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DESULFURIZATION TECHNIQUES OF HEAVY OIL FRACTIONS. REVIEW

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ABSTRACT

Strategies for desulfurization of heavy oil have been investigated through scrutinizing the practicality of differing heavy oil procedures along with reviewing literature regarding the topic. These methodologies include hydrodesulfurization, extractive desulfurization, oxidative desulfurization, and biodesulfurization. Each possesses its iterations along with modified versions through repeated performance for improved results. Nevertheless, these techniques do not function properly. They particularly strive to desulfurize viscous oil. This constraint exists mainly since heavy oil possesses intrinsic attributes like elevated sulfur concentration, viscosity, boiling point, and the elastic character of sulfur compounds. Since fuels must exhibit maximal environmental compatibility, ever more restrictive statutes now oversee the sulfur constituent of these fuels. Additionally, crude oil grade and its byproducts diminished and a need for remaining fuels persists, revealing the importance of sulfur removal, notably in viscous oils. The existence of detailed thiophenic compounds imparts important quantities of sulfur to these oils rendering elimination via typical high-pressure hydrodesulfurization methods arduous.

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1. INTRODUCTION

Desulfurization constitutes an obligatory process during crude oil refinement to yield coveted end products (2,3). Rules concerning the levels of sulfur within transport fuels have progressively tightened over time, also a collection of petrochemical compounds get produced virtually sulfur-free currently. Thus, sulfur extraction out from oil is among the vital transformation necessities within many refineries (2). This extraction substantially influences the value and handling expenditures of unrefined petroleum.

The global demand for cleaner fuels is augmenting because progressively strict environmental statutes superintend the sulfur content of transportation fuels, notably marine fuels. Additionally, crude oil along with its components diminishes in caliber because the requirement persists regarding leftover fuels, therefore eliminating sulfur turns important, notably within viscous oils. Considering these commodities include substantial quantities of sulfur predominantly within detailed thiophenic configurations, established high-pressure desulfurization techniques battle for its extraction.

Furthermore, unprocessed substances should be immaculate. This immaculateness is paramount for the petrochemical industry. The durability of equipment, the efficiency of processing, and the quality of products in this industry directly hinge on the purity of raw materials.

Petrochemical products like plastics, polymers, fertilizers, together with other chemicals require raw materials. Superior raw materials are requisite to product quality. Absent pristine base components, the resultant item degrades, thus curtailing worth and utility.

Refining progressions become more efficient when the petrochemical sector employs pure feedstocks. Elevated levels of sulfur, nitrogen, and additional pollutants may impair catalysts given their propensity for diminishing reaction velocity and efficacy (11). Conversely, pristine feedstock eases superior equipment performance while concurrently diminishing energy expenditure.

Equipment safeguard is paramount: Raw materials occasionally harbor pollutants. Sulfur along with metal compounds, for instance, result in corrosion in addition to wear. This elevates repair expenditures and induces premature equipment failure. Conversely, should we utilize pure raw materials, this will lengthen equipment life coupled with diminished maintenance requirements.

Conservation of the environment remains quite important. Employing purified raw material consequently aids in diminishing environmental repercussions. Sulfur along with noxious materials discharged copiously augment emissions to the ecosphere, which taints the atmosphere inducing diverse ecological predicaments. Clean feedstocks ease cleaner production processes as well as a decline in these emissions.

Accordingly, feedstocks should exhibit high purity within the petrochemical sector since that remains important for economic efficiency plus product quality, together with environmental protection and regulatory compliance.

Some scholars observed that hydrodesulfurization (HDS) coupled with carbon rejection methodologies are principal industrial techniques (3,11). Coking and fluid catalytic cracking (FCC) represent instances involving these carbon rejection techniques for desulfurization of heavy oil. Although efficacious regarding sulfur reduction, these methodologies possess a prominent carbon impact.

Furthermore, high-temperature processes, which produce hydrogen for HDS, engender elevated processing costs financially along with environmentally, especially when they process heavier and sulfur-rich crude oils. Consequently, alternate desulfurization pathways are undergoing investigation amid growing consideration (5,12).

Several reviews concerning this topic have been composed. Desulfurization publications typically have concentrated mainly on sulfur extraction from refining portions such as naphtha, distillate, and light vacuum gas oil. However, the aim of this review is to comprehensively survey the processes for converting heavy fractions. Here, we will scrutinize each desulfurization method. We shall ascertain its capability regarding viscous crude oil. The desulfurization methods documented in the literature are adapted for lighter fractions, also as we examine the discussions that have taken place, it becomes clear that they are unsuitable regarding heavy oil. Therefore, this evaluation shall rest upon the degree to which such processes can desulfurize heavy oil.

