



Review

Oxidative Desulfurization of Heavy Oils with High Sulfur Content: A Review

Sara Houda ^{1,2} , Christine Lancelot ¹, Pascal Blanchard ¹, Line Poinel ²
and Carole Lamonier ^{1,*} 

¹ Université Lille, CNRS, Centrale Lille, ENSCL, Université Artois, UMR 8181-UCCS- Unité de Catalyse et Chimie du Solide, F-59000 Lille, France; christine.lancelot@univ-lille.fr (C.L.); pascal.blanchard@univ-lille.fr (P.B.)

² SEGULA Technologies, 19 Rue d'Arras, 92000 Nanterre, France; sara.houda@segula.fr (S.H.); line.poinel@segula.fr (L.P.)

* Correspondence: carole.lamonier@univ-lille.fr; Tel.: +33-320434950

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Abstract: The demand for clean fuels is increasing throughout the world, with more stringent environmental regulations for transportation fuels including marine fuels, particularly regarding their sulfur content. Moreover, the quality of crude oil and derived petroleum cuts is getting lower while fossil fuels are still in high demand. Heavy oils are characterized by high sulfur content where most sulfur is found in bulky thiophenic structures difficult to remove using conventional high pressure hydrodesulfurization process. However they appeared more reactive in oxidative desulfurization (ODS) process, carried out at mild conditions without hydrogen pressure. This review focuses for the first time on the heavy fuels initially containing more than 0.5 wt.%S and upgraded by the ODS process. Different attractive approaches of the literature towards ODS are reported using homogeneous and heterogeneous catalysis. Recent developments in ODS assisted with ultrasound technology and the use of ionic liquid to enhance ODS efficiency will be fully detailed and discussed to better understand their viability when applied to high sulfur content, high viscosity, and high boiling point feeds.

Keywords: oxidative desulfurization; heavy oil; ultrasonic process; ionic liquids

1. Introduction

As reported by the International Energy Agency, global energy requirements have risen more slowly than in the past but are still expected to increase by 30% [1] between today and 2040, with oil demand continuing to grow until 2040 mainly due to the dynamism of China and India. The way that the world meets these growing energy needs is changing with the lead now being taken by natural gas, the rapid rise of renewables, and by energy efficiency. However, the era of oil is not over yet and oil demand growth remains robust in the New Policies Scenario partly due to the rising consumption of road transport, aviation, and shipping. The rapid switch to electric cars pushed by extra policy and infrastructure support is not sufficient to trigger a major turnaround in global oil use.

Among the different petroleum fractions obtained from crude oil (Figure 1), high market demand for light/middle distillates is observed. However, at the same time there is lower availability of light oils yielding high proportion of light/middle distillates used for transportation fuels. Accordingly, the main industrial challenge is to adapt refineries to process heavier crude oils as well as to refine heavier cuts in order to produce light distillates. These crude and residual cuts are mainly known as a complex mixture of high molecular weight hydrocarbons along with impurities such as sulfur, nitrogen, aromatics, asphaltenes, and heavy metals. Among these impurities, sulfur is known as the most hazardous undesirable contaminant. Environmental regulations have therefore been introduced in many countries

to drastically reduce the sulfur content of transportation fuels (gasoline and diesel) to 10–15 ppm. The International Maritime Organization (IMO) has also proposed a reduction to the maximum permitted sulfur content of marine fuels and heavy fuel oil as described in MARPOL Annex VI. Since 2015, a greatly more regulated shipping emissions sector loomed into view in the Sulfur Emissions Control Areas (SECAs) with a maximum sulfur mass content permitted in marine fuels equal to 0.1%. For ships operating outside designated emission control areas the current limit for sulfur content of ships' fuel oil is still 3.5%, nevertheless a substantial cut will be observed in 2020 where the sulfur content will be limited to only 0.5%. These specifications, beneficial from an environmental point of view, present a major technical and economic challenge for the petroleum refining industry for adapting refineries to process heavier crude oils. Hydrotreatments are the most commonly used processes for upgrading heavy fractions to better quality fuels. To accommodate the increasingly stringent regulations on permissible sulfur levels in fuels more severe conditions of temperature and pressure and increasing hydrogen consumption are required. However, increasing the amount of hydrogen has economic and environmental impacts, notably, by increasing the use of fossil fuel and natural gas reforming and the quantity of CO₂ generated by current hydrogen production technologies.

Significant advances have been made for developing alternative nonhydrogenation processes. Such processes for obtaining ultra-low sulfur diesel (ULSD) include desulfurization by adsorption, reactive adsorption, oxidative desulfurization, extractive desulfurization with solvents or ionic liquids, and biodesulfurization, as detailed in the review of Stanislaus et al. in 2008 [2]. Among these methods, oxidative desulfurization forming sulfones from sulfur with the use of an oxidizing agent has received much attention because of its specificity towards sulfur molecules and high oxidative reactivity of 4,6-dimethyldibenzothiophene (DMDBT), known as a refractory sulfur molecule of diesel feed, higher than that of dibenzothiophene (DBT). The sulfone products are further removed mainly by extraction or adsorption. The nature of this process makes it well suited as a finishing process for moderately hydrotreated fuels.

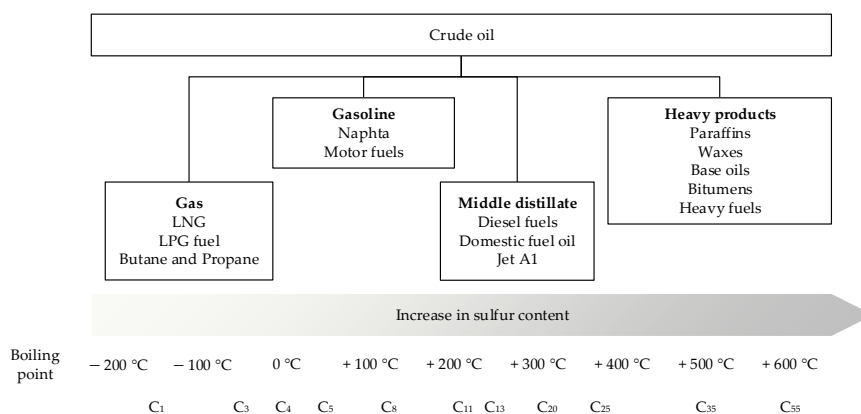


Figure 1. Petroleum fractions from crude oil and properties.

As reported in Figure 2, a large increase in the number of publications related to the oxidative desulfurization (ODS) process is observed since 2007, corresponding to environmental regulations setting up sulfur limitations at 10 ppm for road diesel in Japan and Europe.

A major part of these publications is dedicated to ODS process performed on model molecules mostly dibenzothiophene (DBT) and dimethyldibenzothiophene (DMDBT). ODS process on real fuels such as diesel has also been investigated starting from hydrotreated diesel containing a low initial sulfur amount (<500 ppmS) for the use of ODS as finishing process. It has indeed been reported that the catalytic behavior may differ in the ODS of model and real feeds [3]. Only one study by Oh et al. in 2017 [4] focused on the ODS of marine diesel. The initial sulfur content was low (230 ppm) and does not match the sulfur content of real feeds. We noticed several recent reviews in the literature dealing

with the progress in the technologies for desulfurization of crude oil, but they considered the whole technologies without paying particular attention to the ODS process [5–7].

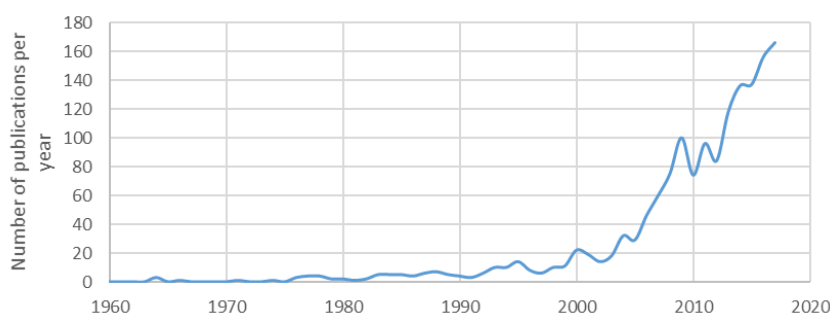


Figure 2. Evolution of the number of papers reporting oxidative desulfurization in bibliographic records. Source: Scopus (keyword: Oxidative desulfurization).

Taking into account the use of heavier crude oils and the interest to develop not only a finishing process but a global desulfurization process without using the expensive hydrogen reactant, this review focuses on the ODS process applied to high sulfur content fuels having a sulfur content above 0.5 wt.%S and highlights the upgrading of heavy fuels by ODS particularly suitable for marine fuels for which legislation is currently becoming more and more extreme. The use of many petroleum fractions are reported in the literature and their denomination in the referenced articles are listed in Table 1, together with their sulfur content.

Table 1. Petroleum fractions referenced in the literature, their denomination in the corresponding article, and their sulfur content.

Fraction	Designation Used in Article	Sulfur Content (%)	References
Gasoline	Naphtha	2.00	Imtiaz et al. 2013 [8]
	Gasoline	1.30	Kulkarni et Afonso. 2010 [9]
	Light Gas Oil (LGO)	0.005	Estephane et al. 2018 [3]
	SR-LGO	1.33	Otsuki et al. 2000 [10]
	Light Cycle Oil (LCO)	0.80	Prasad et al. 2008 [11]
	Diesel fuel	0.86	Anisimov et al. 2003 [12]
	LCO	0.63	Toteva et al. 2009 [13]
	LGO	1.20	
	Heavy Gas Oil	4.00	Imtiaz et al. 2013 [8]
	Straight Run Diesel Fraction	1.19	Krivtsov et al. 2013 [14]
Diesel	Gas Oil	0.57	Trakarnpruk et al. 2009 [15]
	Gas Oil	2.87	Zannikos et al. 1995 [16]
	Straight Run Gas Oil (SRGO)	1.56	Hassan et al. 2013 [17]
	Marine Diesel	0.02	Oh et al. 2017 [4]
	Crude Diesel	0.83	Mokhtar et al. 2016 [18]
	Diesel Fuel	0.72	Najafi et al. 2011 [19]
	Marine Diesel Oil	0.17	Wan et Yen. 2007 [20]
	Diesel Oil	0.77	Mei et al. 2003 [21]
	Hydrotreated Petroleum Product	3.60	Mello et al. 2009 [22]
Vaccum gas oil	Vaccum Gas Oil (VGO)	2.17	Otsuki et al. 2000 [10]
	Diesel Mixture (VGO+diesel)	0.63	Rakhmanov et al. 2015 [23]
	Vaccum Gas Oil	1.98	Shiraishi et Hirai. 2004 [24]
Heavy fuel oil	Heavy Fuel Oil (HFO)	1.80	Ogunlaja et al. 2017 [25]
	HFO	2.75	Farshi et Shiralizadeh. 2015 [26]
	HFO	3.85	Flores et al. 2004 [27]
Residual Oil	Bunker C Oil	3.17	Tang et al. 2013 [28]
	Residual Fuel	2.86	Kazakov et al. 2016 [29]
	Residual Oil	0.04	Tetrisyanda et al. 2017 [30]
Crude Oil	Crude Oil	1.60	Mohammed et al. 2012 [31]
	Crude Oil	1.12	Abu Bakar et Ahmed. 2016 [32]
	Crude Oil	0.10	Rafiee et al. 2016 [33]
	Crude Oil	2.50	Otaibi et al. 2015 [34]
	Crude Oil	5.20	Hosseini et Hamidi. 2014 [35]
	Crude Oil	1.19	Haruna et al. 2018 [36]

2. ODS Technology and Efficiency Evaluation

The oxidative desulfurization process is considered as a two-step reaction. At first, bivalent sulfur is oxidized to the hexavalent corresponding sulfone in the presence of an oxidant: it consists of adding two oxygen atoms to the sulfur without breaking any carbon–sulfur bonds; an intermediate is a sulfoxide compound (Figure 3). With appropriate conditions (i.e., excess of oxidant), sulfones are obtained and no sulfoxide detected. Then, a purification step is performed in which oxidized sulfur compounds are separated from oils due to their different chemical and physical properties from the original sulfur compounds such as boiling point and polarity. In most studies efficiency of the process is evaluated after extraction, and expressed as a global sulfur removal rate.

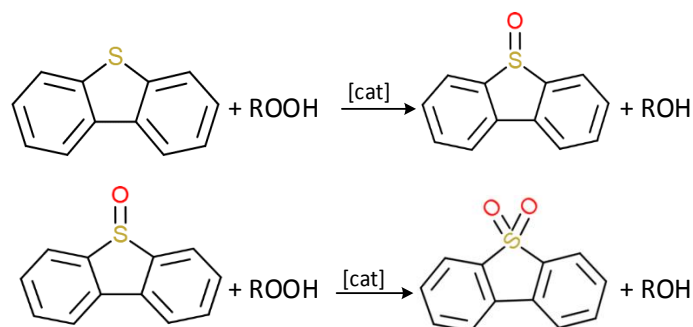


Figure 3. Oxidative desulfurization reaction pathway.

2.1. Sulfones Separation

The purification step can be performed using liquid–liquid extraction, adsorption, precipitation or chemical decomposition. Among separation methods, liquid–liquid solvent extraction is principally used. Extraction solvent can be directly added with the oxidizing agent in the fuel [37–39] or after oxidation of sulfur compounds [40–42]. After extraction, the desulfurized fuel can be obtained by separation of the solvent polar phase and the fuel nonpolar phase, distillation is sometimes used for separation and solvents are often reused for several extraction cycles. Solvent extraction enables separation of desired components based on their variable solubility using specific liquid solvents characterized by their polarity and dielectric constant. Even though this method seems relatively simple, the separation is mainly achieved by the appropriate association of solvent, oil, and selected extracted component. After the oxidative desulfurization reaction, solvent extraction has been applied on a single molecule feed, mixed model feed, as well as real feedstock in particular diesel fraction. The challenge is to maintain a selective extraction of sulfones with high efficiency starting from oxidized real feedstocks with high initial sulfur content.

With the purpose of optimizing extraction of only sulfones from the complex hydrocarbon mixture, several parameters are defined for selecting the best solvent required for sulfones extraction:

- Solvent selectivity toward sulfones
- Solvent capacity: solubility of sulfones in the solvent
- Recoverability of solvent for reuse
- Low solubility of hydrocarbon mixture to avoid loss of fraction in the solvent
- Partition ratio and number of extraction stages.

