



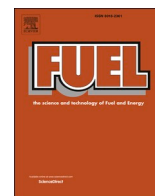
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Review article

Data-driven hydrodesulfurization of heavy feeds: from model compounds to refinery-relevant catalyst design, soft sensing, and process optimization

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ABSTRACT

Hydrodesulfurization (HDS) remains the primary industrial route for sulfur removal, but increasingly heavy and complex feedstocks make deep desulfurization more challenging. This review examines the evolution of HDS from model sulfur compounds to refinery-relevant heavy feeds, including vacuum gas oils, residues, biomass-derived oils, and waste tire and plastic pyrolysis oils. The distribution and reactivity of inorganic and organic sulfur species are discussed, with particular emphasis on refractory thiophenic compounds, and the competing direct desulfurization and hydrogenation pathways. The effects of temperature, hydrogen pressure, liquid hourly space velocity, and feed sulfur content are evaluated in relation to sulfur conversion, hydrogen consumption, catalyst deactivation, and process economics. The emerging role of machine learning (ML) in HDS research is assessed. ML enables quantitative mapping of catalyst descriptors, feedstock properties, and operating conditions to catalytic performance, enhancing catalyst screening, structure–activity analysis, sulfur-content prediction, soft sensing, multi-objective optimization of operating conditions, and catalyst lifetime prediction. The review further highlights hybrid physics-aware models, explainable ML, digital twins, and adaptive learning as promising approaches for bridging laboratory-scale models with dynamic refinery operation. Unlike conventional trial-and-error approaches, these data-driven methods can reveal complex interactions among catalysts, feedstock, and process variables while reducing experimental effort and enabling real-time decision support. Some barriers remain, including data quality, training-deployment data mismatch, model transferability, interpretability, and limited long-term industrial datasets. Integrating mechanistic HDS knowledge with ML promises a pathway toward faster catalyst development, optimized operation, improved catalyst utilization, and more sustainable heavy-feed desulfurization.

Abbreviations: AARE, Average absolute relative error; ADS, Adsorptive desulfurization; AI, Artificial intelligence; ANN, Artificial neural network; APC, Advanced process control; API, American Petroleum Institute gravity; BDS, Biodesulfurization; BSR, Bacterial sulfate reduction; BT, Benzothiophene; CCR, Conradson carbon residue; CUS, Coordinatively unsaturated sites; DBT, Dibenzothiophene; DDS, Direct hydrodesulfurization; DFT, Density functional theory; DPF, Diesel particulate filters; DS, Desulfurization; ECFP, Extended-connectivity fingerprint; EDS, Extractive desulfurization; FAIR, Findable, Accessible, Interoperable, and Reusable; GC, Gas chromatography; GC×GC, Comprehensive two-dimensional gas chromatography; GNN, Graph neural network; GPF, Gasoline particulate filters; GPR, Gaussian process regression; GRU, Gated recurrent unit; HDAs, Hydrodeasphaltenes; HDM, Hydrometallization; HDN, Hydrodenitrogenation; HDO, Hydrodeoxygenation; HDS, Hydrodesulfurization; HDT, Hydrotreating; HTE, High-throughput experimentation; HTL, Hydrothermal liquefaction; HYD, Hydrogenation; IC, Ion chromatography; ICP, Inductively coupled plasma; ISC, In-situ combustion; LCA, Life cycle assessment; LHSV, Liquid hourly space velocity; LIME, Local Interpretable Model-agnostic Explanations; LSTM, Long short-term memory; MAE, Mean absolute error; ML, Machine learning; MoDTC, Molybdenum dithiocarbamate; MOF, Metal-organic framework; MOGP, Multi-output Gaussian process; MPC, Model predictive control; MS, Mass spectrometry; NCP, Neural circuit policy; ODS, Oxidative desulfurization; PAH, Polycyclic aromatic hydrocarbon; PINN, Physics-informed neural network; PLS, Partial least squares; PM, Particulate matter; QSAR, Quantitative structure–activity relationship; RF, Random forest; RMSE, Root mean square error; RNN, Recurrent neural network; RUL, Remaining useful life; SCR, Selective catalytic reduction; SHAP, Shapley Additive Explanations; SMR, Steam methane reforming; SVR, Support vector regression; TEA, Techno-economic analysis; TEM, Transmission electron microscopy; ULS, Ultra-low-sulfur; VGO, Vacuum gas oils; WABT, Weighted average bed temperature; WPPO, Waste plastic pyrolysis oils; WPTO, Waste pyrolysis tire oil; XAI, Explainable artificial intelligence; XGBoost, Extreme Gradient Boosting; XRD, X-ray diffraction; ZDDP, Zinc dialkylidithiophosphate.

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1. Introduction

The long-term sustainability of global liquid fuel and petrochemical supply is increasingly challenged by the gradual depletion and reduced availability of easily accessible light crude oil resources [1,2]. Although conventional light crudes remain highly desirable because of their relatively low sulfur content, high hydrogen-to-carbon ratio, and ease of refining, their declining share in many refining portfolios has intensified interest in heavier and more complex feedstocks. To maintain energy security and meet persistent global demand for transportation fuels, chemicals, and industrial energy carriers, refineries are propelled toward the utilization of feedstocks that were once considered less attractive or technically difficult to process.

In this context, heavy feeds have become strategically important as alternative carbon resources for future fuel production. These feeds include not only heavy crude oils, vacuum gas oils, atmospheric and vacuum residues, bitumen-derived fractions, and extra-heavy petroleum streams [3,4], but also an expanding range of non-conventional and waste-derived liquids [5]. Among these, biomass residues [6,7], pyrolysis tire oil [8,9], waste plastic pyrolysis oil [10], used lubricating oil re-refining streams [11], and coal- [12,13] or shale-derived liquids [14] are increasingly being explored as supplementary refinery feedstocks. Their growing relevance stems from two converging pressures: the need to compensate for the expected decline in high-quality light crude supply and the parallel demand to valorize low-value, carbon-rich waste and residual resources within a more circular and resource-efficient energy system (Fig. 1).