2. OBJECTIVE

The main objective of this review is to provide a comprehensive and critical analysis of existing desulfurization methods applied to vacuum gas oil, with particular emphasis on the transformation and removal of sulfur-containing aromatic compounds such as dibenzothiophene, benzonaphthothiophene, and their alkylated derivatives.

This study aims to evaluate the effectiveness of various desulfurization approaches, including oxidative, hydrodesulfurization, and emerging alternative techniques, in terms of sulfur removal efficiency, reaction mechanisms, and operational conditions.

Furthermore, the review seeks to examine how different process parameters—such as oxidizing systems, temperature, reaction time, and reagent ratios—influence the reactivity, stability, and conversion pathways of sulfur compounds. Special attention is given to the structural changes in sulfur-containing aromatics during treatment processes and their impact on downstream thermal conversion, such as cracking.

Within this framework, the review will:

- summarize and compare different desulfurization technologies reported in the literature;
- analyze the transformation behavior of sulfur-containing aromatic compounds under various treatment methods;
- evaluate the influence of process conditions on desulfurization efficiency;
- review reported kinetic studies related to sulfur compound decomposition and transformation;
- identify current challenges, research gaps, and future directions in the field of deep desulfurization of heavy petroleum fractions.

3. SULFUR IN CRUDE OIL

Following carbon and hydrogen, sulfur constitutes petroleum's third most copious element (1,4). Unrefined petroleum commonly shows sulfur densities that extend in scope from 0.03 to 7.89% via mass (4) . Sulfur constituents within petroleum are generally categorized. The two categories include inorganic and organic (1). Inorganic sulfur including elemental sulfur, hydrogen sulfide (H2S), and pyrite may occur dissolved within as well as suspended. Concurrently, organic sulfur compounds represent the principal sulfur-containing components within crude oil. These include thiols, sulfides, and thiophenic constituents.

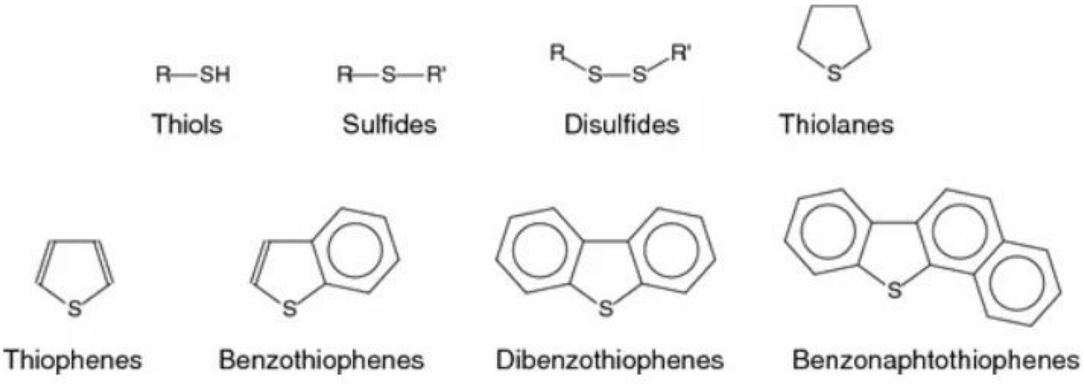

Figure 1. *Some prominent classes of organosulfur compounds*

Fluctuations are obvious in the density and constitution of sulfurous elements across the distillation spectrum. Per Table 1, sulfur quantity within the distillation portion rises alongside greater boiling temperatures because the densest portion exhibits maximum sulfur quantity. Per Table 2, sulfur compounds gain stability as the boiling point elevates, including thiols, sulfides, also thiophene among naphtha to benzothiophene compounds displaced during distillation. In vacuum gasoil as well as vacuum residues, dibenzothiophene compounds represent the foremost route of sulfur presence. Sulfur's chemical makeup immediately impacts its removal process for aliphatic sulfur-bearing compounds like thiols and sulfides are simpler to desulfurize than aromatic sulfur compounds like thiophenes (3,11).