Solvent capacity and its selectivity toward sulfones are considered as the main parameters for high efficiency. The solvent should have high capacity to solubilize sulfones only. Different types of solvents have been reported in the literature for their sulfones extraction use and are reported in Table 2 with their properties and typical conditions of their use.

Comparison of solvents used for extraction was carried out in several studies and different results were obtained depending on feedstock nature and operating conditions. Most studies used

highly polar solvents like acetonitrile, N, N-dimethylformamide (DMF), methanol, butyrolactone, or N, N-dimethylpyrrolidone for extraction. While for the model feed containing initially DBT or 4,6-DMDBT acetonitrile and methanol has been demonstrated as a very efficient extraction solvent [28,43–45], the nature of the feedstock influences the choice of solvent for high sulfur content and heavy feedstock. Acetonitrile was found suitable for the extraction due to its relatively low boiling point at 355 K compared to sulfones (550 to 950 K) which facilitates separation and reuse of solvent. Acetonitrile was chosen for extraction after ODS of diesel oil [21], vacuum gas oil [24], and heavy fuel oil [26]. Methanol was for example selected for extraction of oxidized gas oil by Zannikos et al. [16]. However, the comparison between DMF, acetonitrile, and methanol indicated that the solvent with higher polarity extracted more sulfone compounds, thus DMF was the most suitable among them for the extraction of oxidized vacuum gas oil [10]. Complete desulfurization of a 2.17 wt.%S vacuum gas oil was noticed after 10 cycles of extraction with DMF. Similarly, in 2016 Mokhtar et al. [18] chose DMF for extraction of oxidized crude diesel. DMF was also reported as more adapted for extraction from more complex mixtures like crude oil [34]; however the DMF is classified as a substance of very high concern by the European Chemicals Agency (ECHA) since 2012. Unexpectedly, a nonpolar solvent, n-heptane, was proposed by Mohammed et al. [31] for the extraction of oxidized crude oil. The extraction with this solvent was compared to extraction using methanol. A high percentage of sulfur reduction (85%) from 1.494 wt.%S to 0.217 wt.%S was obtained with n-heptane versus only 31% sulfur removal using methanol. Using n-heptane as a extraction solvent after heavy cuts ODS may precipitate asphaltene molecules further separated from the fuel. To increase the extraction of sulfones from oxidized real feedstock Imtiaz et al. 2013 [8] proposed a two steps extraction with a mixture of solvents: extraction using water–methanol followed by acetonitrile–methanol mixture. After the extraction sequence, the desulfurization rates of the different petroleum fractions (naphtha, light gas oil, heavy gas oil, and bitumen) were respectively 83%, 85%, 69%, and 64% and strongly depended on the nature of the petroleum fraction.

Table 2. Properties of solvents used for extraction and desulfurization rates (D.R.) results.

Extraction Solvent.	Dipole Moment (Debye)	Dielectric Constant	Solvent to Oil Ratio S/O	Petroleum Fraction	Sulfur Content (ppm)	D.R. (%)	Extraction Steps	Reference
N, N- dimethylformamide (DMF)	3.24	36.71	1	VGO + Diesel Fraction	6300	90%	3	Rakhmanov et al. 2015 [23]
Acetonitrile	3.53	35.94	1	HFO	27,500	59%	1	Farshi et Shiralizadeh. 2015 [26]
Acetonitrile + water (80:20)	-	-	1	Naphtha	20,000	83%	1	Imtiaz et al. 2013 [8]
followed by	-	-	-	LGO	12,000	85%	1	-
methanol-water (80:20)	-	-	-	HGO	40,000	69%	1	-
	-	-	-	Bitumen	50,000	64%	1	-
n-Heptane	-	-	2	Crude oil	14,940	85%	1	Mohammed et al. 2012 [31]
Methanol	2.87	32.66	1	Gas oil	24,000	90%	1	Zannikos et al. 1995 [16]
Acetonitrile	3.53	35.94	1	VGO	19,800	89%	1	Shiraishi et Hirai.2004 [24]
DMF	3.24	36.71	1	SR-LGO	13,500	92%	-	Otsuki et al. 2000 [10]
DMF	3.24	36.71	1	VGO	21,700	100%	10	-
Acetonitrile	3.53	35.94	0.5	Diesel	7,744	99%	1	Mei et al. 2003 [21]
Acetonitrile	3.53	35.94	1	HFO	38,500	35%	1	Flores et al. 2004 [27]
DMF	3.24	36.71	1	Diesel	8,286	90%	4	Mokhtar et al. 2016 [18]

Along with the type of solvent, the heavy nature of hydrocarbons implies restrictions in the operating extraction conditions. A high solvent/feed ratio of 1 could be required. Mohammed et al. [31] have shown that the increase of the solvent/feed ratio from 1 to 3 enhanced the desulfurization rate. Extraction can be carried out at mixing temperature higher (70 °C) than room temperature [10] and several extraction stages, up to 10, can be required to reach the lowest sulfur levels [18,22].

Separation techniques are not exclusively limited to solvent extraction; several studies carried out separation using adsorption. Oxidized sulfur compounds are preferentially adsorbed and removed by the adsorbent compared to nonoxidized sulfur compounds. The adsorbent can be reused by regeneration at high temperatures. Different types of adsorbent have been used (alumina oxides, activated carbon, zeolites, and polymers). It is important to ensure that the sorbent has high affinity toward sulfone molecules leaving nonpolar hydrocarbons (HCs) in the fuel. Comparing adsorption to solvent extraction

Chen et al. 2010 [46] found that adsorption using alumina of oxidized diesel with 0.88 wt.%S content gave better removal efficiency in comparison with solvent extraction using acetonitrile (68% instead of 28%).

In the work reported by Otsuki et al. for oxidized diesel SRGO solvent extraction was followed by adsorption, considering one method of separation was not sufficient to remove all oxidized compounds [10]. Other works have also noticed the adsorption of sulfones when using a heterogeneous catalyst acting as an absorbent and inducing a washing step to recover the whole quantity of sulfones formed during the ODS process [3,47]. In these studies, different retention rates (sulfones adsorption on the catalyst surface) were observed depending on the nature of the feed and real fuels appeared favorable to sulfone dissolution with lower retention rates observed than with the model fuel.

2.2. Efficiency Evaluation

Despite these works dealing with sulfone adsorption, for real feeds, and in particular high sulfur content feeds, ODS catalytic activity is mainly evaluated measuring the global sulfur content after the extraction step (S_{final}) compared with the initial sulfur content (S_{init}) with conversion (X in %) expressed as $X = (S_{\text{init}} - S_{\text{final}}) / S_{\text{init}} \times 100$, this global sulfur content being evaluated by a fluorescence technique. As early as 2001, by using GC-MS and GC-FID equipment, Hulea et al. [48] have also determined the global sulfur removal of kerosene (1310 ppmS) mixed with a suitable solvent (acetonitrile or ethanol) and hydrogen peroxide using Ti-containing molecular sieves. Conversion values in these cases report the oxidation step performance together with the extraction step efficiency. Some studies, such as that reported by Flores et al. [27], have clearly shown that this extraction step could retain sulfide species together with the sulfones indicating that the conversion rate evaluates a global sulfur removal capacity (sulfones and sulfur) rather than ODS conversion. To get around this problem, Flores et al. have initially used acetonitrile for extracting sulfur compounds before oxidation from heavy fuel oil containing 3.85 wt.%S, leading to a 18.4% sulfur reduction, demonstrating the solvent capacity to retain nonoxidized sulfur compounds. It is however clear that higher desulfurization rates are obtained when using oxidized fuels. They are related to the specific affinity between sulfones and solvent. In this case, when catalytic results are based on global sulfur evaluation, they should be considered as a global sulfur removal rate and not an ODS conversion.

Together with the fluorescence method enabling total sulfur evaluation, the gas chromatography method associated with a flame ionization detector (FID) coupled (or not) with a MS detector has already been reported in the literature for qualitative observation of sulfur or sulfone model molecules [49] (Safa et al. 2017). For quantitative measurement of sulfur conversion, this technique is often devoted to model feed analysis containing one, or a limited number, of specific sulfur molecules and their corresponding sulfones, characterized by a specific peak easily identified on the chromatogram. The model molecule conversion is calculated from the intensity decrease of the corresponding peak in the chromatogram [50–52].

Using gas chromatography (GC) technique with a PFPD detector, Chica et al. [53] studied the ODS of a partially hydrotreated commercial diesel (330 ppmS) containing mono-, di-, and tri-methyl DBT in a continuous fixed bed reactor and calculated oxidation conversion of the sulfur compounds from GC-PFPD chromatograms. Recently in 2018 Estephane et al. [3] have also determined sulfide conversion into sulfones in a prehydrotreated LGO (light gas oil) 50 ppmS containing only alkyl-dibenzothiophenes (the most refractory compounds to HDS) using the GC technique with a specific sulfur detector. Their work was extended to a diluted straight run diesel (2000 ppmS) feed containing an important number of substituted BT and DBT sulfur species. Due to the overlap of alkyl-benzothiophenes (Cx-BTs) sulfones retention times with those of alkyl-dibenzothiophene (Cx-DBT) sulfides, the conversion calculations for each molecule could not be done in this case and was thus restricted to Cx-BTs sulfides and to DBT.

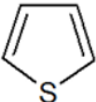
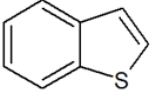
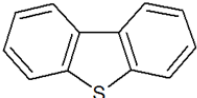
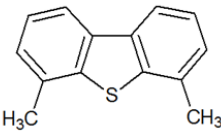
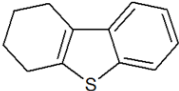
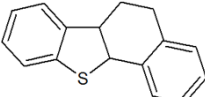
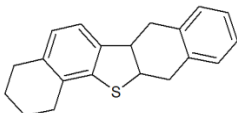
For high sulfur content fuels (> 0.5 wt.%S) without previous prehydrotreatment, this GC method has not yet been reported in the literature. Thus, until now, there is no analytical method evaluating sulfide conversion to sulfones for high sulfur content real feeds. Desulfurization rates are generally

obtained after separation, keeping in mind that a part of sulfides molecules can also be extracted through the sulfones separation process.

2.3. Sulfur Molecules Reactivity

To go further in the understanding of ODS, few studies have reported on sulfur molecules reactivity when using heavy feedstocks. With model fuels containing a mixture of well-defined and well-known sulfide molecules, it was shown that one of the advantages of ODS process compared to HDS was that reactivity was observed in the reversed order, with the following order for ODS: 4,6-DMDBT > DBT > BT [10,54]. This behavior was related to the higher electron density found on the sulfur atom with attached electron rich aromatic rings, favorable to the electrophilic addition mechanism for the oxidation of sulfur. It was also reported that alkyls groups attached to aromatic groups were able to further increase sulfur atom electron density to explain better reactivity for 4,6-DMDBT compared to that of DBT [2]. Nevertheless, sulfur density values for these two molecules are very similar (Table 3). Others studies with model mixtures [50,55] showed these alkyl groups also induce a sulfur atom steric hindrance leading to ODS reactivity decrease [3].

Table 3. Representative structures and electron densities on the sulfur atom for various sulfur-containing compounds.

Sulfur Compound	Structure	Electron Density
Thiophene		5.696
Benzothiophene		5.739
Dibenzothiophene		5.758
4,6-dimethyldibenzothiophene		5.76
Tetrahydrodibenzothiophene		5.923
Tetrahydrobenzophthothiophene		5.921
Octahydrodinaphthothiophene		5.926

Using GC equipped with a specific sulfur detector (GC-PFPD or GC-SCD) Estephane et al. (2018) [3] and Safa et al. (2017) [49] were able to recently report on the reactivities of different sulfur molecules remaining after hydrotreatment of a gas oil (LGO 50ppmS) and a middle distillate (339 ppmS), respectively. Both studies confirmed the negative effect of the steric hindrance of alkyl substituents around the sulfur atom (positions 4 and 6) as well as the size of the alkyl groups. Unexpectedly, works with diluted SRGO (2000 ppmS) only treated by ODS demonstrated that the

global reactivities of BT and DBTs were found to be similar in this real feed contrary to results generally obtained using mixture of model molecules.

Reactivity studies have also been reported when performing ODS on high loaded sulfur fractions. Shiraishi et al. 2004 [24] studied the reactivities of sulfur compounds during the oxidative desulfurization of vacuum gas oil using acetic acid and hydrogen peroxide. The works were carried out on polyaromatic thiophenic sulfur compounds in VGO that do not exist in light feeds. The authors found that polyaromatic compounds having naphthenic rings adjacent to the thiophenic rings (dinaphthothiophene, tetrahydrodibenzothiophene, and octahydrodinaphthothiophene) have higher electron density on the sulfur atom (Table 3) thus better reactivity in comparison to thiophenic compounds, and this makes VGO oxidation easier than for light oils.

Moreover, in 2014 Krivstov and Golovko [14] introduced another factor affecting thiophenic molecules reactivities (substituted benzo and dibenzo thiophene) during the oxidative desulfurization of VGO using hydrogen peroxide and formic acid. They found that in addition to the increased electron density on the sulfur atom and steric hindrance due to the alkyl substituents, the inductive effect has a positive influence ameliorating reactivity rate. It extends over the C–C bond chain and leads to an increase of the electron density in the conjugated aromatic system facilitating reaction. They obtained desulfurization rates decreasing in the following order: 2-ethylDBT > DBT > 4-ethylDBT. The steric effect of the ethyl groups dominates in the 4th ethyl position, thus 4-ethylthiophene was less reactive than DBT. Nonetheless, the positive inductive effect was dominating in the case of 2-ethylthiophene enabling better reactivity in comparison to thiophene. Besides the nature of the sulfur molecule on reactivity, for heavy fractions and typically residual cuts, the presence of heavy molecules like asphaltenes (whose typical molecular structures are presented in Figure 4) is considered an extensively significant factor influencing desulfurization rate. Bukowski et al. (1983) [56] considered these stable compounds as inhibitors terminating free radical reactions through recombination and disproportionation. For Herrington (2004) [57], asphaltenes can also suppress radical chain formation and the catalytic decomposition of organic sulfur compounds by peroxides and hydroperoxides.