Despite their promise, these heavy and unconventional feeds are significantly more challenging to upgrade than conventional light crudes [15]. They typically contain elevated levels of sulfur, nitrogen,

oxygen, metals, aromatics, resins, asphaltenes, and coke precursors, together with broad compositional variability and poor physicochemical stability. For example, pyrolysis tire oil is particularly rich in sulfur-containing compounds due to the sulfur vulcanization chemistry of waste tires [16], while biomass-derived residual oils such as hydrothermal liquefaction biocrudes may contain complex mixtures of sulfur-, nitrogen-, and oxygen-containing molecules [17] that require severe processing prior to refinery integration. Similarly, petroleum-derived heavy residues are often enriched in refractory heteroatoms species and catalyst-poisoning contaminants, making them among the most difficult feedstocks to upgrade efficiently [18].

Although petroleum-derived heavy feedstocks, such as vacuum residues, atmospheric residues, heavy crude oils, and vacuum gas oils remain the primary industrial feedstocks processed in hydrodesulfurization units, growing environmental concerns and circular economy initiatives have stimulated increasing interest in integrating renewable and waste-derived oils into existing refinery infrastructure. In contrast to conventional petroleum residues, biomass-derived oils, waste plastic pyrolysis oils, tire pyrolysis oils, and used lubricating oils are currently considered primarily as supplementary or co-processing feedstocks rather than direct replacements for petroleum streams [19,20]. Their incorporation into refinery operations aims to improve resource utilization, reduce reliance on fossil resources, and facilitate the production of lower-carbon transportation fuels while taking advantage of existing hydrotreating infrastructure [21]. However, these alternative feedstocks possess substantially different chemical characteristics, including higher oxygen contents, greater compositional variability, and distinct impurity profiles, which introduce additional challenges for catalyst design, process optimization, and reactor operation. Consequently, understanding both the similarities and the

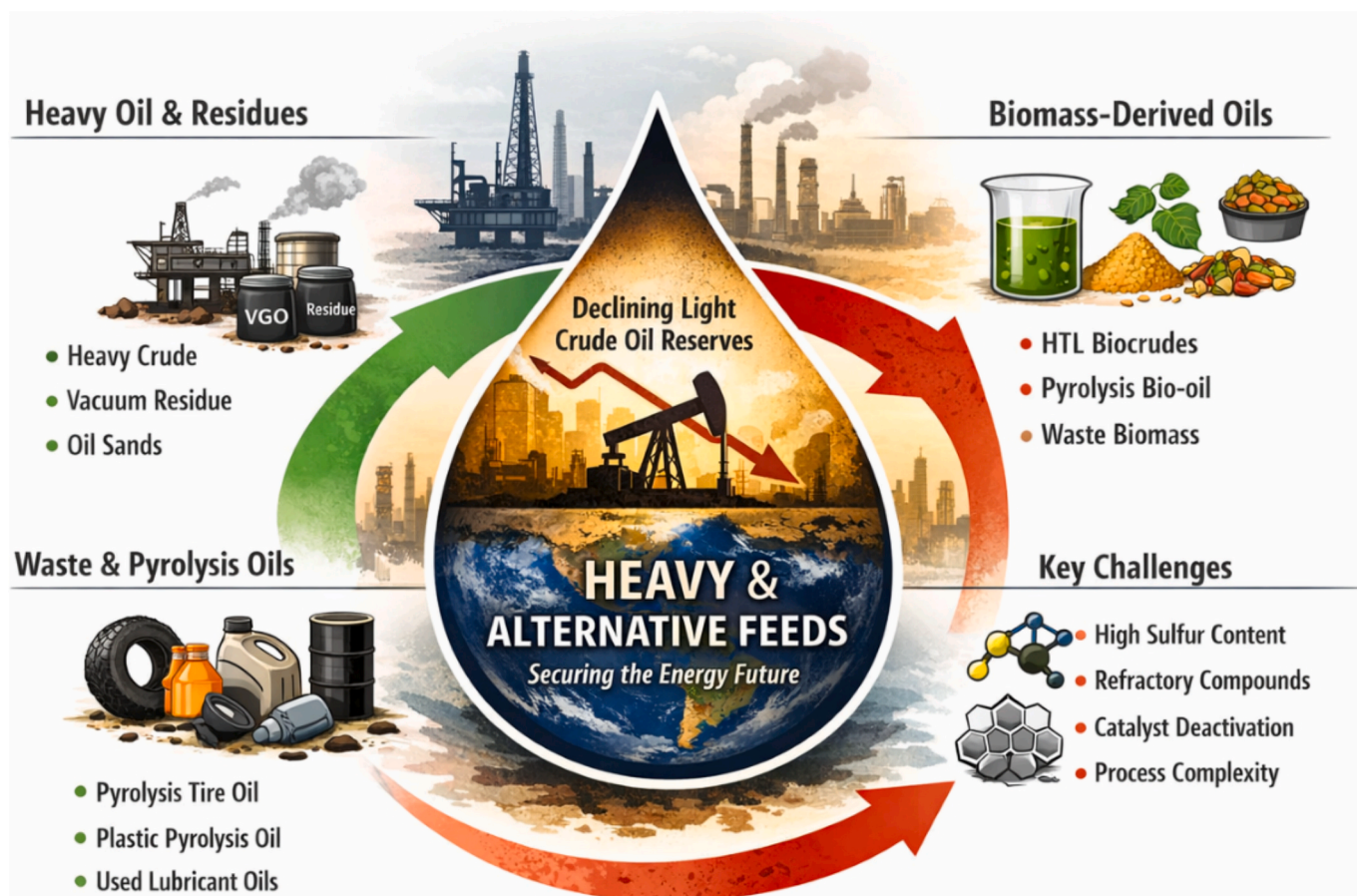


Fig. 1. The shift towards heavy feed for refining.

differences between conventional petroleum residues and emerging alternative feedstocks is essential for developing hydroprocessing strategies that are technically effective, economically viable, and compatible with future refinery decarbonization.