Table 1. *Distribution of sulfur compounds across the distillation range of crude oil with a total sulfur content of 1.2%*

Distillation range(°C)	Sulfur content	Distribution of sulfur compounds (%)			
		Thiols	Sulfides	Thiophenes	Other[a]
70-180(naphta)	0.02	50	50	Trace	-
160-240(kerosene)	0.2	25	25	35	15
230-350(distillate)	0.9	15	15	35	35
350-550(vacuum gasoil)	1.8	5	5	30	60
>550(vacuum residue)	2.9	Trace	Trace	10	90

[a] *Benzothiophenes, dibenzothiophenes and heavy sulfides*

Table 2. *Physical properties of selected sulfur-containing compounds*

Compounds	Normal boiling point (°C)	Melting temperature(°C)	Density at 20°C(kg/m^3)
1-Ethanethiol (ethyl mercaptan)	35	-144.4	839.1
Dimethyl sulfide	37.3	-98.3	848.3
1-Propanethiol (propyl mercaptan)	67	-113.3	841.1
Thiophene	84.2	-38.2	1064.9
Diethyl sulfide	92.1	-103.8	836.2
1-Butanethiol (butyl mercaptan)	98.4	-115.7	833.7
Dimethyl disulfide	109.7	-84.7	1062.5
Tetrahydrothiophene(thiolane)	121.1	-96.2	998.7
Dipropyl sulfide	142.4	-102.5	837.7
Thiophenol	168.7	14.8	1076.6
Dibutyl sulfide	185	-79.7	838.6
Benzthiophene (thianaphthene)	221	32	1148.4
Dibutyl disulfide	226	-[a]	938.3
Dibenzthiophene	332	99	-[a]

[a] *No information is provided in the reference.*

Detailed sulfur constituents typically exhibit elevated concentrations in unrefined oils displaying heightened viscosities and densities. Hydrodesulfurization procedures or thermal manipulation may eliminate unbranched aliphatic sulfides (thioethers). The identical procedures or remedy may readily eliminate cyclic sulfides (thiolanes). Conversely, sulfur integrates within aromatic cycles including thiophene and relevant analogs like benzothiophene, dibenzothiophene, also benzonaphthothiophene. Hydrodesulfurization or thermal conversion methods possess increased impediments regarding its removal.

3.1 Sulfur in heavy oil cuts

Sulfur is present within dense oil fractions while its effects form a petroleum industry concern. Petroleum refinement and refining operations engender elevated-ebullition viscous oil constituents. Oil quality as well as refining processes, along with final products' properties, are considerably affected via the sulfur amount within these fractions.

Detrimental ecological consequences from sulfur's existence within fuel commodities and petroleum derivatives are possible. Furthermore, sulfur may impair catalysts throughout oil refining and diminish their efficacy, and this degrades the procedure's efficiency and economics.

Viscous oil constituents are subjected to differing processes for sulfur reduction. Every method contains intrinsic merits and deficiencies. The oil's composition in conjunction with the refining process requirements determine their choice. In this scientific work, various methods for removing sulfur as well as sulfur-containing compounds in heavy oil fractions will be studied also each's positive and negative aspects will be listed. Fundamentally, sulfur regulation of dense oil constituents affects sustainable advancement for the petroleum sector. Therefore, researchers must consistently cultivate applicable technologies.

4. DESULPHURIZATION TECHNOLOGIES

4.1 Hydrodesulfurization (HDS)

Hydrodesulfurization represents the foremost technique toward decreasing crude oil's sulfur content within the petroleum sector (3,11). HDS commonly entails introducing oil as well as H2 into a fixed bed reactor. The reactor embraces a fitting HDS catalyst, and the induction exists concurrently. NiMo/Al2O3 and CoMo/Al2O3 represent some of the most frequently utilized HDS catalysts (3). Nevertheless, further possibilities do exist. H2S arises when the sulfur of organic sulfur compounds is transformed throughout HDS.

Selecting a specific catalyst variant hinges upon the present application. NiMo catalysts, according to, excel at hydrogenation while CoMo catalysts are better regarding hydrogenolysis. As a consequence, CoMo catalysts exist as the favored choice for HDS processes when such processes include unsaturated hydrocarbon streams, like streams derived from fluid catalytic cracking (FCC), while NiMo catalysts exist as the favored choice for fractions that do require intensive hydrogenation. Substances like NiMo have been observed to be more efficacious in the HDS of constituents like DMDBT. NiMo catalysts are favored where hydrogen flux is uninhibited yet exposure duration is constrained, characteristic of flow reactors, although CoMo catalysts can be more productive in batch reactors. Hydrotreating conditions commonly span from 200 to 425 °C and 1 to 18 MPa, and particular parameters are adjusted for the intended level of desulfurization and the proportion of sulfur compounds inside the feedstock.