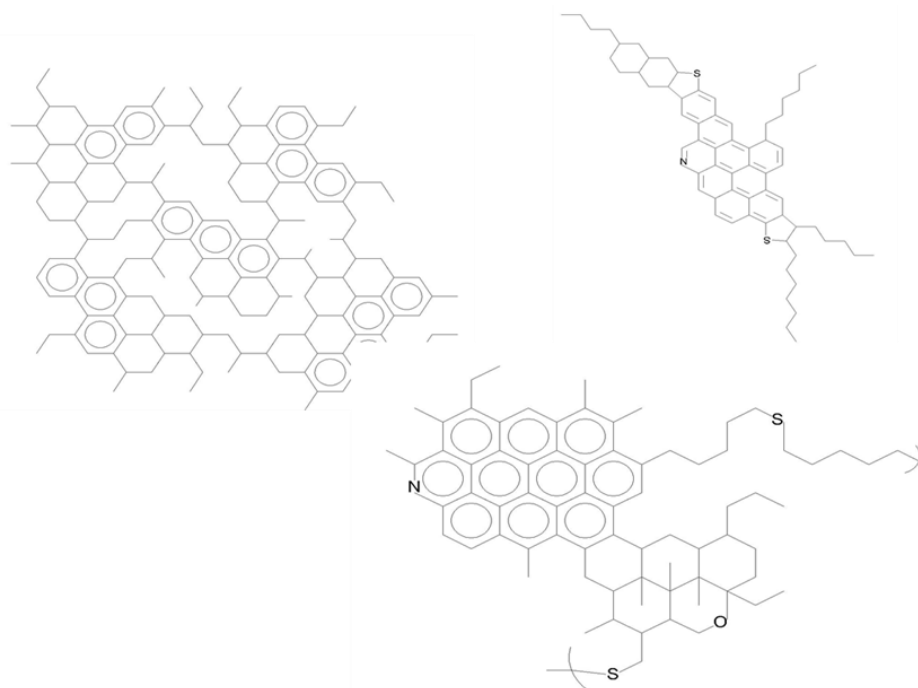


Figure 4. Presentation of typical asphaltenes molecular structures.

2.4. Noncatalytic Process

The use of a noncatalytic process based on the direct chemical oxidation of sulfur molecules has been scarcely explored and was dedicated to heavy feedstocks treatment.

Nitrogen oxides were proposed as chemical oxidants at the beginning of the 1970s by Guth et al. (1975) [58] who patented a continuous oxidative desulfurization process using them, and obtained a desulfurization rate of 86% after 4 min oxidation at 155 °C on a residual oil initially containing 2.2 wt.% S. Autoxidation using air was later studied in 2012 by Javadli et De Klerk [5] with a reaction carried out with a tar sand bitumen containing 5.2% of sulfur. Using air, sulfur is removed as sulfones as well as sulfur dioxide. Several conditions were tested to optimize the reaction. When increasing reaction temperature up to 175 °C the viscosity increased and bitumen hardening was noticed; this was explained by the authors through free radical reaction and side reactions caused by the complex nature of bitumen showing that attention must be paid to the optimization of reaction conditions in order to limit hazardous effects. At optimized conditions corresponding to a temperature of 145 °C for 3 h, a 46% desulfurization rate was obtained after oxidation followed by solvent extraction using water. In 2016 Kazakov et al. [29] reported the use of ozone for the noncatalytic oxidative desulfurization of residual fuel. The sulfur content was reduced from 2.5 wt.%S to 0.46 wt.%S within 3 min at only 50 °C under 0.1 MPa pressure of ozone. These different studies showed that desulfurization using noncatalytic methods performed using selective oxidizing agents as air, ozone, or nitrogen oxides presents a main drawback: the emission of the reaction product SO₂ is detrimental to environmental protection since it is that product we are trying to avoid by removing the sulfur from the fuel before combustion.

The use of liquid oxidants such as nitric acid, potassium permanganate, and sodium hypochlorite without the use of catalysts has also been reported in two studies on low grade coal desulfurization. Coal contains sulfur as both combustible (sulfides, thiophene, thiols, etc.) and noncombustible (mainly in sulfate form) components which respectively are oxidized to SO₂, and remain in the ash during combustion [59]. The use of liquid oxidants enabled the transformation of combustible sulfur compounds into sulfate phases captured in the ash, avoiding SO₂ release after combustion; however a high volume of oxidant (100 mL) is required to treat 20 g of coal. Guru et al. (2007) [59] successfully used nitric acid for the ODS of coal at ambient temperature with a desulfurization rate up to 35%. Using potassium permanganate and ferric sulfate as oxidants, Irum et al. 2017 [60] obtained desulfurization levels up to 94% and 71% respectively, starting from a coal containing 5 wt.% of sulfur after a 1 h reaction at 80 °C. Similarly, sulfur was transformed to sulfate and captured in the ash during the combustion.

Beside the simple oxidation process, the catalytic oxidation is considered as the most promising nonconventional method for upgrading different petroleum fractions. The main advantages relate to the high economic benefit obtained due to the mild operating conditions: low temperature and atmospheric pressure; and to better efficiency enabled by the use of a catalyst following the green principle chemistry nine. The ODS catalytic systems used are categorized into homogenous or heterogeneous catalysts; enzymatic catalysts have never been reported in the literature until now.

3. Homogeneous Catalytic Systems

The high efficiency due to the one phase catalysis system promoted the extensive use of homogeneous catalyst in the oxidative desulfurization process for heavy and high sulfur feedstock. Previous reviews have established a systematic comparison between homogeneous and heterogeneous catalysis [61], but model sulfur compounds were mostly considered as well as mechanism and reactivity parameters, without providing information about the efficiency of these systems with high sulfur feedstock such as diesels, vacuum gas oil, heavy fuel oil, or crude oil. This part of the review therefore focuses on results obtained using homogeneous catalysis for treating these different heavy fractions. Several parameters are discussed such as the nature and quantity of oxidant used, reaction temperature, reaction time, and mixing conditions.

3.1. Homogeneous Catalysts

The main type of homogeneous catalysts reported in the literature are carboxylic acids as well as homogeneous metallic systems such as polyoxometalates.

Formic and acetic acids are considered the most used catalysts in ODS among the carboxylic acids. With their use, the reaction is carried out according to the following steps: peracids (RCOOOH) are produced by the reaction of hydrogen peroxide and the carboxylic acid, then the formed peracid reacts with the sulfur compound to give the corresponding sulfone (Figure 5). Water is formed as byproduct.

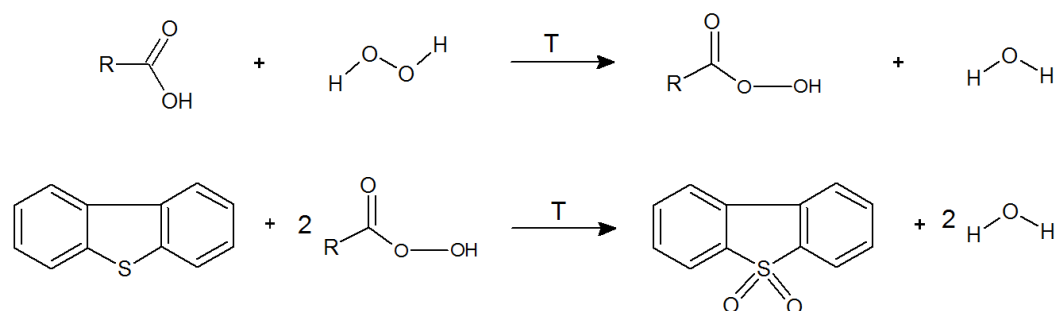


Figure 5. Mechanism of oxidative desulfurization reaction of dibenzothiophene (DBT) using carboxylic acid.

Different types of hydrocarbon fractions were targeted and used with this system. The use of formic acid has been studied by Aida in 1993 [62] who established a patent for oxidative desulfurization of heavy fuel oil using formic acid and hydrogen peroxide. The sulfur content in heavy fuel oil after oxidation and extraction decreased from 1.87 wt.%S to 0.21 wt.%S with this catalytic system.

Along with formic acid, acetic acid was widely used in ODS. In 1995 Zannikos et al. [16] applied oxidative desulfurization for a 2.87 wt.%S gas oil using hydrogen peroxide with a molar ratio of oxidant to sulfur equal 3 and acetic acid at $T = 90^\circ\text{C}$. After a one-hour reaction and extraction with methanol they achieved desulfurization down to 0.11 wt.%S in the gas oil.

Some articles compared the efficacies of formic acid and acetic acid. In 2015, Farshi & Shiralizadeh [26] and Otaibi et al. [34] concluded that better ODS results were obtained using acetic acid. Farshi et al. [24] found that the use of formic acid for oxidizing heavy fuel oil led to formation of byproducts such as sticky polymer materials. In the same way, for Otaibi et al. [32], the desulfurization rate for crude oil decreased using formic acid compared to acetic acid due to the higher acidity of formic acid, leading to an incomplete oxidation along with change in quality of the resulting oil.

With most of the systems mentioned previously, a huge amount of oxidant is being used with oxidant/sulfur ratio reaching up to 100. A major development in homogeneous catalysis was the application of peroxometalates as catalysts. These catalysts used in ODS process are salts of transition metals which form peroxycomplexes, improving catalytic performances.

Anisimov et al. (2003) and Fedorova et al. (2002) [12,63] oxidized a diesel fuel fraction using hydrogen peroxide as oxidant and vanadium peroxocomplexes as catalyst. Starting from 0.86 wt.%S, the sulfur reduction reached 0.2 wt.%S in the fuel after 3 h of the reaction. A catalytic system of polyoxometalates and hydrogen peroxide-acetic acid system was also investigated by Trakarnpruk and Rujiraworawut in 2009 [15]. At 70°C , a significant removal of sulfur was obtained with tungsten based heteropolyanions. Comparing the efficiency of heteropolyanions in the catalytic system, tungsten-based heteropolyanions were more active than those based on molybdenum. They enabled desulfurization of diesel fuels from 0.57 wt.%S to 0.01 wt.%S. Lately, in 2015, it was interesting to find a patent by Koseoglu and Bourane [64] about ODS of bunker fuel oil using homogeneous catalysis. Bunker fuel was mixed with hydrogen peroxide, acetic acid, and tungsten based polyoxoanions, the oxidant to sulfur molar ratio was fixed to 5, desulfurization with sulfur content from 3.5 wt.%S

to 3 wt.%S was noticed after an hour and a half with a loss of 53% of the oil fraction giving low fuel recovery (47 %); which makes the process unacceptable.

3.2. Effect of Reaction Temperature

Reaction temperature is a critical parameter evolving with the feedstock used, it was further investigated. A range of temperatures was tested across the literature. Oxidation reactions are generally carried out at temperatures between 35 and 90 °C. Oxidation of petroleum feed at 35 °C was investigated by Krivstov and Golovko (2013) [14]. The oxidation of high sulfur diesel SRGO by hydrogen peroxide and formic acid with an oxidant to acid molar ratio $\text{H}_2\text{O}_2:\text{HCOOH}$ of 3:4 followed by adsorption of oxidized products with silica gel reduced the total sulfur from 1.19 wt.%S to 0.05 wt.%S within eight hours. In these works, the composition of the fuel before and after adsorption was further analyzed. The authors found a change in the composition of diesel fuel. The relative amount of saturated HCs increased due to the removal of oxidized aromatic hydrocarbons and sulfur compounds after ODS reaction and adsorption. Otsuki et al. [10] carried out ODS of SRGO with 1.35 wt.%S and VGO containing 2.17 wt.%S using formic acid and hydrogen peroxide with the same quantity of oxidant for both fractions. They mixed 800 mL of fuel with 105 mL of formic acid and 480mL of hydrogen peroxide. Their works gave us the opportunity to compare ODS efficiency for two different petroleum fractions: the oxidation of SRGO was carried at 50 °C but a higher temperature (70 °C) was used for oxidizing VGO, taking into consideration the complexity and the higher viscosity of the gas oil mixture. The removal of sulfur by ODS reaction and extraction with DMF was very effective with a resulting sulfur content of 0.01 wt.%S and 0.1 wt.%S, respectively, starting from 2.17 wt.%S for VGO and 1.35 wt.%S for SRGO. Beside the expected direct effects improving kinetics and reaction rate, the use of higher temperatures was also investigated because of its expected effect to decrease the viscosity of highly viscous petroleum fractions, therefore permitting better diffusion of sulfur molecules and thus improving oxidation conversion. Mohammed et al. [31] performed oxidation of crude oil containing 1.494 wt.%S at 90 °C. After 15 min of reaction using a mixture of acetic acid and hydrogen peroxide with a oxidant/catalyst volume ratio of 1 and a catalyst/sulfur mass ratio of 8, followed by solvent extraction using n-heptane, the total sulfur content was reduced to 0.318 wt.%S. Several publications (Farshi & Shiralizadeh, 2015; Tetrisyanda et al., 2017; Toteva et al., 2009) [13,26,30] focused on the effect of temperature on ODS reaction. In most studies, increasing temperature from 35 °C to 90 °C enhanced sulfur reduction but above 90 °C, the increase in temperature had a reverse effect mainly due to the degradation of oxidant used and the formation of resins and asphaltenes [13].

3.3. Reaction Time

Reaction time is also a major parameter because it influences the possibility of scaling up the ODS process to an industrial scale. In ODS, it is quite rare to find an efficient oxidant–catalyst system allowing desulfurization in a few minutes. Oxidation time varies mostly between 1 and 10 h [13,14,16,23,36]. However, Mohammed et al. [31] have demonstrated desulfurization of crude oil in 15 min (results mentioned above), while Otsuki et al. (2010) [10] reported the oxidation of SRGO and VGO using $\text{H}_2\text{O}_2/\text{HCOOH}$ in 36 h. This long reaction time was mainly related to the multiple steps used for the addition of oxidant and acid in small fractions. Krivstov et Golovko (2014) [14] reported that increasing the reaction time enabled more sulfur reduction and highest desulfurization so that a sulfur content down to 0.046 wt.% S in the product was observed after 8 h compared to 0.194 wt.% S after 1 h. However, Toteva et al. (2009) [13] noticed that reaction time higher than 2 h decreased sulfones concentration due to their oxidation into sulfates when treating 0.6 wt.% S light cycle oil (LCO) with hydrogen peroxide and acetic acid.