It should be noted that the primary objective of hydroprocessing varies with the nature of the feedstock and the downstream refinery application. For diesel-range feedstocks, hydrotreating is designed not only to achieve ultra-low sulfur specifications—typically ≤ 10 ppm for EURO 5 compliance—but also to improve fuel quality through partial aromatic saturation, resulting in higher cetane number and lower density [22,23]. For feedstocks intended for fluid catalytic cracking (FCC) and hydrocracking pretreatment, particular emphasis is placed on hydrodenitrogenation (HDN), because nitrogen compounds are potent inhibitors that strongly poison downstream cracking catalysts. In residue upgrading, hydroprocessing is commonly integrated with hydrocracking to reduce the boiling range while simultaneously removing sulfur, nitrogen, and contaminant metals (e.g., nickel and vanadium) that would otherwise deactivate downstream catalysts [24,25]. In contrast, catalytic upgrading of biomass-derived pyrolysis oils and hydrothermal liquefaction (HTL) biocrudes primarily targets hydrodeoxygenation (HDO) and stabilization to produce refinery-compatible intermediates or drop-in fuels, whereas sulfur removal generally plays a secondary role due to the relatively low sulfur content of most biomass-derived feedstocks [26–28].

Ultra-low-sulfur (ULS) fuel specifications—typically ≤ 10 – 15 ppm for diesel and gasoline—have become a central requirement of modern refining [29–31]. Critically, however, these specifications are not independent targets; they are established instrumentally to enable compliance with increasingly stringent emissions standards (e.g., Euro VI, US EPA Tier 3, IMO 2020) that mandate reductions in NO_x , particulate matter (PM), and SO_x emissions. Sulfur present in transportation fuels is oxidized during combustion to form sulfur oxides (SO_x), which are major precursors of acid rain, particulate pollution, atmospheric haze, and adverse human health effects [32]. Beyond direct emissions, sulfur also interferes with the performance of advanced emission-control systems such as three-way catalysts [33], diesel oxidation catalysts [34,35], and particulate filters [36], leading to catalyst poisoning and reduced efficiency in automotive after-treatment technologies. The adoption of these sulfur-sensitive aftertreatment systems—selective catalytic reduction (SCR), diesel particulate filters (DPF), and gasoline particulate filters (GPF)—has further reinforced the dependence on ULS fuels, as these technologies require low-sulfur feeds to maintain durability, efficiency, and regulatory compliance over their operational lifetime. Consequently, deep sulfur removal is essential not only to meet fuel quality specifications, but also to ensure compliance with global clean-air standards and to enable the broader deployment of cleaner engines and exhaust treatment systems.

From a refining and process perspective, sulfur-free fuels are also critical for improving the downstream compatibility, operational reliability, and sustainability of fuel production systems. Sulfur-containing compounds—especially refractory thiophenic species commonly found in heavy feeds—can accelerate corrosion, deactivate catalysts in downstream upgrading units [37,38], and reduce the quality and stability of refined products. As the refining industry increasingly incorporates heavy petroleum fractions, waste-derived oils [39], and biogenic residual feeds [40], the challenge of sulfur removal becomes even more significant because these resources often contain higher and more complex sulfur burdens than conventional light crude fractions [41,42]. Therefore, the development of efficient desulfurization strategies is indispensable for securing cleaner fuels from increasingly difficult feedstocks, while simultaneously supporting environmental protection, refinery integration, and long-term energy resilience.

Alongside the rapid advancement of hydroprocessing technologies, recent years have witnessed a paradigm shift toward data-driven research in petroleum refining and heterogeneous catalysis. Machine learning (ML), deep learning, and artificial intelligence (AI) are

increasingly being integrated with experimental investigations, first-principles calculations, and process simulations to accelerate catalyst discovery, establish structure–performance relationships, optimize operating conditions, and facilitate intelligent refinery operation through digital twins and advanced process control [43,44]. Recent studies have demonstrated the considerable potential of ML for industrial hydroprocessing applications. For example, Yang et al. [45] developed an attention-based encoder–decoder recurrent neural network (A-ED-RNN) framework incorporating bio-inspired neural circuit policies (NCPs), gated recurrent units (GRUs), and long short-term memory (LSTM) networks to predict diesel and jet fuel production rates in an industrial hydroprocessing unit. Using plant operating variables—including feed flow rates, reactor temperatures and pressures, hydrogen makeup, and purge gas flow rate—as model inputs, the proposed NCP-A-ED-RNN achieved comparable prediction accuracy while requiring significantly fewer trainable parameters, resulting in shorter training times and lower computational demands. Such lightweight architectures are particularly attractive for industrial deployment, where computational efficiency and memory usage are critical considerations.

Machine learning has also demonstrated significant potential for optimizing hydroprocessing systems beyond conventional petroleum refining. Chen et al. [46] integrated ML models with process simulation and multi-objective optimization to optimize the hydrodeoxygenation of biomass-derived pyrolysis oil, simultaneously balancing fuel quality, hydrogen consumption, carbon utilization, and greenhouse gas emissions. Their work illustrates how data-driven optimization can identify optimal operating conditions that satisfy multiple and often competing performance objectives, highlighting the growing role of AI in sustainable fuel production. More recently, Ta and Liu [47] developed a multi-output Gaussian process (MOGP) surrogate model for an industrial hydrotreating unit using historical operating data collected over six catalyst cycles and multiple operating regimes. The model simultaneously predicted several key process indicators—including product sulfur concentration, product yields, hydrogen consumption, and cetane index—while quantifying predictive uncertainty. Such surrogate models provide interpretable operating maps that support process optimization, catalyst management, and real-time refinery decision-making.

Beyond process optimization, recent advances in heterogeneous catalysis have underscored the importance of integrating high-throughput experimentation, computational modeling, and interpretable machine learning to accelerate catalyst development. ML-assisted catalyst screening enables the identification of key physicochemical descriptors governing catalytic performance, thereby substantially reducing the time, cost, and experimental effort associated with conventional trial-and-error approaches [48]. Collectively, these developments indicate that future hydroprocessing research will increasingly rely on the synergy between mechanistic understanding and data-driven methodologies to address the complexity of refinery-relevant heavy feedstocks while simultaneously improving hydrogen utilization, catalyst lifetime, process efficiency, and operational sustainability [44].