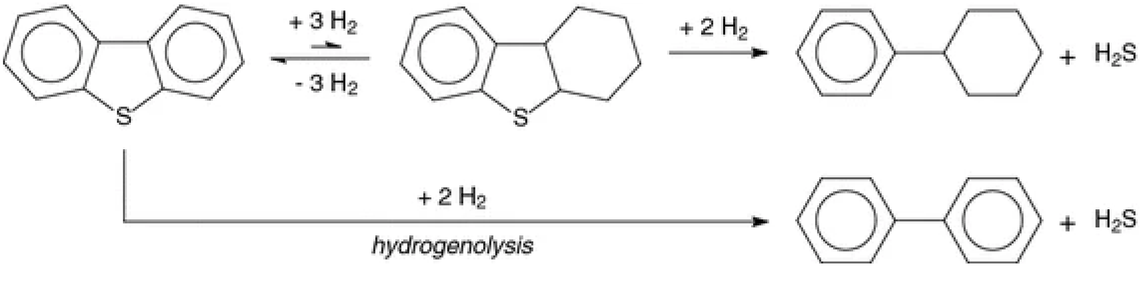

Figure 2. *Desulfurization mechanisms*

Thiophene rings pose increased difficulties regarding sulfur removal. The π-electron constitution for the conjoined C=C framework features restricted skill. Sulfur's singular electron pair is the entirety which it includes. Despite stabilization via resonance of roughly 120–130 kJ mol-1, less than benzene's stabilization of 160–170 kJ mol-1, it markedly impedes HDS. Two discrete pathways elicit desulfurization (Figure 2). Hydrogenolysis constitutes the mechanism with less hydrogen. Nonetheless, the resonance stabilization involving sulfur inside the thiophene ring impedes straightforward hydrogenolysis. This equilibration begets the primary HDS route where the ring saturates prior to desulfurization. Nonetheless, strong dehydrogenation to aromatize compels the hydrogenated product's equilibrium concentration to persist minimally.

Due to thiophene's resonance stabilization, scission is likewise impeded, which elucidates why thiophene-bearing sulfur compounds predominantly generate coke during fluid catalytic cracking. Hydrocracking improves aromatic hydrogenation, which permits sulfur removal via cracking as well as hydrogenation. For improving distillate quality, achieving selective ring opening is the primary goal via hydrocracking heavy oil rather than increasing HDS. HDS is routinely employed for the enhancement of heavy oils. The efficacy of HDS is impeded by the attributes of viscous oils:

(a) High metal content engenders catalyst deactivation as well as precipitate formation.

(b) Coking as well as fouling stem from particular predispositions. Consequently, catalyst inactivation occurs.

(c) Minute catalyst pores constrain approach toward molecular size.

(d) HDS adsorption proves arduous because steric impedance impacts thiophene sulfur.

4.2. Extractive desulfurization

Extractive desulfurization skillfully eliminates organosulfur constituents from sulfur (6,7). Particular solvents will dissolve compounds, easing the process for removal. Within this process, liquid-liquid extraction requires that the two liquid phases remain immiscible. Elements for extractive desulfurization are represented in Figure 3.

The raw material and the dissolving agent initially merge inside some blending reservoir easing assimilation of organosulfur constituents into the dissolving agent with their great solubility. A separator divides the hydrocarbon and solvent phases thereafter. Subsequently, the refined hydrocarbon exhibiting diminished sulfur content undergoes additional treatment. The organosulfur compounds are segregated from the solvent during distillation allowing solvent reclamation. Following retrieval, it is returned into the mixing tank.

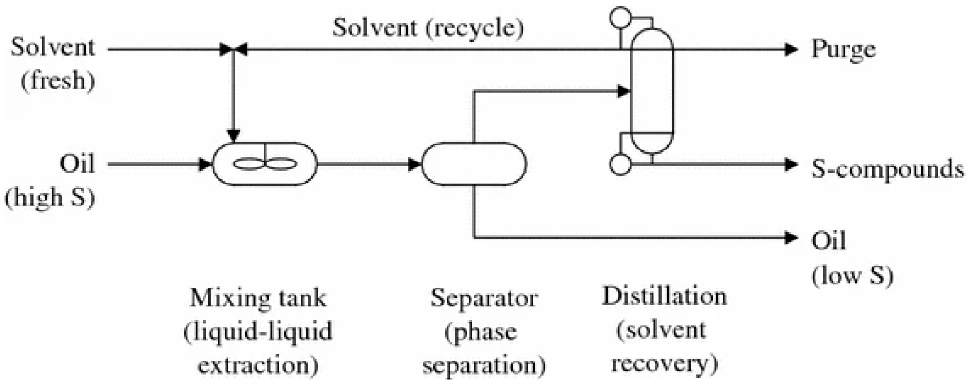

Figure 3. *General process of extractive desulfurization, using low-boiling solvent extraction as an example*