3.4. Oxidant

The quantity of oxidant used could also be one of the major factors affecting desulfurization efficiency. The stoichiometric oxidant/sulfur molar ratio (Ox/S) for ODS reaction forming a sulfone molecule is 2:1.

The effect of this ratio was extensively studied [13,23,26,30,32]. In many cases, oxidation reaction of petroleum mixture was performed using a molar ratio of oxidant:sulfur of 2. In Abu Bakar's study (2016) [32] starting from a crude oil with 1.13 wt.%S, the increase in oxidant to sulfur ratio from 1:1 to 5:1 enabled an increase in desulfurization activity such that the final sulfur content could be improved from 0.74 wt.%S (at $O_x/S = 1$) to 0.43 wt.%S (at $O_x/S = 5$). For economic reasons, the best ratio of oxidant:sulfur to use was reported as 2 because sulfur content was down to 0.58 wt.%S, showing no significance change with ratios higher than 2. Similarly, Farshi and Shiralizadeh (2015) [26] demonstrated that the increase of the ratio favored sulfur removal for the oxidative desulfurization of a 2.75 wt.%S heavy fuel oil. From $O_x/S = 5$ to $O_x/S = 10$, sulfur content reached 1.43 wt.%S instead of 2.15 wt.%S. Without further study of optimal O_x/S ratio, O_x/S ratio higher than the stoichiometry are sometimes preferred, as reported by Otaibi et al. (2015) [34] using a ratio of 8 when performing an ODS reaction of a crude oil fraction containing 2.5 wt.%S. This high ratio could be explained, not only by the initial sulfur content, but also by the heavy nature of the petroleum fraction used requiring high oxidant amount due to side reactions that can proceed, such as oxidation of aromatic hydrocarbons. This ratio was remarkably increased in the study of Shiraishi and Hirai (2004) [24] who reported the ODS of a 1.98 wt.%S vacuum gas oil diluted with decane using a huge oxidant to sulfur ratio of 100. The mixture was reacted with hydrogen peroxide and acetic acid with a molar ratio acid/sulfur of 50. After 3 h, using this massive excess of oxidant and acid and after solvent extraction, sulfur content was decreased from 1.98 wt.%S to 0.032 wt.%S.

The use of a mixed homogeneous oxidant system containing together hydrogen peroxide and potassium permanganate was reported by Haruna et al. (2018) [36] for crude oil ODS. Hydrogen peroxide, potassium permanganate, and formic acid were mixed in equal quantity (5 mL each) to 15 mL of crude oil with sulfur content of 1.19 wt.%S at 60 °C for 2 h. Reaction was followed by solvent extraction using dimethyl sulfoxide (DMSO). The authors demonstrated better results using this combined oxidant system compared to the use of potassium permanganate oxidant, with sulfur contents after reaction evaluated at 0.32 and 0.60 wt.%S, respectively.

Indeed, for environmental and economic reasons, minimizing the quantity of oxidant is a target in the development of ODS.

3.5. Reactivity of Different Fractions of a Heavy Fuel

Captivating work was realized by Otaibi et al. (2015) [34] and by Abu Bakar et al. (2016) [32]. The authors compared oxidative desulfurization rates for various petroleum fractions from the same crude oil, initially containing 1.12 wt.%S for Abu Bakar et al. and 2.5 wt.%S for Otaibi et al. Oxidation was carried out using hydrogen peroxide and acetic acid followed by extraction with DMF. After oxidation, the crude oil was further distilled into fractions and total sulfur content was determined for each cut. Results of desulfurization efficiency were distinctive. According to Abu Bakar et al. [32], the maximum sulfur reduction was attained for the residuum cut with 75% desulfurization after 20 min. The reductions of sulfur content were 32% in gasoline, 45% in kerosene, and 69% in diesel. The sharper decrease for diesel was attributed to the presence in diesel feed of high amount of thiophenic compounds like dimethylbenzothiophene known as refractory in hydrodesulfurization process but considered as easily oxidized. For Otaibi et al., from a global desulfurization rate of 38% of the crude oil obtained after 60 min, desulfurization rates were then calculated for different fractions and observed to decrease in the following order: gasoline–diesel (59%) > VGO fraction (38%) > VR (13%) residue. In this case, the lowest desulfurization achieved with the residue was explained by its complex nature.

3.6. Stirring Conditions

Another factor that highly affects reaction efficacy is mixing conditions. In ODS, researchers aim to have a perfectly mixed medium in which intimate contact between the phases occurs. To achieve this, uniform contact is mostly desired. In the case of mixing highly viscous petroleum feeds, achieving uniformity is often a difficult challenge, but not impossible. To decrease the viscosity of petroleum fractions, some researchers tended to dilute the sample with an organic solvent, thus facilitating

mixing conditions. Shiraishi and Hirai (2004) [24] used decane as solvent to increase the fluidity of vacuum gas oil. Other studies proposed to substitute the magnetic stirrer applied to lighter feeds with electrical stirring for perfect mixing conditions in the case of ODS of viscous crude oil [34] and heavy fuel oil [26]. In this latter work, Farshi & Shiralizadeh (2015) [26] reported oxidative desulfurization of heavy fuel oil using hydrogen peroxide and acetic acid. The reaction was followed by solvent extraction using acetonitrile. The resulting sulfur content was 1.14 wt.%S, reduced from 2.75 wt.%S. In the 1990s, Tam et al. (1990) [65] demonstrated oxidative desulfurization of an atmospheric gas oil using a continuous electric stirred reactor. Oxidation reaction was performed at 25 °C with nitric acid as the oxidant and acetic acid as the catalyst with the acid to oil ratio 0.03. The use of such a system allowed the sulfur content of the atmospheric gas oil to be reduced from 1.12 wt.%S to 0.38 wt.%S.

3.7. Additional Reagents

Additional chemical reagents were also introduced to the system containing fuel, oxidant, and catalyst with the purpose of accelerating reaction. Rakhamanov et al. (2016) [23] mentioned the use of phase transfer agents (PTA) reinforcing reaction, for the desulfurization process of a mixture of light gas oil with vacuum gas oil having 0.68 wt.%S, using the formic acid/hydrogen peroxide system with an oxidant to sulfur ratio of 4 and an acid to oxidant ratio of 1. Phase transfer catalyst was then added. The results showed that after 6 h of reaction and after 3 extractions with DMF the desulfurization rate obtained was 90%. For the same purpose of facilitating reaction, sulfuric acid was introduced to the hydrogen peroxide/acetic acid system to 0.63 wt.% S gas oil (Yazu et al., 2001 [66]). It was reported that more acid was added to the medium to increase acidity and thus the catalytic activity. Desulfurization up to 90% was obtained. Similarly, sulfuric acid was used in the oxidative desulfurization of 0.63 wt.% S light cycle oil carried out by Toteva et al. in 2009 [13]. LCO was mixed with hydrogen peroxide, acetic acid, and sulfuric acid in the molar ratios: acid/sulfur = 2:1 and H₂SO₄/S = 1:1. Interestingly, the analysis of products before and after oxidation was further done using Fourier transform infrared (FTIR) spectroscopy. The FTIR served as analytical qualitative tool only comparing the intensity of sulfide peaks before and after oxidation as well as detecting sulfones peaks and comparing their intensities when changing reaction temperature without further study of overall desulfurization. Analyses were carried out after solvent extraction. The effect of reaction time was studied for reaction at 50 °C in the presence of oxidant with a molar ratio to sulfur equal to 3. Results indicated that increasing reaction time above 120 min had a negative effect reducing the quantity of sulfones formed due to the oxidation into sulfates detected using the FTIR. After extraction using DMF, the desulfurization rate was 90%.

In their works, Imtiaz et al. (2013) [8] proposed a phase transfer catalyst as phase transfer agent: an amphiphilic quaternary ammonium heteropolyoxometalate salt together with formic acid with a combination of two oxidants (hydrogen peroxide coupled to bubbled air) for performing oxidative desulfurization of several liquid fuels. For the same volume of fuel (20 mL) and oxidant (5 mL of hydrogen peroxide) different Ox/S ratios could be calculated and evaluated to 10, 20, 6, and 5, respectively, for naphtha (2 wt.%S), light gas oil (1.2 wt.%S), heavy gas oil (4 wt.%S), and bitumen (5 wt.%S). Reactions were carried at 80 °C for 30 min using ratio of oxidant/acetic acid = 2:1. It was shown by the authors that in the presence of the PTA, desulfurization efficiency was improved and reaction time was minimized. Desulfurization rates for the different fractions were evaluated after a two-step solvent extraction by acetonitrile–water (80:20) followed by methanol–water (80:20). Desulfurization yields were 83%, 85%, 69%, and 64% for naphtha, light gas oil, heavy gas oil, and bitumen, respectively. Comparable to Otaibi et al. [34] desulfurization rates decreased with heavier fractions. The result is always attributable to the heavier and more complex nature of compounds existing in the heavier feeds.

Feedstock complexity led researchers to apply homogeneous catalysis facilitating the contact between oxidant and sulfur molecules together with catalysts to obtain efficient sulfur removal. However, the use of homogeneous ODS industrial processes is still limited because homogeneous

catalysts are molecularly dispersed with the reactant, making the recovery of products and solvents difficult.

4. Heterogeneous Catalysts

Accordingly, attention has turned to heterogeneous catalytic systems for oxidation reactions. One of the advantages of heterogeneous systems is related to the easy product and catalyst separation. As previously observed for homogeneous ODS systems, heterogeneous catalysts have also been mostly used to model feedstock as well as hydrotreated middle distillate fractions with low amounts of sulfur, the ODS reaction being used as a finishing process.

In articles focusing on the ODS of high sulfur content fractions (> 0.5 wt.%S), heterogeneous catalysts are mainly composed of one active phase (often based on transition metals) dispersed on a support with large specific area. Among transition metals, the use of molybdenum [67–71], vanadium [72,73], and tungsten [74–76] as active phases has been reported. Comparative studies of the various active phases have been conducted [50,51] and various supports have been considered, including alumina [39,45,50,51,77], silica [38,78], and zeolites [79,80]. Interest is also growing in molecular sieves such as mesoporous silicates as well as activated carbon [48,81,82]. The various catalytic systems were mainly tested on model feedstocks and low sulfur light oils.

For heterogeneous systems, the use of tert-butylhydroperoxide (tBHP) has been patented for ODS of low sulfur feedstock (Kocal, 2001; Karas et al., 2008 [83,84]) and is often reported for oxidative desulfurization of diesel and heavy fuel oil fractions. Its main advantage is the one phase reaction medium enhancing mass transfer and allowing reactions in continuous fixed bed reactor.

Another type of catalyst, based on the presence of functional polymer, was studied by Ogunlaja et al. (2017) [25] and applied to the oxidative desulfurization of aromatic fraction of heavy fuel oil using tert-butyl hydroperoxide. Authors used nanofibers for adsorption of corresponding sulfones. The sulfur level decreased from 1.8% to 0.89%. The quantity of oxidant used was 10 times higher than that required by the stoichiometry of the reaction (oxidant to sulfur ratio equal to 20), which was justified by the authors by the nature of the fuel.

Hydrogen peroxide use was also noted for oxidation of crude oil and diesel oil. With this oxidant, the presence of two phases is reported, an aqueous polar phase containing the oxidant and an oil nonpolar phase. As a result, mass transfer problems can occur making the oxidation reaction more difficult by the separation of reactants. A study by Rafiee et al. (2016) [33] reported the ODS of crude oil in the presence of hydrogen peroxide oxidant with an Ox/S = 10 and 12% tungstophosphoric acid supported on montmorillonite as catalyst. After solvent extraction using acetonitrile sulfur content dropped from 0.1 wt.%S to 0.04 wt.%S.

Despite the complex nature of real feeds and the stringent conditions to apply, there are some efficient oxidant–catalyst systems that do not require high Ox/S ratios, with reported ratios close to stoichiometry. Prasad et al. (2008) [11] carried out ODS on light cycle oil having 0.8 wt.% sulfur using tert-butyl hydroperoxide as oxidant and 15% MoO₃/Al₂O₃-SiO₂ with promoted with 3% bismuth. Desulfurization to 0.02 wt.%S was obtained after solvent extraction using N-Methyl-2-pyrrolidone NMP. Despite the high sulfur amount and the presence of substituted benzothiophene and dibenzothiophene low oxidant to sulfur ratio (Ox/S = 2.5) was used. The authors claimed that the deactivation of the catalyst caused by the adsorption of the sulfones during the ODS reaction was inhibited by the presence of bismuth acting as a promotor. The use of promoted catalyst was also investigated by Mokhtar et al. (2016) [18]. In this study complete desulfurization of 0.8wt.%S crude diesel was achieved after oxidation with tert-butyl hydroperoxide with a molar ratio oxidant to sulfur equal 3, in the presence of 16% molybdenum on alumina promoted by 4% tungsten and 2% vanadium, followed by 5 times solvent extraction using DMF. It has been reported that the catalyst was recyclable and 5 times usage of the catalyst was possible at laboratory scale.

The preparation method of the catalyst can also have a role in evaluating catalyst efficacy. A recent work was published by Palomeque-Santiago et al. (2018) [85] testing a tungsten zirconia

supported catalyst. It was prepared using two different methods: traditional incipient wetness impregnation using ammonium metatungstate precursor and anionic exchange at low pH using peroxotungstic acid. In DBT oxidation the catalysts prepared using anion exchange had better activity in comparison to those prepared by the impregnation method and were thus tested in the ODS of SRGO 1.63% of sulfur. This diesel fraction was obtained from heavy crude oil. The reaction was carried out in the presence of tBHP with a high molar ratio of oxidant to sulfur equal to 20. After reaction and further extraction with butyrolactone, sulfur content decreased to 0.48 wt.%S, achieving 70% desulfurization. From the authors' point of view, the absence of WO_3 octahedral crystallites with the presence of tetrahedral species explained the enhanced catalytic activity.

One can notice the very limited application of heterogeneous catalysts for heavy fractions even though its use has always been convenient for model feedstock and light oils. However, growing opportunities are favoring the use of advanced heterogeneous catalytic systems due to the easy products and catalyst separation, high productivity, and also eco-compatibility.