Although numerous review articles have summarized hydrodesulfurization catalysts, reaction mechanisms, sulfur chemistry, operating variables, and alternative desulfurization technologies, these topics have largely been discussed independently. Existing reviews predominantly emphasize catalyst development, mechanistic understanding, or process engineering, whereas recent advances in artificial intelligence, machine learning, digital twins, and refinery data analytics have received comparatively limited and fragmented attention. Consequently, there remains a lack of a comprehensive review that systematically integrates catalytic fundamentals with data-driven methodologies for industrial hydrodesulfurization.

In this review, we bridge this gap by connecting molecular sulfur chemistry, hydrodesulfurization mechanisms, catalyst behavior, and operating conditions with emerging machine-learning approaches for

catalyst design, soft sensing, process optimization, catalyst lifetime prediction, and refinery decision support. Rather than treating machine learning as a standalone topic, we demonstrate how sulfur speciation, catalyst descriptors, reaction conditions, and process variables can be translated into informative features for predictive models, thereby linking mechanistic understanding with data-driven optimization.

Furthermore, unlike previous reviews that primarily focus on petroleum feedstocks or laboratory-scale model compounds, this review extends the discussion to refinery-relevant heavy feeds, including vacuum gas oils, petroleum residues, biomass-derived oils, waste tire pyrolysis oils, and waste plastic pyrolysis oils. Particular emphasis is placed on the transition from conventional experimental optimization toward integrated, data-driven workflows capable of accelerating catalyst development, reducing experimental effort, improving hydrogen utilization, and enabling real-time refinery optimization. This integrated perspective provides practical guidance for future intelligent hydroprocessing of increasingly complex feedstocks.

2. Sulfur chemistry in the heavy hydrocarbon feedstock

Sulfur content varies widely across different heavy and unconventional feedstocks, reflecting both their origin and the processes used for their production. In general, biomass-derived oils tend to exhibit lower sulfur levels than fossil-derived feeds, although this is highly dependent on the type of biomass and its contamination history. Wood-derived bio-oils are the most extensively researched and typically contain the lowest sulfur concentrations, ranging from tens to hundreds of $\text{mg}\cdot\text{kg}^{-1}$ [49]. For instance, softwood bio-oil sourced from the Finnish Technical Research Centre (VTT) was found to contain only $68\text{ mg}\cdot\text{kg}^{-1}$ of sulfur [50]. These trace amounts frequently fall below the $100\text{ mg}\cdot\text{kg}^{-1}$ detection threshold of standard elemental analyzers using infrared or thermal conductivity detectors. Consequently, researchers may encounter false-negative data, leading to the incorrect assumption that sulfur is entirely absent [51–53]. However, exceptions exist; eucalyptus bio-oil has shown levels as high as $2000\text{ mg}\cdot\text{kg}^{-1}$ [54]. In contrast, feedstocks such as herbaceous biomass or oilseed waste generally yield higher sulfur concentrations [49], with rice husk and rapeseed cake bio-oils reaching $0.2\text{ wt}\%$ and $0.58\text{ wt}\%$, respectively [55,56]. The highest levels are often found in protein-dense materials like algae, where sulfur content can approach $1\text{ wt}\%$ [49].

In contrast, waste-derived and pyrolysis oils often exhibit more variable and, in some cases, elevated sulfur content depending on the nature of the waste stream. For example, waste pyrolysis tire oil (WTPO) is well known for its relatively high sulfur concentration, which originates from sulfur used in the vulcanization of rubber during tire manufacturing. WTPO typically contains $1.0\text{--}2.5\text{ wt}\%$ of sulfur [57–60], far exceeding standard fuel regulations. Similarly, waste plastic pyrolysis oils (WPPO) may contain sulfur of 0.1 to over $0.2\text{ wt}\%$ [61,62] if the feedstock includes sulfur-containing polymers or contaminants. Meanwhile, used lubricating oils and refinery waste streams can also carry sulfur compounds along with degradation products, additives, and metals. Typically, sulfur concentration of this type is about $0.42\text{--}0.79\text{ wt}\%$ [61,63]. Among all heavy feedstocks, heavy crude oils and petroleum residues typically contain the highest and most structurally complex sulfur fractions [64]. Sulfur content in these materials can range from moderate to very high levels of more than $5\text{ wt}\%$ depending on the origin of oil [65–67].

Generally, sulfur in heavy hydrocarbon feedstocks exists in a wide range of chemical forms that can be broadly classified into inorganic and organic sulfur species, each exhibiting distinct chemical behavior and implications for desulfurization. This distinction is important because the reactivity, distribution, and removal pathways of sulfur strongly depend on its chemical state and association with the hydrocarbon matrix. Therefore, a clear understanding of both categories is essential for interpreting sulfur reactivity in heavy feeds and for designing effective upgrading strategies.

2.1. Inorganic sulfur

Inorganic sulfur in biomass-derived oil.

In biomass-derived oils, inorganic sulfur is generally present in relatively low concentrations compared to organic sulfur [68]; however, its impact on upgrading processes can be disproportionately significant [69]. These inorganic species primarily originate from the mineral content of the biomass feedstock, as well as from external contaminants introduced during collection, handling, or processing. Typical sources include sewage sludge, manure, agricultural residues, and certain industrial or municipal wastes, which may contain sulfur in the form of sulfates (SO_4^{2-}), sulfites (SO_3^{2-}), and metal-associated sulfur compounds [70]. During thermochemical conversion processes such as pyrolysis or hydrothermal liquefaction (HTL), these inorganic sulfur species may partially transform, dissolve into aqueous or oil phases, or remain associated with solid residues, depending on process conditions [71,72].