This method presents several benefits, including its facile application, the lack of hydrogen, and the capacity for performance below near-ambient conditions (6). The feedstock remains chemically unaltered, it should be noted, also extraction is physical. Nevertheless, by utilizing this procedure, diverse impediments exist that warrant resolution:

(a) Desulfurization via extraction exhibits natural efficacy when the organic sulfur constituents are soluble in the specified solvent. Thus, solvent selection must be performed with large care. Maximum desulfurization efficacy can be attained thus. An abundance of solvents like acetone, ethanol, and polyethylene glycols were scrutinized, with scrutiny revealing desulfurization rates from 50% to 90%, contingent on extraction cycles employed during the process.

(b) Physically isolating the solvent and oil phases efficiently is vital if the separation process triumphs. Furthermore, the solvent needs diminished stable solubility within the oil. This keeps the process solvent from undergoing depletion.

(c) Augmenting mixing along with extraction efficiency requires diminishing oil viscosity. Diminishing solvent viscosity remains important too. Nevertheless, heavy oil confronts obstacles herein, generally requiring its fractionation amid heightened temperatures to diminish viscosity. This constraint might require operators extracting under duress, which additionally confounds the procedure.

(d) It is imperative that the solvent possesses a disparate boiling point from the sulfur compounds extracted from the oil. While an individual favors selecting a dispersant possessing an elevated boiling point compared to the sulfur constituents since the dispersant's magnitude is generally greater with respect to what they derive from the sulfur constituents, heavy oil procurement commonly mandates utilizing a dispersant exhibiting a diminished boiling point. The expenditures linked to solvent retrieval escalate markedly as a result.

(e) The resultant solvent from extraction could possibly still contain particular constituents. These constituents had been isolated out of the oil yet still cannot undergo efficacious separation via distillation. As routine sanitation diminishes such accumulation, the density of those constituents steadily accrues throughout solvent reclamation.

The utilization of less dense solvents in extractive desulfurization processes regarding viscous oil introduces predicaments concerning the fiscal efficacy of those processes, notably the peril of solvent depletion and dissolution inside the viscous oil's detailed framework.

Sulfur compounds like S-compounds, (as shown in Figure 1) in products like gasoline and diesel fuel, act as contributors regarding sulfur oxides (SOX) emission throughout combustion. These discharges diminish combustion efficacy, neutralize three-way converters, and escalate releases regarding carbon monoxide (CO) and particulates. Thus, desulfurization of feedstocks is of paramount importance in the oil refining process.

Hydrodesulfurization (HDS) is at this moment prevalently employed within industry. It mainly includes the interaction of S compounds within petroleum via hydrogen utilizing Co-Mo/Al2O3 and Ni-Mo/Al2O3 catalysts. HDS faces predicaments, though, particularly since certain nations aim for sulfur thresholds in petroleum to possess zero sulfur content with elevated rigor. Originally, the European directive concerning transport fuels constrained sulfur content to 150 ppm for gasoline and 350 ppm for diesel in 1998, then diminished it to 50 ppm within five years, and currently promotes levels below 10 ppm. The United States along with Japan have likewise levied taxes on transport fuels. Those fuels' sulfur concentration exceeds 10 ppm.

HDS is efficacious because it mainly eliminates aliphatic S-compounds like thiols, thioethers, and disulfides, along with thiophene (TS), benzothiophene (BT), dibenzothiophene (DBT), and their derivatives, given that steric hindrance arises during adsorption onto the catalyst surface. Achieving lower sulfur content levels through HDS requires more stringent conditions, including high temperatures (approximately 400°C), high pressures (approximately 20 MPa) and more active noble catalysts, and that results in increased costs and potential oil losses, especially in the form of alkenes.

Scientists explored alternate avenues for confronting these matters. They employed extraction, oxidation, adsorption, and biodesulfurization. Extractive desulfurization (EDS) materializes as a feasible procedure among these methodologies since it is able to function under amenable and plain circumstances without modifying the fuel oils' compounds' chemical constitution. Furthermore, extracted sulfur compounds also can become feedstock that is recycled.