Promising advances in lighter fuel ODS have included the use of titanium-containing catalyst in particular for treating diesel or kerosene [48,83,86–89]. As early as the 2000s, patents have been published regarding desulfurization without solvent use by Corma et al. [87–89] and using flow-type reactors by Kocal et al. for UOP LLC [83,86]; this opens the doors to the use of solid catalysts for ODS processes. Important factors need to be taken into consideration when it comes to residue feeds. At first, as mentioned before, heavy fuel oil as well as heavier cuts have high viscosity, therefore, mixing conditions are very important to ensure a perfectly mixed system. Catalyst optimization and adaptation to the heavy nature of the feedstock is a must to facilitate the diffusion of large complex molecules and to avoid deposition of large molecules of asphaltenes and metal chelates on the catalysts surface.

5. Assisted ODS Process

5.1. Ultrasound Technology

Interesting progress and noticeable results have been obtained using ODS technology for fuels with high sulfur content, nevertheless a main drawback making the industrial application of such a process difficult appeared to be the long reaction times due to low oxidizing rates. Reviewing heterogeneous catalytic systems for heavy fuels ODS, mass transfer problems have been previously identified as limiting the overall sulfur removal rate despite the use of active catalysts. To increase the reaction rate, strong stirring is required. Ultrasonic technology can be used in a broad range of industrial applications. Whilst they are not widely used yet, they could easily be implemented, for example in food processing. Energy produced from ultrasound can provide an extremely fine emulsion of immiscible liquids or assist mass transfer and surface activation (in a solid–liquid system). Cavitation created from ultrasound creates microbubbles that further grow and reach a critical size causing their collapse. Shock waves are formed producing very high temperatures and pressures thus increasing chemical reactivity [90]. Moreover, ultrasonication is also used as an upgrading method lowering feed viscosity and preventing asphaltene flocculation [91] thus facilitating oxidative desulfurization of heavy crudes.

For all these reasons, ultrasound assisted ODS process appears promising for sulfur removal.

Nevertheless, the application of ultrasound assisted oxidative desulfurization (UAOD) has been lately (after 2011) reported in the literature for low sulfur light gas oil (<0.22 wt.%S) [92–95] as well as model feedstock ($S < 1000$ ppm) [69,96,97].

In comparison with conventional ODS, the use of ultrasound waves enhanced considerably the results obtained in the same operating conditions. A paper by Hosseini & Hamidi (2014) [35] concerned the oxidative desulfurization of a crude oil using ultrasounds. Experiment was performed using acetic acid and hydrogen peroxide. Sulfur content was reduced from 5.2 wt.%S to 0.36 wt.%S after 20 min. Without ultrasound desulfurization efficiency was only 62% which indicates its important

beneficial effect. Similar to conventional ODS, conditions such as temperature and feedstock type were considered and determined in ultrasound setup. Reaction temperature varied from 25 to 100 °C. Increasing temperature from 25 to 80 °C favored sulfur removal rate improvement from 10.26 to 34.84% in the case of UAOD of bunker fuel containing 3.5 wt.%S and using tert-butyl hydroperoxides as oxidant. Preferentially, reaction temperature was 75–80 °C. As for conventional ODS, temperature above 100 °C led to oxidant degradation decreasing desulfurization rate [28]. Moreover, authors took into consideration the complexity of the feed tested and the resulting consequence of handling difficulty due to the high viscosity; hence, to ensure the fluidity of Bunker-C oil, it was diluted with n-heptane solvent at volume ratio of 1/5 leading to a solution lighter in sulfur at 0.7 wt.%S.

Using ultrasounds, in addition to conventional operating conditions, other parameters such as ultrasound reactor type, ultrasound frequency, and power should be considered. Reactor technology could influence kinetics of the reaction. Gaudino et al. (2014) [96] investigated the effect of reactor type on UAOD of model molecule DBT. Figure 6 presents three types of reactors used for desulfurization: (a) cup-horn like emitting plate (called also ultrasonic bath in which transducers are located at the bottom of the reactor and ultrasound irradiations transmit into the system indirectly), (b) a single horn system mostly used at the laboratory scale (a cylindrical probe immersed in the liquid transmits the waves into the medium directly), and (c) a sonitube (cylindrical tube at a position of 90°). The authors also used a multihorns system with horizontal flow reactor (continuous system). From the authors' point of view, considering energy consumption and efficiency, sonitube reactor offered the best compromise. In comparison to the other systems (probe type and cup-horn), this sonitube reactor was also considered by Gogate et al. (2011) more effective due to the uniform acoustic field, higher surface area of the sonicator as well as the geometry of the reactor [98].

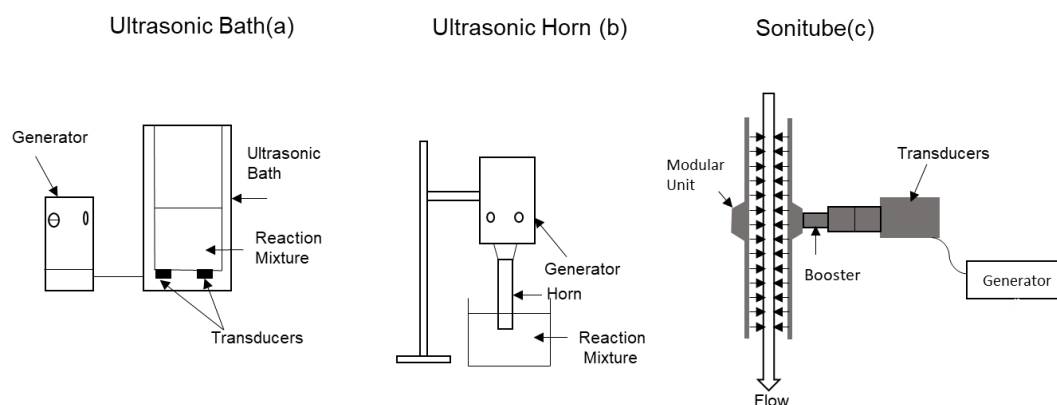


Figure 6. Schematics of different sonochemical reactors: (a) Ultrasonic Bath. (b) Ultrasonic Horn. (c) Sonitube adapted from [98].

With high sulfur feed, Wan et Yen (2008) [99] studied the UAOD for marine gas oil using two types of reactor: tubular reactor (vertical probe type reactor with several transducers) and probe type reactor (ultrasonic horn). Under similar conditions, they compared oxidative desulfurization using the two ultrasonic devices at different frequencies. Better desulfurization rates were obtained using the probe type reactor at a frequency $f = 20$ kHz (98.8% sulfur removal) in comparison with tubular reactor operating at $f = 40$ kHz (95.3% sulfur removal). However, in the attempt to scale up the UAOD process, continuous reaction was tried [99] and both ultrasound generators were compared (probe type and tubular sonoreactor). In the large scale continuous reaction, the sonoreactor gave better results: 90% desulfurization was obtained in 30 min using 200 W power output. In addition to the desulfurization results, economic aspects have been considered, the capacity of the sonoreactor was 25 times larger than that of the probe type offering a larger irradiation area which can be more efficient in scaled up system. This result points out the significant importance of reactor design on desulfurization rate. An optimized reactor enables better sulfur removal and lower energy consumption.

In addition, ultrasound frequency is a crucial parameter affecting desulfurization efficiency. In the literature, with low sulfur feeds the frequencies used varied from 20 to 200 kHz. Indeed, at low frequencies, it was reported that less cavitation bubbles were produced, with more violent collapse giving a better sonophysical effect. The evaluation of frequency for low sulfur feed indicated that the optimal rate was between 20 and 40 kHz which was applied on high sulfur feeds.

The ultrasonication power was further investigated in the range between 100 to 800 W. Najafi et al. (2011), Tang et al. (2013), and Hosseini & Hamidi (2014) [28,35,100] studied the role of wave power amplitude by a set of experiments with different radiation conditions on high sulfur feeds diesel fuel (0.72 wt.%S), Bunker-C oil (3.6 wt.%S), and crude oil (5.2 wt.%S). As a result, they found that increasing wave power from 100 to 800 W enhanced sulfur removal; a higher intensity of ultrasound is introduced to the reaction which can accelerate oxidation reaction. However, notable attention must be paid to hazardous effect of high levels of wave powers. Tang et al. [28] reported that for UAOD of Bunker-C oil, increasing wave power can produce high volatile hydrocarbons due to the cracking of fuel oil. Thus, for side reaction and energy consumption considerations, it is not recommended to work with the highest power possible.

The use of phase-transfer catalysts (PTC) promoting reactions between reagents and facilitating the transport of reactants between phases is often associated with ultrasound technology. Tetraoctyl ammonium bromide is one of the most used PTC. Najafi et al. (2011) [19] studied the effect of phase-transfer catalyst for UAOD of diesel fuel, with phosphoric acid as PTC. Up to 10 g of phosphoric acid was added to 750 mL of diesel. They found that increasing its quantity from 3 to 10 g enhanced the sulfur conversion from 51% to 63%. However, with more than 10 g, its presence lowered the number of oxygen radicals and thus led to reduction of the conversion rate. Wan et Yen (2007) [20] studied the type of PTA to use for UAOD of marine diesel oil. They started with a comparison between two types of quaternary salts (tetraoctyl ammonium bromide TOAB and fluoride TOAF) on model feedstock. Results indicated that tetraoctyl ammonium fluoride gave better sulfur conversion in comparison with TOAB due the smaller molecular size of its anion. Thus, TOAF was further used for UAOD of marine gas oil with sulfur content 0.17%. After 10 min at 70 °C and 20 kHz frequency using PTA as catalyst, the desulfurization rate was 98%. The recovery of spent catalyst was evaluated and the desulfurization performance with the used catalyst was the same as the new catalyst which is promising for lowering capital cost and waste in the ultrasound process.

Without ultrasound, time needed to oxidize sulfur compounds for heavy high sulfur feeds can go up to several hours. With an ultrasound system, the reaction time decreased to minutes and sonication times reported in the different publications for model and real fuels ranged from 5 to 60 min. Different works also showed that slightly increasing sonication time increases desulfurization. Chen et al. (2010) [46] carried out ODS for pyrolysis oil containing 0.88 wt.%S. The increase of sonication time from 5 to 25 min increased desulfurization rate of pyrolysis oil from 21.2% to 43.6%. However, in 2004 Flores et al. study [27], the reaction time increased from 7.5 to 20 min in the UAOD of heavy fuel oil containing 3.8 wt.%S led to a decrease in sulfur reduction. The authors accounted this different result to the nature of the heavy fuel oil, where higher reaction time can favor secondary reactions such as recombination of heavy molecules.

Ultrasound technology was firstly and mainly applied using hydrogen peroxide as an oxidant because its major role was to improve mass transfer limited by the presence of aqueous and oil phases. Most researches were carried out using 30% hydrogen peroxide as oxidant.

With hydrogen peroxide, for economic reasons and for safety, it is recommended to work using low concentrations, and the effect of the percentage of hydrogen peroxide was studied by Kamal et al. (2017) [100] on a bitumen fraction with initial sulfur content of 5.2 wt.%S. Twenty milliliters of hydrogen peroxide with concentration varying from 0 to 30% were therefore added to 1 g of bitumen. Higher desulfurization yields were obtained when increasing concentration of hydrogen peroxide but above 5% H₂O₂, no significant difference in desulfurization was reported demonstrating that low concentrations of hydrogen peroxide are applicable in UAOD.

Likewise, Flores et al. (2004) and Wan et Yen (2007) [20,27] studied the effects of concentration of H₂O₂ on UAOD of heavy fuel oil and marine gas oil. Similar results were found indicating the possibility of using a highly diluted hydrogen peroxide solution for a safer process.

For the high sulfur feedstock, UAOD was applied almost exclusively using homogeneous catalysts such as phosphotungstic acid [20,21,46,99], acetic acid [22,35], phosphoric acid [19], and Fenton-like catalysts [27]. Only one work of Tang et al. (2013) [28] was devoted to UAOD with a heterogeneous system using a molybdenum oxide powder.

For better desulfurization efficiency, some researchers used more than one ultrasound unit. Chen et al. (2010) [46] combined two units connected in series for continuous UAOD (20 kHz, 500 W) followed by solid adsorption using alumina for pyrolysis waste oil containing 0.88 wt.%S. With two units better desulfurization results were observed giving 0.08 wt.% residual sulfur instead of 0.22 wt.%S with one unit. In addition, Wan et Yen (2008) [99] connected two parallel sonoreactors to reach higher sulfur reduction (92% instead of 90%).

To summarize, ultrasound assisted oxidative desulfurization was notably investigated using homogeneous catalytic systems. Its capacity of accelerating oxidation reaction was demonstrated at mild conditions with high efficiencies. UAOD was effective and has potential usage in the petroleum industry on different feedstocks.

However, since no industrial scale production was reported, a transition from laboratory scale to an industrial one is an important step to achieve. Developments should therefore focus on scale-up optimization to ensure uniform cavitation activity. In addition, more heterogeneous systems should be evaluated in ultrasound oxidation before reaching a commercial stage process.

5.2. Ionic Liquids

Amongst the nonconventional routes for oxidative desulfurization process, ionic liquids (ILs) have emerged and demonstrated their potential use. Ionic liquids were first known as molten salts. They are defined as liquids composed entirely of ions that are liquid at or below 100 °C. Ionic liquids are composed of organic cations and inorganic anions with side chains of alkyl or different functional groups such as alkylsulfates, alkylphosphates, or halogen containing anions. The most presented cations are imidazolium, ammonium, pyridinium, phosphonium, and sulfonium.

Properties distinguishing some ILs can include nonvolatility, solubility, high thermal and chemical stability, good catalytic activity, and recyclability. These properties induced their usage in various chemical processes in the fields of catalysis, bio catalysis, synthetic chemistry, and electrochemistry [101–103]. Their application has been widely extended in recent years mainly due to the need to have green chemicals less harmful for the environment. The distinctive properties of ionic liquids allow them to not only to have multiple applications in different chemical reactions, but also versatile utilizations for desulfurization. Many reviews [9,104–110] have reported in details the various applications of ILs for desulfurization as catalysts or as co-catalysts in oxidative desulfurization, as well as solvents for extraction. Together with these applications, the reviews included the study of several ILs parameters such as the quantity used, the temperature effect and their recovery.