A particularly important form of inorganic sulfur in biomass-derived oils is dissolved gas of hydrogen sulfide (H_2S), which can be generated in situ during thermal decomposition [73]. In addition, trace amounts of metal sulfides (e.g., Al, Fe, Zn and Ca) may be present either as suspended particulates or as precursors that can form under reducing conditions [74,75]. Although these species are often more reactive and easier to remove than organic sulfur compounds, they pose several operational challenges. For instance, H_2S is highly corrosive and toxic, requiring careful handling and separation [76], while metal-associated sulfur can contribute to fouling, catalyst poisoning, and equipment degradation.

Inorganic sulfur in waste pyrolysis oil.

Inorganic sulfur in waste-derived pyrolysis oils is generally present at lower concentrations than organic sulfur, but it remains highly relevant because of its disproportionate impact on upgrading operations, catalyst stability, and equipment integrity. These sulfur species originate primarily from sulfur-containing additives, fillers, contaminants, and inorganic impurities present in the parent waste materials [77,78]. During pyrolysis, such compounds can undergo thermal decomposition, reduction, and redistribution between gas, liquid, and solid phases, generating volatile sulfur species, sulfur-containing particulates, and sulfur-bearing ash residues. The obtained WTPO consists of thousands of organic compounds, primarily composed of carbon and hydrogen [79,80], which impart a predominantly hydrophobic nature. In contrast, inorganic sulfur species typically display hydrophilic behavior, making them poorly dispersed or difficult to uniformly dilute within the WTPO matrix. However, since zinc oxide is commonly added to the tire manufacturing process to enhance the serviceability and life of the tire [80], there is a potential of some trace amount of ZnS_2 or ZnSO_4 in the WTPO [81].

In waste plastic pyrolysis oils (WPPOs), inorganic sulfur content is typically lower than in WTPO [82], but sulfur contamination may still arise from sulfur-containing polymers, additives, pigments, flame retardants, or mixed-waste contamination during feed preparation [83]. In fact, post-consumer plastic waste streams are rarely compositionally pure, and the presence of multilayer packaging, elastomeric contaminants, or residual food and industrial residues can introduce sulfur-bearing inorganic impurities. During pyrolysis, these contaminants may decompose into H_2S , sulfur oxides precursors, or sulfur-containing ash species, some of which may remain dispersed in the pyrolysis oil. Although sulfur levels in WPPOs are often moderate, their highly variable feedstock composition makes sulfur speciation and removal less predictable compared with more uniform petroleum-derived feeds.

Inorganic sulfur in used lubricating oil.

Similarly, used lubricating oil re-refining streams can contain inorganic sulfur species originating from degraded lubricant additives, engine wear debris, fuel contamination, and accumulated inorganic particulates during service life [84]. Sulfur-containing antiwear and detergent additives, such as zinc dialkyldithiophosphates (ZDDPs), molybdenum dithiocarbamate (MoDTC), can decompose during thermal

processing to form sulfur-bearing inorganic residues, including metal sulfides, sulfates, and ash-forming compounds [85]. These contaminants can persist through pretreatment and pyrolysis or re-refining operations, thereby increasing the complexity of downstream desulfurization.

Inorganic sulfur in heavy oil and residues.

The provenance of sulfur within petroleum remains a fundamental area of geochemical study. While historical research has provided significant insights into the molecular architecture of these compounds [86], the biological origin of this sulfur is complex. Although sulfur is abundant in living cells, primarily within proteins, it is typically lost during post-mortem decomposition. Instead, sulfur isotope analysis indicates that petroleum-based sulfur originates largely from inorganic sulfates [87]. While the geospheric sulfur cycle involves a sophisticated integration of biological and chemical processes, bacterial sulfate reduction (BSR) serves as the main mechanism for converting inorganic sulfur in the sediment into the organic sulfur compounds [88,89]. Hence, inorganic sulfur generally constitutes a smaller fraction of total sulfur than organically bound sulfur species, yet it remains an important contributor to corrosion, catalyst poisoning, and operational complexity during refining. Inorganic sulfur in these feedstocks is typically present as dissolved hydrogen sulfide (H_2S), elemental sulfur, metal sulfides, and sulfur-bearing mineral particulates appear throughout the entire boiling range of crude oil, however, it is more concentrated in the heavy fraction [90,91]. Although their concentration is generally much lower than that of organic sulfur compounds, their high reactivity makes them disproportionately significant in refining operations.

Among inorganic sulfur species, hydrogen sulfide is the most prevalent and industrially important. Sour heavy crudes and residues frequently contain dissolved H_2S , either originating directly from sulfur-rich reservoirs or generated through thermal decomposition and transformation of sulfur-containing compounds during upstream and downstream processing. Hyne reported that under conditions involving steam injection, the concentration of H_2S in produced gases can reach levels as high as 2000 ppm, with lower bounds around 30 ppm [92]. Using in-situ combustion (ISC) method for heavy oil recovery, the H_2S produced was reported to be at an excessive 3000 ppm and could reach 20,000 ppm in severe cases [93–95]. H_2S is highly toxic and corrosive, and its presence promotes sulfide stress cracking, equipment corrosion, and safety hazards throughout refinery operations. Along with diluted H_2S , H_2S accumulated during hydrodesulfurization reactions and recirculated in the hydrogen-rich recycle gas can significantly influence hydrodesulfurization kinetics by participating in sulfiding–desulfiding equilibria on catalyst surfaces and by competitively adsorbing at active sites during hydrotreating [96,97]. Under industrial operating conditions, the in situ generated H_2S is generally the dominant source affecting catalyst performance, whereas dissolved H_2S initially present in the fresh feedstock usually plays a much smaller role.

Heavy oils and residues may also contain metal-associated sulfur species, particularly iron sulfide (FeS), pyrite (FeS_2), and other transition-metal sulfides introduced from reservoir minerals, corrosion products, or contamination during production and storage [98]. These sulfur-bearing solids are especially relevant in vacuum residues, oil sands bitumen, and other solids-rich heavy feedstocks, where entrained mineral matter and asphaltene-associated particulates are more abundant [99]. Such particulate sulfur species can contribute to erosion, fouling, and catalyst bed plugging and deactivation, particularly in fixed-bed hydrotreating systems [67,100].

