsorption desulfurization technology requires not only the innovation of reaction mechanism and materials, but also the optimization of the desulfurization process.
- For oxidative desulfurization (ODS), different types of reactor design have been used in many previous studies such as batch reactor [65], fixed bed reactor [66], trickling bed reactor [67], and

fluid bed reactor [68] which have shown different effects on the removal performance of sulfur compounds in ODS process, but the oxidative desulfurization (ODS) of kerosene by oscillating baffled reactor (OBR) has not been addressed before, making it a future challenge.

8. Conclusions

Sulfur in transportation fuels has been shown to be a major hazard, as sulfur oxide is emitted into the atmosphere, causing acid rain. At the same time, sulfur poisons vehicle catalytic converters at a very rapid rate, emitting toxic gases that pose health risks to humans. One of the most recent technologies for removing sulfur from fuels is fuel desulfurization, a process that consumes a lot of energy and costs a lot of capital; in addition, it has not been successful in removing sulfur at very low levels, especially for some stubborn sulfur compounds. By finding a decentralized technology, based on absorption, extraction, photocatalytic or biosulfur, which can complete the fuel desulfurization process either in the same plant or in separate units, the overall process means milder conditions, better economics and better environmental acceptance, which will benefit society in general and the refining business. A wide range of conventional and unconventional methods for desulfurization of sulfur-containing petroleum distillates are presented in this manuscript. Further studies are needed before we can claim to understand the bacterial partners in the metabolism of heterocyclic sulfur compounds in order to fully understand the BDS domain.

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