Ionic liquids have been used as room temperature solvents for extraction of sulfur compounds [111–115] or as extractant of oxidized sulfur compounds after oxidative desulfurization reaction [40,116,117]. Extractive desulfurization studies have been performed using neutral ILs such as imidazolium- or pyridium-based ILs or acidic ILs for which it has been proposed that their Lewis acidity helped for better extraction of aromatic model sulfur compounds. It was also found that the IL extraction efficiency was improved when the sulfur compounds were first oxidized. The desulfurization of model feed containing DBT was about 12–22% while a better desulfurization was obtained up to 33–60% when achieving ODS using H₂O₂ (Ox/S = 11) and the same IL [117]. As a drawback, the extraction of sulfur compounds using ILs for extractive desulfurization could be limited by the co-extraction of aromatic compounds of the feed.

The main disadvantage of the system oxidant/ILs is the high amount of oxidant required with oxidant to sulfur ratio reported above 10 for model feedstocks. In the attempt of lowering the amount of oxidant required, researchers tended to use ILs as a co-catalyst, meaning that it is acting as a phase transfer agent added to the reaction medium containing the catalyst and oxidant, for activating the reaction. ILs were added to ODS reactions performed with different types of catalysts, mainly polyoxometalates [115,118,119]. Zhu et al. [117] compared the ODS efficiency using a homogeneous tungsten based catalyst $[\text{WO}(\text{O}_2)_2\text{Phen}\cdot\text{H}_2\text{O}]$ with H_2O_2 as the oxidizing agent, and the same system with the addition of the $\text{Bmim}^+\text{BF}_4^-$ ionic liquid. After 3 h at 70 °C they obtained 50% desulfurization of the model molecule, DBT; while in the presence of IL, the desulfurization reached up to 99%. These studies highlight the remarkable advantage of introducing ILs to catalytic reactions, the combination of ILs/catalysts offering a compatible system enhancing reaction efficiency.

Lately, the use of supported ILs aim to overcome shortcomings of one phase processes in which ILs are dissolved in the reaction media making their recovery difficult. Supported ILs catalysts were developed and tested [120], combining the advantages of ILs along with an easy separable system. The supported ionic liquid $[\text{Bmim}]\text{FeCl}_4/\text{Am TiO}_2$ system used by Xun et al. (2015) [121] led to complete desulfurization of DBT at 60 °C after 1 h using H_2O_2 with $\text{Ox/S} = 4$. Desulfurization efficiency remained at 100% with recyclability up to 25 uses of the same catalyst. However, in this case attention must be paid to the ionic liquid loading on support to avoid the problem of leaching of the ionic liquid into the reaction medium. In these experiments, ionic liquids with tetrafluoroborate or hexafluorophosphate anions are used for extraction; however Freire et al. have demonstrated they are sensitive to hydrolysis, even at low temperature, which describe their instability [122].

In all of the systems mentioned, the work was carried out on model feedstock. One example in 2010 was achieved on real diesel feedstock containing 0.8% of sulfur. Kulkarni et Afonso [9] investigated real gasoline ODS in the presence of 30% hydrogen peroxide and $\text{BMIM}^+\text{PF}_6^-$. After 10 h, sulfur content was reduced from 0.8 wt.%S to 0.13 wt.%S.

Ionic liquids show a great potential for future application as a novel approach for ODS but consideration must be taken in the selection of ionic liquids with regards to Green Chemistry principle. However, researchers must focus on the application of these systems to high sulfur feedstock in order to evaluate their performance in the presence of real feeds and the consequent problems related to their regeneration.

5.3. Ultrasound and Ionic Liquid

One study has been conducted by Chan et al. (2008) [123] for oxidative desulfurization of diesel and heavy fuel oil samples combining ultrasound and ionic liquids together with superoxide oxidant. The main idea of this work was to find alternative highly efficient oxidant, cheaper, and easier to produce and to store in comparison with hydrogen peroxide and they proposed solid super oxides. These solids, like hydrogen peroxide, are known as reactive oxygen species and can generate other reactive oxygen species including hydrogen peroxide, hydroxyl radical, and perhydroxyl radical by a series of free radical reactions (Foote, 1995) [124]. Despite their limited application in ODS process, Chan et al. (2008) [123] attempted the UAOD (20 kHz) of diesel and heavy fuel oil using potassium superoxide KO_2 . All experiments were carried out at 70 °C using an oxidant (KO_2 or H_2O_2), acetic acid, tetraoctylammonium bromide as phase transfer catalyst, and 1-n-butyl-3-methylimidazolium-hexafluorophosphate. It was interesting to notice that ionic liquid was used as a co-catalyst. Tested samples were sour diesel with 0.8 wt.%S and heavy fuel oil with 2.6 wt.%S. Ninety-five percent desulfurization was achieved after 6 h for diesel using KO_2 with molar $\text{Ox/S} = 2.8$. The same results were obtained for desulfurization of the same diesel but using H_2O_2 with $\text{Ox/S} = 18$. The results highlight the advantageous effect of using KO_2 because even though similar sulfur removal was obtained, a lower quantity of KO_2 was needed, which will limit oxidant consumption and storage capacity in the overall process. The same experiment using KO_2 was carried

out for heavy fuel oil with a 65% sulfur decrease after 6 h of reaction, demonstrating the feasibility of the reaction for heavy and residual fractions.

6. Conclusions

The development of ODS process has been ongoing for over 30 years, mainly to respond to the growing demand for ULSD. Oxidative desulfurization reaction can serve as a finishing step after hydrodesulfurization to remove from diesel the last few hundreds ppm of sulfur compounds like dialkyl dibenzothiophenes which are more refractory to HDS due to the steric hindrance caused by the alkyl derivatives. These compounds are easily oxidized to their corresponding sulfones in the presence of oxidant and catalyst at atmospheric pressure and relatively low temperature.

Advances in oxidative desulfurization systems mainly focus on simple model feedstock, or low sulfur and light petroleum fractions. However, upgrading the residue fractions is of immediate interest nowadays. At the same time, specifications for heavy petroleum products, such as bunker fuels, are more and more stringent to respond to sanitary and environmental concerns. These requirements highlight the need to purify heavier streams to obtain more valuable clean fuels. As a consequence, ODS process is further studied as an alternative or complementary process to HDS to avoid or reduce the economic deficiency related to operating conditions of HDS with high temperature, high pressure, and high hydrogen consumption.

Therefore, in this review, we intended to present and discuss the works carried out on oxidative desulfurization of high sulfur fractions of petroleum to better understand the viability of this method applied to high sulfur content, high viscosity, high boiling point feeds, and to point out the state of art on ODS of heavy oil with a highlight of the major breakthroughs.

To date, few studies report oxidative desulfurization of heavy fuels. In most papers, desulfurization rates are reported after a purification step through extraction or adsorption with no calculation of the actual conversion rate of sulfides to sulfones. Despite major developments in heterogeneous catalysis and its advantageous catalyst recovery, most of the reactions reported were carried out using homogeneous catalysis, mainly to overcome the problem of reaction in the presence of two phases. Heterogeneous catalysts deactivation and reuse also remain to be improved before scale-up of the process.

To increase exchanges between phases, and as an alternative to thermal energy to drive the oxidation reaction, ultrasound assisted oxidative desulfurization was reported for heavy sulfur feeds and despite its success in reaching low sulfur concentration, it was also mainly used with homogeneous catalysis. Recent applications to heavy crude oil suggest possibilities for heavy fuel oil as well.

Along with ultrasounds, ionic liquids have emerged and demonstrated their potential use for low sulfur diesel and model feedstock with no demonstration to high sulfur feeds.

Overall, the pragmatic analysis of papers reported indicates significant difficulties to perform ODS on heavy feeds, in which most of the sulfur is contained in polyaromatic structures, with high metal and asphaltene contents. Whilst ODS is not reported to reduce sulfur concentration in initially high sulfur heavy feeds to ppm level yet, preliminary results down to moderate to low concentration demonstrate its feasibility and encourage further developments. Application of ultrasound as well as ionic liquids will flourish with more efforts in residue heterogeneous catalytic systems development for increasing efficiency.

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Abbreviations

DBT	Dibenzothiophene
DMDBT	Dimethyldibenzothiophene
DMF	N,N-Dimethylformamide
GC	Gas chromatography
HFO	Heavy Fuel Oil
IL	Ionic Liquid
LCO	Light Cycle Oil
ODS	Oxidative desulfurization
PTA	Phase Transfer Agents
PTC	Phase Transfer Catalysts
SR-LGO	Straight Run Light Gas Oil
SRGO	Straight Run Gas Oil
TAOF	Tetraoctyl ammonium fluoride
tBHP	tert-butylhydroperoxide
TOAB	Tetraoctyl ammonium bromide
UAOD	Ultrasound Assisted Oxidative Desulfurization
ULSD	Ultra-Low Sulfur Diesel
VGO	Vacuum Gas Oil

References

1. WEO 2017. Available online: <http://www.iea.org/weo2017/#section-2-1> (accessed on 21 June 2018).
2. Stanislaus, A.; Marafi, A.; Rana, M.S. Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. *Catal. Today* **2010**, *153*, 1–68. [[CrossRef](#)]
3. Estephane, G.; Lancelot, C.; Blanchard, P.; Toufaily, J.; Hamiye, T.; Lamonier, C. Sulfur compounds reactivity in the ODS of model and real feeds on W-SBA based catalysts. *RSC Adv.* **2018**, *8*, 13714–13721. [[CrossRef](#)]
4. Oh, H.; Kim, J.M.; Huh, K.-S.; Woo, H.C. Oxidative desulfurization of marine diesel using WO_x/SBA-15 catalyst and hydrogen peroxide. *Korean Chem. Eng. Res.* **2017**, *55*, 567–573. [[CrossRef](#)]
5. Javadli, R.; de Klerk, A. Desulfurization of Heavy Oil—Oxidative Desulfurization (ODS) As Potential Upgrading Pathway for Oil Sands Derived Bitumen. *Energy Fuels* **2012**, *26*, 594–602. [[CrossRef](#)]
6. Aitani, A.M.; Ali, M.F.; Al-Ali, H.H. A Review of Nonconventional Methods for the Desulfurization of Residual Fuel Oil. *Pet. Sci. Technol.* **2000**, *18*, 537–553. [[CrossRef](#)]
7. Lin, L.; Hong, L.; Jianhua, Q.; Jinjuan, X. Progress in the Technology for Desulfurization of Crude Oil. *China Pet. Process. Petrochem.* **2010**, *12*, 1–6.
8. Imtiaz, A.; Waqas, A.; Muhammad, I. Desulfurization of liquid fuels using air-assisted performic acid oxidation and emulsion catalyst. *Chin. J. Catal.* **2013**, *34*, 1839–1847. [[CrossRef](#)]
9. Kulkarni, P.S.; Afonso, C.A.M. Deep desulfurization of diesel fuel using ionic liquids: Current status and future challenges. *Green Chem.* **2010**, *12*, 1139–1149. [[CrossRef](#)]
10. Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Imai, T.; Kabe, T. Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction. *Energy Fuels* **2000**, *14*, 1232–1239. [[CrossRef](#)]
11. Prasad, V.V.D.N.; Jeong, K.-E.; Chae, H.-J.; Kim, C.-U.; Jeong, S.-Y. Oxidative desulfurization of 4,6-dimethyl dibenzothiophene and light cycle oil over supported molybdenum oxide catalysts. *Catal. Commun.* **2008**, *9*, 1966–1969. [[CrossRef](#)]
12. Anisimov, A.V.; Fedorova, E.V.; Lesnugin, A.Z.; Senyavin, V.M.; Aslanov, L.A.; Rybakov, V.B.; Tarakanova, A.V. Vanadium peroxocomplexes as oxidation catalysts of sulfur organic compounds by hydrogen peroxide in bi-phase systems. *Catal. Today* **2003**, *78*, 319–325. [[CrossRef](#)]
13. Toteva, V.; Georgiev, A.; Topalova, L. Oxidative desulphurization of light cycle oil: Monitoring by FTIR spectroscopy. *Fuel Process. Technol.* **2009**, *90*, 965–970. [[CrossRef](#)]
14. Krivtsov, E.B.; Golovko, A.K. The kinetics of oxidative desulfurization of diesel fraction with a hydrogen peroxide-formic acid mixture. *Pet. Chem.* **2014**, *54*, 51–57. [[CrossRef](#)]