2.2. Organic sulfur

Organic sulfur in biomass-derived oil.

Organic sulfur in biomass-derived oils originates primarily from sulfur-containing biomolecules inherently present in biomass or from sulfur-rich contaminants associated with residual and waste biomass feedstocks [101]. While clean lignocellulosic biomass generally contains only trace sulfur, sulfur levels can increase substantially in feedstocks

such as sewage sludge, manure, algae, and industrial organic wastes due to the presence of proteins and sulfolipids [102]. During thermochemical conversion processes such as pyrolysis and hydrothermal liquefaction (HTL), sulfur-containing precursors undergo thermal decomposition, cyclization, and recombination reactions, generating a diverse range of sulfur-containing organic compounds that partition into the oil phase [69,103].

Compared with petroleum-derived feedstocks, the molecular distribution of organic sulfur compounds in biomass-derived oils is often more heterogeneous and less systematically characterized. Advanced sulfur-speciation analyses of pyrolysis bio-oils have identified thiols, sulfides, disulfides, thiophenes, benzothiophenic derivatives, and sulfur-containing oxygenated compounds as major sulfur-bearing constituents [104]. In particular, hydrogen sulfide, methanethiol, dimethyl disulfide, and thiophenic compounds have been reported as dominant sulfur-containing species in lignocellulosic pyrolysis oils, indicating that both aliphatic and heterocyclic sulfur structures can be formed during biomass thermochemical conversion [73]. In HTL biocrudes derived from protein- and sulfur-rich feedstocks, sulfur may additionally be incorporated into larger heteroatom-rich aromatic and polar molecules through condensation under harsh conditions [105].

Although the total sulfur content of biomass-derived oils is generally lower than that of heavy petroleum residues or pyrolysis tire oil, the removal of organic sulfur from these feeds remains challenging because sulfur compounds are embedded within chemically unstable matrices rich in oxygenates, nitrogen compounds, and reactive polar species [106–108]. Such compositional complexity promotes competitive adsorption, polymerization, and coke formation during catalytic upgrading, thereby reducing sulfur removal efficiency and accelerating catalyst deactivation. Furthermore, sulfur-containing compounds in biomass-derived oils often coexist with oxygen- and nitrogen-containing heterocycles, making selective hydrodesulfurization difficult under conventional hydrotreating conditions. As highlighted in previous upgrading studies, the feedstock-dependent nature of HTL and pyrolysis biocrudes results in markedly different hydrotreating behavior, emphasizing the need for improved sulfur speciation and feed characterization prior to catalyst and process design [109].

Despite increasing interest in biomass-derived liquid fuels, the chemistry of organic sulfur in these feedstocks remains less understood than that of petroleum sulfur compounds. More comprehensive molecular-level characterization is therefore needed to establish structure–reactivity relationships for sulfur-containing species in biomass-derived oils and to enable the development of targeted upgrading strategies for renewable heavy-feed integration into refinery hydroprocessing infrastructure.

Organic sulfur in waste pyrolysis oil.

Organic sulfur constitutes the dominant sulfur fraction in most waste-derived pyrolysis oils and is a major obstacle to their direct utilization as transportation or refinery fuels. Unlike inorganic sulfur species, which are often present as volatile H_2S or sulfur-bearing particulates, organic sulfur compounds are chemically incorporated into the hydrocarbon matrix and therefore require catalytic bond cleavage for effective removal [110]. Their concentration and molecular distribution depend strongly on the composition of the original waste feedstock and the thermal condition of the pyrolysis process [110,111]. As a result, sulfur speciation in waste pyrolysis oils is highly heterogeneous and varies considerably among tire-derived, plastic-derived, and lubricant-derived pyrolysis streams.

Among waste pyrolysis oils, WTPO contains the highest concentration and broadest distribution of organic sulfur compounds due to the sulfur vulcanization chemistry used in tire manufacturing [112]. Investigations into the chemical profile of tire pyrolysis oil have frequently highlighted the prevalence of sulfurous compounds. For instance, Williams and Bottrill identified numerous sulfur-containing polycyclic aromatic hydrocarbons (PAHs) in these oils [113], a finding further supported by Pakdel et al., who confirmed the existence of thiophene

derivatives in the resulting liquid fractions [114]. The formation of these complex hydrocarbons is often attributed to Diels–Alder reactions between sulfur species and polycyclic aromatic structures [113]. Furthermore, research by Diez et al. demonstrated that increasing the final pyrolysis temperature leads to a greater release of sulfur into both the gas and liquid outputs, while notably finding that chlorine levels remained insignificant across different thermal conditions [115]. Numerous sulfur-speciation studies have shown that sulfur in WTPO is predominantly present as thiophenes, benzothiophenes, dibenzothiophenes, and their alkylated derivatives, with benzothiophenic compounds often reported as the dominant sulfur class in diesel-range fractions [116,117]. The prevalence of these aromatic sulfur heterocycles contributes to the refractory nature of WTPO during hydrodesulfurization, as their aromatic stabilization and steric hindrance reduce susceptibility to C–S bond cleavage.

In waste plastic pyrolysis oils (WPPO), organic sulfur content is generally lower than in WTPO because the major commodity plastics (e. g., polyethylene and polypropylene) contain little intrinsic sulfur. Nevertheless, sulfur-containing organic compounds may still be present when mixed plastic waste includes sulfur-bearing additives, elastomeric contaminants, multilayer packaging, or contaminated post-consumer residues. Under such circumstances, sulfur introduced from feed impurities may be converted during pyrolysis into light sulfides, thiophenic compounds, and substituted aromatic sulfur species [62], although the exact sulfur distribution is highly feedstock-dependent and less systematically characterized than for tire pyrolysis oils. Previous studies on mixed-waste pyrolysis fuels have reported that sulfur concentrations in plastic-derived oils can vary widely depending on sorting efficiency and contamination level, highlighting the importance of feed pretreatment and quality control [61].

Organic sulfur in lubricating oil.