For use in EDS, dimethylsulfoxide, pyrimidinone, imidazolidinone as well as polyalkylene glycol, like several molecular solvents, have been assessed. Nevertheless, the capricious disposition of such molecular dissolvents coupled alongside the constraint that appropriate extractors exist scantily has deterred individuals from wide-ranging EDS utilization throughout industrial functions. Solvent differs, extractants reconstitute with complexity, also these processes considerably impede EDS's commercial implementation.

4.3. Ionic-liquid extraction method

Ionic liquids, when employed for sulfur extraction from fuels such as diesel, represent a compelling substitute to organic solvents because they have the potential to yield ultra-clean diesel fuels (5,12). Numerous investigations have underscored the efficacy of imidazolium, pyridinium, or quinolinium-based ionic liquids. They have depicted as well their propitious extraction attributes for anions like alkyl sulfates, alkyl phosphates, or halogen-containing anions.

Ideally, ionic liquids would pull sulfur out of fuel, barely touch the hydrocarbons, flow easily through pipes, and snap back into two clean layers when the job was done. Yet in the messy reality of working plants, they usually fall short of that laundry list.

They look promising in lab tests that mix pure dibenzothiophene with decane, but when the feed comes straight from the distillation column, the gain shrinks fast. It turns out that ionic liquids behave like many other solvents: they excel on model fluids yet falter with the dirty, complex blends found in everyday refining. The problem grows heavier still when dealing with vacuum gas oils or other high-viscosity cuts.

One way to nudge the system in the right direction is to first oxidize the sulfur compounds into sulfoxides and sulfones. These by-products grab onto the ionic liquid much more tightly, so the same volume of solvent strips a bigger slice of sulfur from the feed.

Despite the tuning, the high boiling points of most ionic liquids still make life harder during solvent regeneration. Pulling off the solvent to recover the sulfur is trickier than with many organic extractants, and any energy penalty cuts straight into the plants bottom line. Several investigators have suggested different strategies to address the difficulties encountered in the use of ionic liquids for desulfurization.

(a) One option is to extract sulfur species directly by vacuum distillation. While distillation works well in principle, the very high boiling points of heavier organo-sulfur compounds-such as alkylated dibenzothiophenes, which exceed 340 C-mandate the use of vacuum technology. Consequently, this pathway is usually limited to light petroleum cuts, where compound volatility is more manageable.

(b) An alternative method employs a low-boiling solvent to re-extract sulfur after the ionic liquid has been loaded. In this process, the ionic liquid is first withdrawn for recycling, then purified with the auxiliary solvent. A second distillation step subsequently separates the sulfur from the solvent used in the earlier extraction.

(c) A third separation route simply adds water to the sulfur-rich ionic liquid. When sufficient water is introduced, the partition coefficient of many sulfur compounds drops close to zero. As a result, sulfur either dissolves with light hydrocarbons, forms a separate aqueous phase, or, in some formulations, precipitates out entirely. This approach works best when the sulfur species are fully oxidized, allowing them to form stable, herbicidal ions that interact with the melt. Before the ionic liquids can be recovered and reused, however, nearly all the water must be stripped from the mixture. Water removal by simple boiling uses far more energy than most practical processes can afford, so a four-stage evaporative scheme, operating at gradually lower pressures and higher temperatures, has been proposed to trim heat overhead. When implemented carefully, this multi-stage strategy can bring the thermal burden down to levels comparable to those seen in standard hydrodesulfurization.

In short, extractive desulfurization with ionic melts inherits the same strengths that solvent extraction offers: high selectivity, mild temperatures, and compatibility with fuel hydrocarbons. Yet technical route is still held back by the steep raw-material costs and pronounced humidity-sensitivity of some ionic melts, which box plants into specially sealed, expensive infrastructure and prevent large-scale adoption.

To the authors knowledge, extractive desulfurization has never yet been tried on heavy fuels, a finding that matches expectations; many researchers have struggled even to treat straight-run distillate with the same chemistry. Consequently, ionic-liquid extraction cannot now be viewed as a practical option for cleaning heavy oil.

4.4. Adsorptıve desulfurızatıon

Adsorptive desulfurization relies on stationary solids that selectively snag organic sulfur species when a fuel passes through their bed (3,17). The overall success of any adsorptive method rests on the design of the sorbent. Key characteristics include its ability to distinguish organic sulfur from hydrocarbons, the maximum amount of sulfur it can hold, its mechanical stability over multiple cycles, and how easily it can be refreshed for further use.

Two broad strategies exist within adsorptive desulfurization:

(a) Physical adsorption relies on weak van der Waals forces, so the sulfur compounds remain chemically intact as they cling to the material. The energy penalty for regeneration in this case scales mostly with how much sulfur is loaded, yet because the bond is weak physisorption itself can be regarded as almost energy-neutral.