15. Trakarnpruk, W.; Rujiraworawut, K. Oxidative desulfurization of Gas oil by polyoxometalates catalysts. *Fuel Process. Technol.* **2009**, *90*, 411–414. [[CrossRef](#)]
16. Zannikos, F.; Lois, E.; Stournas, S. Desulfurization of petroleum fractions by oxidation and solvent extraction. *Fuel Process. Technol.* **1995**, *42*, 35–45. [[CrossRef](#)]
17. Hassan, S.I.; Sif El-Din, O.I.; Tawfik, S.M.; Abd El-Aty, D.M. Solvent extraction of oxidized diesel fuel: Phase equilibrium. *Fuel Process. Technol.* **2013**, *106*, 127–132. [[CrossRef](#)]
18. Mokhtar, W.N.A.W.; Bakar, W.A.W.A.; Ali, R.; Kadir, A.A.A. Development of bimetallic and trimetallic oxides doped on molybdenum oxide based material on oxidative desulfurization of diesel. *Arabian J. Chem.* **2016**. [[CrossRef](#)]
19. Najafi, I.; Makarem, M.A.; Amani, M. Application of ultrasound waves to increase the efficiency of oxidative desulfurization process. *Adv. Pet. Explor. Dev.* **2011**, *2*, 63–69. [[CrossRef](#)]
20. Wan, M.-W.; Yen, T.-F. Enhance efficiency of tetraoctylammonium fluoride applied to ultrasound-assisted oxidative desulfurization (UAOD) process. *Appl. Catal. A Gen.* **2007**, *319*, 237–245. [[CrossRef](#)]
21. Mei, H.; Mei, B.W.; Yen, T.F. A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization [☆]. *Fuel* **2003**, *82*, 405–414. [[CrossRef](#)]
22. Mello, P.D.A.; Duarte, F.A.; Nunes, M.A.G.; Alencar, M.S.; Moreira, E.M.; Korn, M.; Dressler, V.L.; Flores, É.M.M. Ultrasound-assisted oxidative process for sulfur removal from petroleum product feedstock. *Ultrason. Sonochem.* **2009**, *16*, 732–736. [[CrossRef](#)] [[PubMed](#)]
23. Rakhmanov, E.V.; Domashkin, A.A.; Myltykbaeva, Z.K.; Kairbekov, Z.; Shigapova, A.A.; Akopyan, A.V.; Anisimov, A.V. Peroxide oxidative desulfurization of a mixture of nonhydrotreated vacuum gas oil and diesel fraction. *Pet. Chem.* **2016**, *56*, 742–744. [[CrossRef](#)]
24. Shiraiishi, Y.; Hirai, T. Desulfurization of Vacuum Gas Oil Based on Chemical Oxidation Followed by Liquid–Liquid Extraction. *Energy Fuels* **2004**, *18*, 37–40. [[CrossRef](#)]
25. Ogunlaja, A.S.; Alade, O.S.; Tshentu, Z.R. Vanadium(IV) catalysed oxidation of organosulfur compounds in heavy fuel oil. *C. R. Chim.* **2017**, *20*, 164–168. [[CrossRef](#)]
26. Farshi, A.; Shiralizadeh, P. Sulfur reduction of heavy fuel oil by oxidative desulfurization (ODS) method. *Pet. Coal* **2015**, *57*, 1337–7027.
27. Flores, R.; Rodas, A.; Chavarria, W. Desulfurization of fuel oils using an advanced oxidation method. *Am. Chem. Soc. Div. Fuel Chem.* **2004**, *9*, 341–342.
28. Tang, Q.; Lin, S.; Cheng, Y.; Liu, S.; Xiong, J.-R. Ultrasound-assisted oxidative desulfurization of bunker-C oil using tert-butyl hydroperoxide. *Ultrason. Sonochem.* **2013**, *20*, 1168–1175. [[CrossRef](#)] [[PubMed](#)]
29. Kazakov, A.A.; Tarakanov, G.V.; Ionov, N.G. Mechanisms of Oxidative Desulfurization of Straight-Run Residual Fuel Oil Using Ozonized Air. *Chem. Technol. Fuels Oils* **2016**, *52*, 33–37. [[CrossRef](#)]
30. Tetrisyanda, R.; Wiguno, A.; Ginting, R.R.; Dzikrillah, M.C.; Wibawa, G. Residue Oil Desulfurization Using Oxidation and Extraction Method. *Indonesian J. Chem.* **2017**. [[CrossRef](#)]
31. Mohammed, A.D.; Isah, A.G.; Umaru, M.; Ahmed, S.; Abdullahi, Y.N. Comparative study on sulphur reduction from heavy petroleum-Solvent extraction and microwave irradiation approach. *IJEE* **2012**, *3*, 949–960.
32. Abubakar, A.; Ahmed, I.A.M.-D.; Ahmed, A.S. Reduction of Sulphur Content of Urals Crude Oil Prior To Processing Using Oxidative Desulphurization. *NJBAS* **2016**, *24*, 19–24. [[CrossRef](#)]
33. Rafiee, E.; Sahraei, S.; Moradi, G.R. Extractive oxidative desulfurization of model oil/crude oil using KSF montmorillonite-supported 12-tungstophosphoric acid. *Pet. Sci.* **2016**, *13*, 760–769. [[CrossRef](#)]
34. Otaibi, R.L.A.; Liu, D.; Hou, X.; Song, L.; Li, Q.; Li, M.; Almigrin, H.O.; Yan, Z. Desulfurization of Saudi Arabian crudes by oxidation–extraction method. *Appl Petrochem. Res.* **2015**, *5*, 355–362. [[CrossRef](#)] [[PubMed](#)]
35. Hosseini, H.; Hamidi, A. Sulfur Removal of Crude Oil by Ultrasound Assisted Oxidative Method. In Proceedings of the International Conference on Biological, Civil and Environmental Engineering (BCEE-2014), Dubai, United Arab Emirates, 17–18 March 2014; pp. 17–18.
36. Haruna, S.Y.; Faruq, U.Z.; Zubairu, A.Y.; Liman, M.G.; Riskuwa, M.L. Comparative Studies on Reduction of Sulphur Content of Heavy Crude Oil Using $\text{KMnO}_4 + \text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ and $\text{KMnO}_4 + \text{H}_2\text{O}_2/\text{HCOOH}$ Via Oxidative Desulphurization (ODS). *AJAC* **2018**, *6*, 15–24.
37. García-Gutiérrez, J.L.; Fuentes, G.A.; Hernández-Terán, M.E.; Murrieta, F.; Navarrete, J.; Jiménez-Cruz, F. Ultra-deep oxidative desulfurization of diesel fuel with H_2O_2 catalyzed under mild conditions by polymolybdates supported on Al_2O_3 . *Appl. Catal. A Gen.* **2006**, *305*, 15–20. [[CrossRef](#)]

38. García-Gutiérrez, J.L.; Laredo, G.C.; García-Gutiérrez, P.; Jiménez-Cruz, F. Oxidative desulfurization of diesel using promising heterogeneous tungsten catalysts and hydrogen peroxide. *Fuel* **2014**, *138*, 118–125. [[CrossRef](#)]
39. Abdullah, W.N.W.; Ali, R.; Bakar, W.A.W.A. In depth investigation of Fe/MoO₃-PO₄/Al₂O₃ catalyst in oxidative desulfurization of Malaysian diesel with TBHP-DMF system. *J. Taiwan Inst. Chem. Eng.* **2016**, *58*, 344–350. [[CrossRef](#)]
40. Lo, W.-H.; Yang, H.-Y.; Wei, G.-T. One-pot desulfurization of light oils by chemical oxidation and solvent extraction with room temperature ionic liquids. *Green Chem.* **2003**, *5*, 639–642. [[CrossRef](#)]
41. Ali, M.F.; Al-Malki, A.; El-Ali, B.; Martinie, G.; Siddiqui, M.N. Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques. *Fuel* **2006**, *85*, 1354–1363. [[CrossRef](#)]
42. Cho, K.-S.; Lee, Y.-K. Effects of nitrogen compounds, aromatics, and aprotic solvents on the oxidative desulfurization (ODS) of light cycle oil over Ti-SBA-15 catalyst. *Appl. Catal. B Environ.* **2014**, *147*, 35–42. [[CrossRef](#)]
43. Rivoira, L.P.; Vallés, V.A.; Ledesma, B.C.; Ponte, M.V.; Martínez, M.L.; Anunziata, O.A.; Beltramone, A.R. Sulfur elimination by oxidative desulfurization with titanium-modified SBA-16. *Catal. Today* **2016**, *271*, 102–113. [[CrossRef](#)]
44. Yan, X.-M.; Lei, J.-H.; Liu, D.; Wu, Y.-C.; Guo, L.-P. Oxidative Desulfurization of Diesel Oil Using Mesoporous Phosphotungstic Acid/SiO₂ as Catalyst. *J. Chin. Chem. Soc.* **2007**, *54*. [[CrossRef](#)]
45. Wang, Y.; Li, G.; Wang, X.; Jin, C. Oxidative Desulphurization of 4,6-Dimethyldibenzothiophene with Hydrogen Peroxide over Ti-HMS. *Energy Fuels* **2007**, *21*, 1415–1419. [[CrossRef](#)]
46. Chen, T.-C.; Shen, Y.-H.; Lee, W.-J.; Lin, C.-C.; Wan, M.-W. The study of ultrasound-assisted oxidative desulfurization process applied to the utilization of pyrolysis oil from waste tires. *J. Clean. Prod.* **2010**, *18*, 1850–1858. [[CrossRef](#)]
47. Hamiye, R.; Lancelot, C.; Blanchard, P.; Toufaily, J.; Hamieh, T.; Lamonié, C. Diesel HDS performance of alumina supported CoMoP catalysts modified by sulfone molecules produced by ODS process. *Fuel* **2017**, *210*, 666–673. [[CrossRef](#)]
48. Hulea, V.; Fajula, F.; Bousquet, J. Mild Oxidation with H₂O₂ over Ti-Containing Molecular Sieves—A very Efficient Method for Removing Aromatic Sulfur Compounds from Fuels. *J. Catal.* **2001**, *198*, 179–186. [[CrossRef](#)]
49. Safa, M.A.; Al-Majren, R.; Al-Shamary, T.; Park, J.-I.; Ma, X. Removal of sulfone compounds formed in oxidative desulfurization of middle distillate. *Fuel* **2017**, *194*, 123–128. [[CrossRef](#)]
50. Wang, D.; Qian, E.W.; Amano, H.; Okata, K.; Ishihara, A.; Kabe, T. Oxidative desulfurization of fuel oil. *Appl. Catal. A Gen.* **2003**, *253*, 91–99. [[CrossRef](#)]
51. Zapata, B.; Pedraza, F.; Valenzuela, M.A. Catalyst screening for oxidative desulfurization using hydrogen peroxide. *Catal. Today* **2005**, *106*, 219–221. [[CrossRef](#)]
52. Bazyari, A.; Khodadadi, A.A.; Haghghat Mamaghani, A.; Beheshtian, J.; Thompson, L.T.; Mortazavi, Y. Microporous titania-silica nanocomposite catalyst-adsorbent for ultra-deep oxidative desulfurization. *Appl. Catal. B Environ.* **2016**, *180*, 65–77. [[CrossRef](#)]
53. Chica, A.; Gatti, G.; Moden, B.; Marchese, L.; Iglesia, E. Selective catalytic oxidation of organosulfur compounds with tert-butyl hydroperoxide. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2006**, *12*, 1960–1967. [[CrossRef](#)]
54. Qian, E. Development of Novel Nonhydrogenation Desulfurization Process-Oxidative Desulfurization of Distillate. *J. Jpn. Pet. Inst. J.* **2008**, *51*, 14–31. [[CrossRef](#)]
55. Safa, M.A.; Ma, X. Oxidation kinetics of dibenzothiophenes using cumene hydroperoxide as an oxidant over MoO₃/Al₂O₃ catalyst. *Fuel* **2016**, *171*, 238–246. [[CrossRef](#)]
56. Bukowski, A.; Milczarska, T. Asphalts as inhibitors of radical polymerization. *J. Appl. Polym. Sci.* **1983**, *28*, 1001–1009. [[CrossRef](#)]
57. Herrington, P.R. Effect of Concentration on the Rate of Reaction of Asphaltenes with Oxygen. *Energy Fuels* **2004**, *18*, 1573–1577. [[CrossRef](#)]
58. Guth, E.; Diaz, A. Method for Removing Sulfur and Nitrogen in Petroleum Oils. US3847800A, 12 November 1974.
59. Gürü, M. Oxidative Desulfurization of Aşkale Coal by Nitric Acid Solution. *Energy Source Part A Recover. Util. Environ. Eff.* **2007**, *29*, 463–469. [[CrossRef](#)]

60. Irum, S.; Akhtar, J.; Sheikh, N.; Munir, S. Oxidative desulfurization of Chakwal coal using potassium permanganate, ferric sulfate, and sodium hypochlorite. *Energy Source Part A Recover. Util. Environ. Eff.* **2017**, *39*, 426–432. [[CrossRef](#)]
61. Wei, S.; He, H.; Cheng, Y.; Yang, C.; Zeng, G.; Qiu, L. Performances, kinetics and mechanisms of catalytic oxidative desulfurization from oils. *RSC Adv.* **2016**, *6*, 103253–103269. [[CrossRef](#)]
62. Aida, T.; Funakoshi, I. Method of recovering organic sulfur compound from liquid oil. *EP* **1993**, 565324, 10–13.
63. Fedorova, E.V.; Zhirkov, N.; Tarakanova, A.V.; Ivanov, A.A.; Senyavin, V.; Anisimov, A.V.; Tulyakova, E.V.; Surin, S.A. Oxidative desulfurization of diesel fuel with hydrogen peroxide in the presence of vanadium peroxy complexes. *Pet. Chem.* **2002**, *42*, 253–256.
64. Koseoglu, O.R.; Bourane, A. System and Process for Integrated Oxidative Desulfurization, Desalting and Deasphalting of Hydrocarbon Feedstocks. US8980080B2, 17 March 2015.
65. Tam, P.S.; Kittrell, J.R.; Eldridge, J.W. Desulfurization of fuel oil by oxidation and extraction. 1. Enhancement of extraction oil yield. *Ind. Eng. Chem. Res.* **1990**, *29*, 321–324. [[CrossRef](#)]
66. Yazu, K.; Yamamoto, Y.; Furuya, T.; Miki, K.; Ukegawa, K. Oxidation of Dibenzothiophenes in an Organic Biphasic System and Its Application to Oxidative Desulfurization of Light Oil. *Energy Fuels* **2001**, *15*, 1535–1536. [[CrossRef](#)]
67. Sikarwar, P.; Kumar, U.K.A.; Gosu, V.; Subbaramaiah, V. Catalytic Oxidative Desulfurization of DBT Using Green Catalyst (Mo/MCM-41) Derived from Coal Fly Ash. *JECE* **2018**. [[CrossRef](#)]
68. Bakar, W.A.W.A.; Ali, R.; Kadir, A.A.A.; Mokhtar, W.N.A.W. Effect of transition metal oxides catalysts on oxidative desulfurization of model diesel. *Fuel Process. Technol.* **2012**, *101*, 78–84. [[CrossRef](#)]
69. Akbari, A.; Omidkhah, M.; Towfighi Darian, J. Facilitated and selective oxidation of thiophenic sulfur compounds using MoO_x/Al₂O₃-H₂O₂ system under ultrasonic irradiation. *Ultrason. Sonochem.* **2015**, *23*, 231–237. [[CrossRef](#)] [[PubMed](#)]
70. García-Gutiérrez, J.L.; Fuentes, G.A.; Hernández-Terán, M.E.; García, P.; Murrieta-Guevara, F.; Jiménez-Cruz, F. Ultra-deep oxidative desulfurization of diesel fuel by the Mo/Al₂O₃-H₂O₂ system: The effect of system parameters on catalytic activity. *Appl. Catal. A Gen.* **2008**, *334*, 366–373. [[CrossRef](#)]
71. Yang, C.; Zhao, K.; Cheng, Y.; Zeng, G.; Zhang, M.; Shao, J.; Lu, L. Catalytic oxidative desulfurization of BT and DBT from n-octane using cyclohexanone peroxide and catalyst of molybdenum supported on 4A molecular sieve. *Sep. Purif. Technol.* **2016**, *163*, 153–161. [[CrossRef](#)]
72. Tomskii, I.S.; Vishnetskaya, M.V.; Vakhrushin, P.A.; Tomskaya, L.A. Oxidative desulfurization of straight-run diesel fraction on vanadium–molybdenum catalysts. *Pet. Chem.* **2017**, *57*, 908–913. [[CrossRef](#)]
73. Cedeño, L.; Gomez-Bernal, H.; Fraustro-Cuevas, A.; Guerra-Gomez, H.D.; Cuevas-García, R. Oxidative desulfurization of synthetic diesel using supported catalysts: Part III. Support effect on vanadium-based catalysts. *Catal. Today* **2008**, *133*, 244–254. [[CrossRef](#)]
74. Capel-Sanchez, M.C.; Perez-Presas, P.; Campos-Martin, J.M.; Fierro, J.L.G. Highly efficient deep desulfurization of fuels by chemical oxidation. *Catal. Today* **2010**, *157*, 390–396. [[CrossRef](#)]
75. Abdalla, Z.E.A.; Li, B.; Tufail, A. Preparation of phosphate promoted Na₂WO₄/Al₂O₃ catalyst and its application for oxidative desulfurization. *J. Ind. Eng. Chem.* **2009**, *15*, 780–783. [[CrossRef](#)]
76. Long, Z.; Yang, C.; Zeng, G.; Peng, L.; Dai, C.; He, H. Catalytic oxidative desulfurization of dibenzothiophene using catalyst of tungsten supported on resin D152. *Fuel* **2014**, *130*, 19–24. [[CrossRef](#)]
77. Dumont, V.; Oliviero, L.; Maugé, F.; Houalla, M. Oxidation of dibenzothiophene by a metal-oxygen-aldehyde system. *Catal. Today* **2008**, *130*, 195–198. [[CrossRef](#)]
78. Chang, J.; Wang, A.; Liu, J.; Li, X.; Hu, Y. Oxidation of dibenzothiophene with cumene hydroperoxide on MoO₃/SiO₂ modified with alkaline earth metals. *Catal. Today* **2010**, *149*, 122–126. [[CrossRef](#)]
79. Jiang, Z.; Lü, H.; Zhang, Y.; Li, C. Oxidative Desulfurization of Fuel Oils. *Chin. J. Catal.* **2011**, *32*, 707–715. [[CrossRef](#)]
80. Ratnasamy, P.; Srinivas, D.; Knözinger, H. Active Sites and Reactive Intermediates in Titanium Silicate Molecular Sieves. In *Advances in Catalysis*; Academic Press: Cambridge, MA, USA, 2004; pp. 1–169.
81. Yan, X.-M.; Mei, P.; Lei, J.; Mi, Y.; Xiong, L.; Guo, L. Synthesis and characterization of mesoporous phosphotungstic acid/TiO₂ nanocomposite as a novel oxidative desulfurization catalyst. *J. Mol. Catal. A Chem.* **2009**, *304*, 52–57. [[CrossRef](#)]