Similarly, used lubricating or re-refined oils may contain organic sulfur compounds originating from degraded lubricant additives, sulfur-containing antiwear agents, and contamination accumulated during engine service [118–120]. In addition, contamination from fuel dilution and combustion byproducts may further enrich the organosulfur content of waste lubricant-derived oils [84]. The specific structure of organic sulfur compounds in used lube oil is not yet well understood. Al-Lal et al. [61] conducted a GC-FPD Chromatogram study and suggested that the main sulfurous compounds in this type of oil were derived from dimethylsulfide, benzothiophenes and dibenzothiophenes.

Organic sulfur in heavy oil and petroleum residues.

Organic sulfur is the predominant form of sulfur in heavy crude oils and petroleum residues, accounting for the vast majority of total sulfur in these feedstocks. Unlike lighter petroleum fractions, where sulfur may be distributed among relatively simple sulfides and low-molecular-weight thiophenes, sulfur in heavy oils is concentrated in highly substituted, condensed, and aromatic organosulfur structures (Table 1) [121]. Numerous studies have shown that sulfur content generally increases with boiling range and molecular weight during crude oil fractionation, leading to sulfur enrichment in atmospheric residues, vacuum residues, and asphaltene-rich fractions [64,122–124]. Previous

petroleum characterization studies have consistently reported that sulfur in heavy oils may range from moderate to several weight percent, depending on crude origin [125,126].

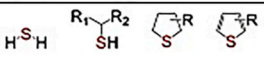
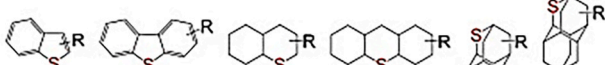
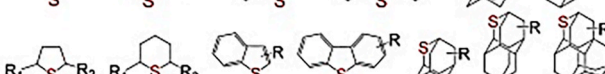
The dominant organic sulfur compounds in heavy petroleum feeds are generally thiophenic species, including thiophenes, benzothiophenes (BTs), dibenzothiophenes (DBTs), benzonaphthothiophenes, and their alkylated derivatives. Among these, dibenzothiophenic compounds and alkyl-substituted DBTs are especially important because they represent the most refractory sulfur species encountered during deep hydrodesulfurization [127,128]. In particular, compounds such as 4,6-dimethyldibenzothiophene are widely recognized as model refractory sulfur compounds due to steric hindrance around the sulfur atom, which limits catalyst access and reduces desulfurization rates [129–132]. Comprehensive sulfur-speciation studies using GC–MS, GC × GC, and high-resolution mass spectrometry have repeatedly identified alkylated DBTs and larger fused-ring thiophenic species as dominant sulfur classes in vacuum gas oils and residue fractions [128].

In the heaviest fractions of crude oil, particularly resins and asphaltenes, sulfur is often incorporated into large polyaromatic molecular architectures containing multiple fused aromatic rings and heteroatoms [133]. These macromolecular sulfur species are believed to include sulfur embedded within condensed aromatic sheets, bridging structures, and heteroatom-rich polar domains [134,135]. Their exact molecular structures remain difficult to fully resolve because of the extreme compositional complexity of heavy petroleum fractions; however, spectroscopic and high-resolution mass spectrometric analyses indicate that sulfur in asphaltenes is predominantly present in aromatic heterocyclic forms rather than aliphatic sulfides or mercaptans [136]. The incorporation of sulfur into such large aromatic frameworks significantly reduces molecular accessibility and contributes to the poor reactivity of heavy residual sulfur under conventional desulfurization processes.

2.3. Sulfur removal challenges

As discussed, sulfur exists as both inorganic and organic species, but these two categories differ markedly in abundance, chemical nature, reactivity, and impact on upgrading performance. Inorganic sulfur—typically present as dissolved hydrogen sulfide (H₂S), elemental sulfur, metal sulfides, sulfates, or sulfur-bearing particulates—generally constitutes a minor fraction of total sulfur but can strongly influence corrosion, catalyst fouling, and process safety due to its high reactivity and mobility. In contrast, organic sulfur overwhelmingly dominates the sulfur inventory of most heavy feeds, particularly in heavy crude oils, petroleum residues, and pyrolysis-derived oils, where sulfur is chemically incorporated into hydrocarbon molecules such as thiols, sulfides, thiophenes, benzothiophenes, dibenzothiophenes, and larger condensed heteroaromatic structures. Unlike inorganic sulfur, which is often readily removed through phase separation, stripping, or reactive scavenging [137,138], organic sulfur requires catalytic bond cleavage—typically via hydrodesulfurization—for effective removal [139]. Furthermore, aromatic and sterically hindered organosulfur

Table 1
Typical sulfur compounds in different crude oil fractions [121].

Distillation Fractions	Structures of main OSCs	Carbon Number
Naphtha		< C ₁₀
Middle Distillate		C ₁₀ –C ₂₅
Residual		C ₂₅ –C ₄₀

species exhibit substantially lower desulfurization reactivity than inorganic sulfur species, particularly when embedded in resin- or asphaltene-rich matrices [140]. Consequently, although inorganic sulfur is important from an operational and corrosion perspective, organic sulfur remains the major challenge in deep desulfurization of heavy feedstocks due to its abundance, structural diversity, and refractory nature. The comparison of inorganic and organic sulfur in heavy hydrocarbon feedstocks is presented in Table 2.

Compliance with stringent sulfur regulations requires the application of various desulfurization techniques, such as adsorptive (ADS), biological (BDS), extractive (EDS), oxidative (ODS), and hydrodesulfurization (HDS). The advantages and limitations of each method are discussed in the section 3. Among them, HDS is predominantly utilized in industrial refineries due to its superior efficiency when treating heavy or heavily contaminated feedstocks [24,141,142]. Despite being the industry standard, HDS remains constrained by significant operational barriers, including substantial energy requirements, the high cost of hydrogen consumption, and the recalcitrant nature of aromatic thiophenic compounds [143,144]. Furthermore, as illustrated in Fig. 2, the effectiveness of HDS is inversely correlated with the complexity of these organic sulfur structures; specifically, reactivity diminishes as the size of the aromatic rings increases or as the degree of alkyl substitution on the ring rises [128].