(b) Reactive adsorption proceeds via a genuine chemical interaction, usually converting the incoming sulfurs to metal sulfides fixed on the sorbent surface. Cleaning the material can then be done either by heating or by flushing it with a suitable solvent. Depending on contaminants and operating conditions, released species may appear as H2S, SOx, or pure elemental sulphur.

Many candidate materials, from metal-organic frameworks to tailored zeolites, have gone through testing to gauge their promise in real-life desulfurization.

Extensive research has assessed the use of solid adsorbents such as activated carbon, zeolites, amorphous silica-alumina, and metal-organic frameworks (MOFs) for removing sulfur from model oils, fluid-catalytic-cracking (FCC) feed, coker naphtha, and distillate streams. Laboratory and pilot tests show that these materials can reach regulatory sulfur targets under relatively mild conditions, yet even the best candidate still falls short when scaled up to full refinery operations. Heavy feeds remain a particular challenge, because bulky sulfur species struggle to navigate narrow pore mouths and steric crowding further limits uptake. As a result, the accessibility limitations that plague catalytic hydrodesulfurization (HDS) are echoed in adsorptive desulfurization, since both techniques depend on molecules physisorbing or chemisorbing to a solid interface.

4.5. Oxidative desulfurization (ODS)

Oxidative desulfurization (ODS) graphically denotes a sequence where an external oxidant reacts with sulfur compounds, thereby making them easier to extract from liquid fuels. The method is frequently presented as a single unified route, yet it actually contains two separate, sequential operations that must occur for successful desulfurization. Oxidative desulfurization (ODS) begins with the oxidation of sulfur species, transforming their chemical profiles. Once oxidized, these species can be selectively separated from unoxidized compounds during a downstream removal stage that exploits the new redox properties (5-8,12).

A series of recent reviews has compiled advances in ODS, revealing sustained scholarly and practical interest evidenced by a growing publication record.

In industrial practice, ODS is routinely applied to convert low-volatility thiols into more easily handled disulfides.

$$2R\text{-}SH + \tfrac{1}{2} O_2 = R\text{-}S\text{-}S\text{-}R + H_2O \quad (1)$$

Conversion occurs in weakly alkaline solution, where hydroxide enhances thiol oxidation kinetics. A moderate NaOH concentration, often supplied as aqueous caustic soda for cost-efficiency, is paired with air as the oxidant. A soluble metal catalyst further accelerates the process, which discriminates strongly between thiols and other sulfur moieties. Heavy-oil fractions typically contain only trace thiols and therefore require no secondary desulfurization step (Table 1).

In oxidative desulfurization, or ODS, the process converts sulfur in sulfide and thiophene bonds into sulfoxides (1) and sulfones (3) through mild oxidation (9,10).

$$R\text{-}S\text{-}R' + \tfrac{1}{2} O2 = R\text{-}(SO)\text{-}R' \qquad (2)$$

$$R\text{-}S\text{-}R' + O2 = R\text{-}(SO2)\text{-}R' \qquad (3)$$

***Table 3**. Dependence of the breaking energy of C-S bonds in sulfur-containing compounds on classification*

Compound classifications[a]	Breaking energy of C-S bonds (kJ/mol)
Unoxidized sulfur	
CH_3S-CH_3	320
PhS-CH_3	290
Oxidized sulfur	
CH_3(SO)-CH_3	230
CH_3(SO_2)-CH_3	280
Ph(SO_2)-CH_3	240
Ph(SO_2)-Ph	290

[a] Ph =Phenyl group, -C_6H_5

Oxidation transforms sulfur-containing species into sulfoxides and sulfones, and these products display two features that support desulfurization. First, the added polar bonds raise overall polarity, which improves selectivity during solvent extraction (18-23). While the redox route does not solve solvent evaporation or the energy burden of recycling, it sharpens the extraction window. Second, oxidation weakens the C-S bond, as summarized in Table 3 (10). Weaker bonds allow the oxidized fragments to be removed much more easily via thermal decomposition. Patent records on oxidative desulfurization (ODS) reveal schemes aimed specifically at upgrading heavy oils, and these schemes vary in their oxidants and reaction conditions.

(a) One popular route relies on acidic oxidation with hydrogen peroxide activated by short-chain carboxylic acids such as formic or acetic acid. Under such conditions oxidation proceeds gently at approximately 50 °C for roughly 6 hours. Subsequent thermal treatment at 350–450 °C cleaves the now-fragile C–S linkages while limiting unwanted breakdown of the hydrocarbon matrix.