82. Xiao, J.; Wu, L.; Wu, Y.; Liu, B.; Dai, L.; Li, Z.; Xia, Q.; Xi, H. Effect of gasoline composition on oxidative desulfurization using a phosphotungstic acid/activated carbon catalyst with hydrogen peroxide. *Appl. Energy* **2014**, *113*, 78–85. [[CrossRef](#)]
83. Kocal, J.A. Process for the Desulfurization of a Hydrocarbonaceous Oil. US6277271B1, 21 August 2001.
84. Karas, L.J.; Han, Y.-Z.; Leyshon, D.W. Organosulfur Oxidation Process. US7270742B2, 18 September 2007.
85. Palomeque-Santiago, J.F.; López-Medina, R.; Oviedo-Roa, R.; Navarrete-Bolaños, J.; Mora-Vallejo, R.; Montoya-de la Fuente, J.A.; Martínez-Magadán, J.M. Deep oxidative desulfurization with simultaneous oxidative denitrogenation of diesel fuel and straight run gas oil. *Appl. Catal. B: Environ.* **2018**. [[CrossRef](#)]
86. Kocal, J.A.; Brandvold, T.A. Removal of Sulfur-Containing Compounds from Liquid Hydrocarbon Streams. US6368495B1, 9 April 2002.
87. Corma Canós, A.; Domine, M.E.; Martinez, C. Method and Catalysts for the Elimination of Sulphur Compounds from the Diesel Fraction. US7371318B2, 13 May 2008.
88. Corma Canós, A.; Domine, M.E.; Martinez Sánchez, C. Process and Catalysts for Eliminating Sulphur Compounds from the Gasoline Fraction. US6846406B2, 25 January 2005.
89. Corma Canós, A.; Domine, M.E.; Martinez, C. Method of Oxidising Sulphur Compounds Present in Gasoline, Kerosene and Diesel Fractions. WO/2003/044129, 31 May 2003.
90. Ja'fari, M.; Ebrahimi, S.L.; Khosravi-Nikou, M.R. Ultrasound-assisted oxidative desulfurization and denitrogenation of liquid hydrocarbon fuels: A critical review. *Ultrason. Sonochem.* **2018**, *40*, 955–968. [[CrossRef](#)] [[PubMed](#)]
91. Avvaru, B.; Venkateswaran, N.; Uppara, P.; Iyengar, S.B.; Katti, S.S. Current knowledge and potential applications of cavitation technologies for the petroleum industry. *Ultrason. Sonochem.* **2018**, *42*, 493–507. [[CrossRef](#)] [[PubMed](#)]
92. Jalali, M.R.; Sobati, M.A. Intensification of oxidative desulfurization of gas oil by ultrasound irradiation: Optimization using Box–Behnken design (BBD). *Appl. Therm. Eng.* **2017**, *111*, 1158–1170. [[CrossRef](#)]
93. Gonzalez, L.A.; Kracke, P.; Green, W.H.; Tester, J.W.; Shafer, L.M.; Timko, M.T. Oxidative Desulfurization of Middle-Distillate Fuels Using Activated Carbon and Power Ultrasound. *Energy Fuels* **2012**, *26*, 5164–5176. [[CrossRef](#)]
94. Dai, Y.; Zhao, D.; Qi, Y. Sono-desulfurization oxidation reactivities of FCC diesel fuel in metal ion/H₂O₂ systems. *Ultrason. Sonochem.* **2011**, *18*, 264–268. [[CrossRef](#)] [[PubMed](#)]
95. Duarte, F.A.; de Mello, P.A.; Bizzi, C.A.; Nunes, M.A.G.; Moreira, E.M.; Alencar, M.S.; Motta, H.N.; Dressler, V.L.; Flores, É.M.M. Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process. *Fuel* **2011**, *90*, 2158–2164. [[CrossRef](#)]
96. Calcio Gaudino, E.; Carnaroglio, D.; Boffa, L.; Cravotto, G.; Moreira, E.M.; Nunes, M.A.G.; Dressler, V.L.; Flores, E.M.M. Efficient H₂O₂/CH₃COOH oxidative desulfurization/denitrification of liquid fuels in sonochemical flow-reactors. *Ultrason. Sonochem.* **2014**, *21*, 283–288. [[CrossRef](#)] [[PubMed](#)]
97. Choi, A.E.S.; Roces, S.; Dugos, N.; Wan, M.-W. Mixing-assisted oxidative desulfurization of model sulfur compounds using polyoxometalate/H₂O₂ catalytic system. *Sustain. Environ. Res.* **2016**, *26*, 184–190. [[CrossRef](#)]
98. Gogate, P.R. Intensification of chemical processing applications using ultrasonic and microwave irradiations. *Curr. Opin. Chem. Eng.* **2017**, *17*, 9–14. [[CrossRef](#)]
99. Wan, M.-W.; Yen, T.-F. Portable Continuous Ultrasound-Assisted Oxidative Desulfurization Unit for Marine Gas Oil. *Energy Fuels* **2008**, *22*, 1130–1135. [[CrossRef](#)]
100. Bin Wan Kamal, W.M.I.; Okawa, H.; Kato, T.; Sugawara, K. Ultrasound-assisted oxidative desulfurization of bitumen. *Jpn. J. Appl. Phys.* **2017**, *56*, 07JE03. [[CrossRef](#)]
101. Pârvulescu, V.I.; Hardacre, C. Catalysis in Ionic Liquids. *Chem. Rev.* **2007**, *107*, 2615–2665. [[CrossRef](#)] [[PubMed](#)]
102. Van Rantwijk, F.; Sheldon, R.A. Biocatalysis in ionic liquids. *Chem. Rev.* **2007**, *107*, 2757–2785. [[CrossRef](#)] [[PubMed](#)]
103. Wei, D.; Ivaska, A. Applications of ionic liquids in electrochemical sensors. *Anal. Chim. Acta* **2008**, *607*, 126–135. [[CrossRef](#)] [[PubMed](#)]
104. Ibrahim, M.H.; Hayyan, M.; Hashim, M.A.; Hayyan, A. The role of ionic liquids in desulfurization of fuels: A review. *Renew. Sustain. Energy Rev.* **2017**, *76*, 1534–1549. [[CrossRef](#)]

105. Vekariya, R.L. A review of ionic liquids: Applications towards catalytic organic transformations. *J. Mol. Liq.* **2017**, *227*, 44–60. [CrossRef]
106. Bhatto, A.W.; Abro, R.; Gao, S.; Abbas, T.; Chen, X.; Yu, G. Oxidative desulfurization of fuel oils using ionic liquids: A review. *J. Taiwan Inst. Chem. Eng.* **2016**, *62*, 84–97. [CrossRef]
107. Dai, C.; Zhang, J.; Huang, C.; Lei, Z. Ionic Liquids in Selective Oxidation: Catalysts and Solvents. *Chem. Rev.* **2017**, *117*, 6929–6983. [CrossRef] [PubMed]
108. Zhao, H.; Baker, G.A. Oxidative desulfurization of fuels using ionic liquids: A review. *Front. Chem. Sci. Eng.* **2015**, *9*, 262–279. [CrossRef]
109. Muzart, J. Ionic Liquids as Solvents for Catalyzed Oxidations of Organic Compounds. *J. Adv. Synth. Catal.* **2006**, *348*, 275–295. [CrossRef]
110. Gharnati, L.; Doring, M.; Arnold, U. Catalytic Oxidation with Hydrogen Peroxide in Ionic Liquids. *Curr. Org. Synth.* **2009**, *6*, 342–361. [CrossRef]
111. Jian-long, W.; Zhao, D.; Zhou, E.; Dong, Z. Desulfurization of gasoline by extraction with N-alkyl-pyridinium-based ionic liquids. *J. Fuel Chem. Technol.* **2007**, *35*, 293–296. [CrossRef]
112. Gao, H.; Zeng, S.; Liu, X.; Nie, Y.; Zhang, X.; Zhang, S. Extractive desulfurization of fuel using N-butylpyridinium-based ionic liquids. *RSC Adv.* **2015**, *5*, 30234–30238. [CrossRef]
113. Holbrey, J.D.; López-Martin, I.; Rothenberg, G.; Seddon, K.R.; Silvero, G.; Zheng, X. Desulfurisation of oils using ionic liquids: Selection of cationic and anionic components to enhance extraction efficiency. *Green Chem.* **2008**, *10*, 87–92. [CrossRef]
114. Mochizuki, Y.; Sugawara, K. Removal of Organic Sulfur from Hydrocarbon Resources Using Ionic Liquids. *Energy Fuels* **2008**, *22*, 3303–3307. [CrossRef]
115. Chen, X.; Lin, H.-Z.; Jiang, S.-G.; Wu, K.-C.; Liu, Y.-J.; Tian, L.-X.; Zhang, Y.-Q.; Niu, J. Dietary supplementation of honeysuckle improves the growth, survival and immunity of *Penaeus monodon*. *Fish Shellfish Immunol.* **2013**, *35*, 161–169. [CrossRef] [PubMed]
116. He, L.; Li, H.; Zhu, W.; Guo, J.; Jiang, X.; Lu, J.; Yan, Y. Deep Oxidative Desulfurization of Fuels Using Peroxophosphomolybdate Catalysts in Ionic Liquids. *Ind. Eng. Chem. Res.* **2008**, *47*, 6890–6895. [CrossRef]
117. Zhu, W.; Li, H.; Jiang, X.; Yan, Y.; Lu, J.; Xia, J. Oxidative Desulfurization of Fuels Catalyzed by Peroxotungsten and Peroxomolybdenum Complexes in Ionic Liquids. *Energy Fuels* **2007**, *21*, 2514–2516. [CrossRef]
118. Leng, Y.; Ge, H.; Zhou, C.; Wang, J. Direct hydroxylation of benzene with hydrogen peroxide over pyridine–heteropoly compounds. *Chem. Eng. J.* **2008**, *145*, 335–339. [CrossRef]
119. Zhang, J.; Wang, A.; Li, X.; Ma, X. Oxidative desulfurization of dibenzothiophene and diesel over [Bmim]₃PMo₁₂O₄₀. *J. Catal.* **2011**, *279*, 269–275. [CrossRef]
120. Riisager, A.; Eriksen, K.M.; Wasserscheid, P.; Fehrmann, R. Propene and 1-Octene Hydroformylation with Silica-Supported, Ionic Liquid-Phase (SILP) Rh-Phosphine Catalysts in Continuous Fixed-Bed Mode. *Catal. Lett.* **2003**, *90*, 149–153. [CrossRef]
121. Xun, S.; Zhu, W.; Zheng, D.; Li, H.; Jiang, W.; Zhang, M.; Qin, Y.; Zhao, Z.; Li, H. Supported ionic liquid [Bmim]FeCl₄/Am TiO₂ as an efficient catalyst for the catalytic oxidative desulfurization of fuels. *RSC Adv.* **2015**, *5*, 43528–43536. [CrossRef]
122. Freire, M.G.; Neves, C.M.S.S.; Marrucho, I.M.; Coutinho, J.A.P.; Fernandes, A.M. Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids. *J. Phys. Chem. A* **2010**, *114*, 3744–3749. [CrossRef] [PubMed]
123. Chan, N.Y.; Lin, T.-Y.; Yen, T.F. Superoxides: Alternative Oxidants for the Oxidative Desulfurization Process. *Energy Fuels* **2008**, *22*, 3326–3328. [CrossRef]
124. Foote, C.S.; Valentine, J.S.; Greenberg, A.; Liebman, J.F. *Active Oxygen in Chemistry*; Springer Science & Business Media: Berlin, Germany, 2012; Volume 2.