(b) Sulfur removal begins with oxidation using an air stream at 80-180 °C. The reaction may be sped up by a non-acidic catalyst, typically a Group 5A metal such as vanadium and Group 8 metals such as nickel, palladium, or platinum. Following this step, an elevated heat-treatment at 200-400 °C, preferably near 300 °C, is applied to convert the sulfur mainly to SO2. Finally, the material undergoes catalytic hydrodesulfurization.

(c) In a second method, the sample is immersed in an acidic aqueous solution and treated with an oxidant until sulfur species become sulfate. The C-S linkages are then cleaved by molten alkali-metal hydroxide, yielding water-soluble polysulfides. These soluble species are easily washed away from the hydrocarbon phase, leaving cleaner organic material.

(d) The sulfur-bearing compounds are oxidized with an external oxidant, typically a hydrogen peroxide solution. The resulting oxidized materials are subsequently extracted with a light paraffinic solvent, which preferentially dissolves the lower-sulfur fraction. This final extraction resembles the classical asphaltene-depletion procedure: when the solvent is gently evaporated, the remaining asphaltenes trap most of the higher-sulfur oxidized species within their structure.

(e) Oxidation of sulfur compounds can be effected with an oxidant such as hydrogen peroxide when the system is buffered by an acidic medium, typically acetic acid, and accelerated by a titanium-containing catalyst. Although optimal yields are reported at approximately 50 °C, the method remains practical over a broader window of 20 to 90 °C. Testing has been performed with model sulfur and nitrogen species as well as with selected cuts drawn from crude oil. Isolation of solvent and target products is then accomplished through standard distillation and solvent-extraction steps.

4.6. Biodesulfurization

Biodesulfurization proceeds at mild temperature and pressure, exploiting the metabolic pathways of specially chosen microbes that can utilize organosulfur substrates as growth factors. With carefully curated microbial consortia, scientists have demonstrated the direct treatment of crude oil without prior fractionation.

Relative to conventional processes, BDS holds promise for lower capital and operating expenditures. Documentation indicates that BDS lines can demand roughly half the initial investment and generate 15% lower ongoing costs when compared to hydrodesulfurization (HDS) units of equivalent capacity.

Recent improvements in reactor design have extended microbial longevity in biodesulfurization-processes from the former 1-2 days to a more viable 8-16 days, or roughly 200-400 hours. Better mass transport has eased resis-tance to flow, permitted higher volumetric rates, and consequently boosted overall process efficiency. Such enhancements mean that conversions can now take place in much smaller reactors, saving space and resources. On the downside, concentrating and separating these more persistent microorganisms has proven difficult, obliging operators to invest in extra equipment for oil-water-emulsion treatment. Even with these advances, commercial biodesulfurization of crude oil remains elusive, chiefly because of logistics related to disinfect-ing, moving, storing, and introducing live cultures in field or refinery settings.

5. RESULTS

A variety of strategies has been proposed to desulfurize heavy-oil fractions, including hydrodesulfurization, extrac-tive desulfurization, oxidative desulfurization, and biodesulfurization (3,5,12). Yet, despite the large number of options recorded in the literature, only a handful prove genuinely workable for treating the high-sulfur content usually present in heavy oil. These difficulties stem from intrinsic characteristics of heavy crude, particularly plentiful sulfur content, high viscosity, elevated boiling range, and the refractory stability of most sulfur species (18-23).

After surveying recent studies and considering practical options for treating heavy oil, several noteworthy points become apparent:

(a) Approaches using solid phases-catalysts or adsorbents-tend to underperform because heavy oil is dense, dirty, and features large, tangled molecules.

(b) Separation routes such as selective extraction or high-temperature distillation struggle with heavy oil's steep viscosity profile and elevated boil-up, even when sulfur compounds are prereduced by alkylation, oxidation, or chlorinolysis.

(c) Although biodesulfurization seems appealing, immutable sulfur bonds, extreme fluidity, and a heterogeneous feed still challenge microbial systems, underscoring the need for transport-tailored organisms with narrow sulfur selectivity.

(d) Finally, selective in-liquid methods that rely on stoichiometric reagents have yet to prove commercially viable for removing sulfur from heavy grades on a meaningful scale. Because heavy oils contain large amounts of sulfur, methods that depend on costly or hard-to-get reagents—most often hydrogen—tend to be uneconomic. As a result, techniques like alkylation, chlorinolysis, and several oxidation-based routes are excluded from serious consideration for their desulfurization (13-16).

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