The predominance of refractory aromatic sulfur compounds in heavy feedstock is one of the principal reasons why these feedstocks require severe hydroprocessing conditions, advanced catalyst formulations, and multistage upgrading strategies for deep desulfurization. Furthermore, sulfur removal is complicated by the simultaneous presence of nitrogen compounds, metals, resins, and asphaltenes, which compete for catalyst active sites and promote deactivation. Therefore, understanding the molecular nature and distribution of organic sulfur species in heavy feeds is essential for catalyst design, kinetic modeling, and the development of predictive desulfurization strategies for refinery-relevant heavy feed upgrading.

Besides, in industrial hydrotreating of heavy petroleum fractions and alternative feedstocks, hydrodesulfurization (HDS) rarely occurs as an isolated reaction but proceeds simultaneously with hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). The coexistence of sulfur-, nitrogen-, and oxygen-containing compounds creates strong competition for catalyst active sites and available hydrogen,

making sulfur removal highly dependent on the overall feed composition [24,145]. Among these heteroatoms, nitrogen compounds are recognized as the most potent inhibitors of HDS because basic nitrogen-containing species, such as quinolines and carbazoles, adsorb much more strongly than organosulfur compounds on the coordinatively unsaturated sites (CUS) of sulfided CoMo and NiMo catalysts [146–148]. This competitive adsorption suppresses both hydrogen activation and the adsorption of refractory sulfur compounds, particularly alkyl-substituted dibenzothiophenes, thereby significantly reducing HDS activity under ultra-deep desulfurization conditions. Kinetic investigations by Ho and Qiao demonstrated that nitrogen species preferentially poison the hydrogenation (HYD) function of sulfided catalysts, resulting in much stronger inhibition of sterically hindered sulfur compounds than unsubstituted dibenzothiophene [149]. Likewise, comprehensive reviews on petroleum HDN have emphasized that efficient nitrogen removal is often a prerequisite for achieving deep sulfur removal because HDN liberates active catalytic sites while reducing ammonia-related inhibition during hydrotreating [150,151].

Unlike petroleum hydrotreating, where hydrodesulfurization is the principal upgrading objective, catalytic upgrading of biomass-derived pyrolysis oils and hydrothermal liquefaction (HTL) biocrudes primarily aim to remove oxygenated and highly reactive compounds through hydrodeoxygenation (HDO) in order to stabilize the oil, improve fuel quality, and produce drop-in refinery feedstocks [152,153]. Consequently, sulfur removal is generally a secondary objective for most biomass-derived feeds, although it becomes increasingly important for sulfur-rich biomass or during co-processing with petroleum feedstocks. The interaction between HDS and HDO becomes increasingly important during the co-processing of renewable feedstocks, such as biomass-derived oils and waste pyrolysis oils, together with petroleum fractions. Oxygenated compounds compete with sulfur-containing molecules for hydrogen and catalytic sites while simultaneously generating water, which can modify catalyst surface chemistry and influence the stability of the sulfided active phase [154]. Consequently, catalyst formulations optimized for conventional petroleum HDS may exhibit altered activity and selectivity during mixed HDS–HDO operation. In addition, HDO generally requires substantial hydrogen consumption to remove oxygen as H₂O [155,156], thereby reducing hydrogen availability for sulfur hydrogenolysis and aromatic hydrogenation. These interactions highlight that sulfur conversion in complex feeds cannot be interpreted solely as a function of sulfur concentration or catalyst activity, but rather as the combined outcome of multiple concurrent hydroprocessing reactions competing for limited catalytic active sites.

In commercial hydroprocessing units, catalyst selection is often tailored according to reactor configuration and process objectives [157,158]. For example, catalyst grading or stacked catalyst beds may combine catalysts with different hydrogenation, hydrodesulfurization, and hydrodenitrogenation functionalities, while residue hydroprocessing commonly integrates hydrotreating catalysts with downstream hydrocracking catalysts to achieve simultaneous heteroatom removal, aromatic saturation, and boiling-range reduction [159]. Consequently, operating severity reflects the combined objectives of sulfur removal, nitrogen removal, hydroconversion, and product quality improvement rather than hydrodesulfurization alone [160].

Beyond their mechanistic importance, sulfur speciation constitutes one of the most informative feature groups used in machine-learning-assisted hydrodesulfurization. Descriptors such as sulfur class distribution, total sulfur concentration, aromaticity, and heteroatom composition are increasingly employed as model inputs for catalyst screening, sulfur conversion prediction, catalyst deactivation analysis, and process optimization. Their role in feature engineering is discussed in Section 7.

3. Comparison of desulfurization technologies

Although hydrodesulfurization (HDS) remains the dominant commercial technology for sulfur removal in petroleum refineries, several

Table 2
Comparison of Inorganic and Organic Sulfur in Heavy Hydrocarbon Feedstocks.

Aspect	Inorganic Sulfur	Organic Sulfur
Typical Forms	H ₂ S, elemental sulfur, sulfates, sulfides, metal sulfides	Thiols, sulfides, disulfides, thiophenes, BTs, DBTs, alkylated DBTs
Primary Origin	Mineral impurities, sulfur decomposition, reservoir gases, additives/contaminants	Native petroleum molecules, sulfur-containing biomass/waste precursors, pyrolytic recombination
Relative Abundance	Minor fraction of total sulfur	Dominant sulfur forms in most heavy feeds
Chemical Association	Free/dissolved, suspended solids, inorganic particulates	Covalently bound within hydrocarbon matrix
Reactivity	High; readily transformed/removed	Lower; often refractory and sterically hindered
Major Operational Concerns	Corrosion, toxicity, catalyst fouling, plugging	Catalyst deactivation, severe HDS conditions, hydrogen consumption
Removal Method	Stripping, solvent extraction and adsorption etc.,	Adsorptive desulfurization, biodesulfurization, extractive desulfurization, oxidative desulfurization and hydrodesulfurization
Importance in Deep Desulfurization	Secondary but operationally significant	Primary limiting factor

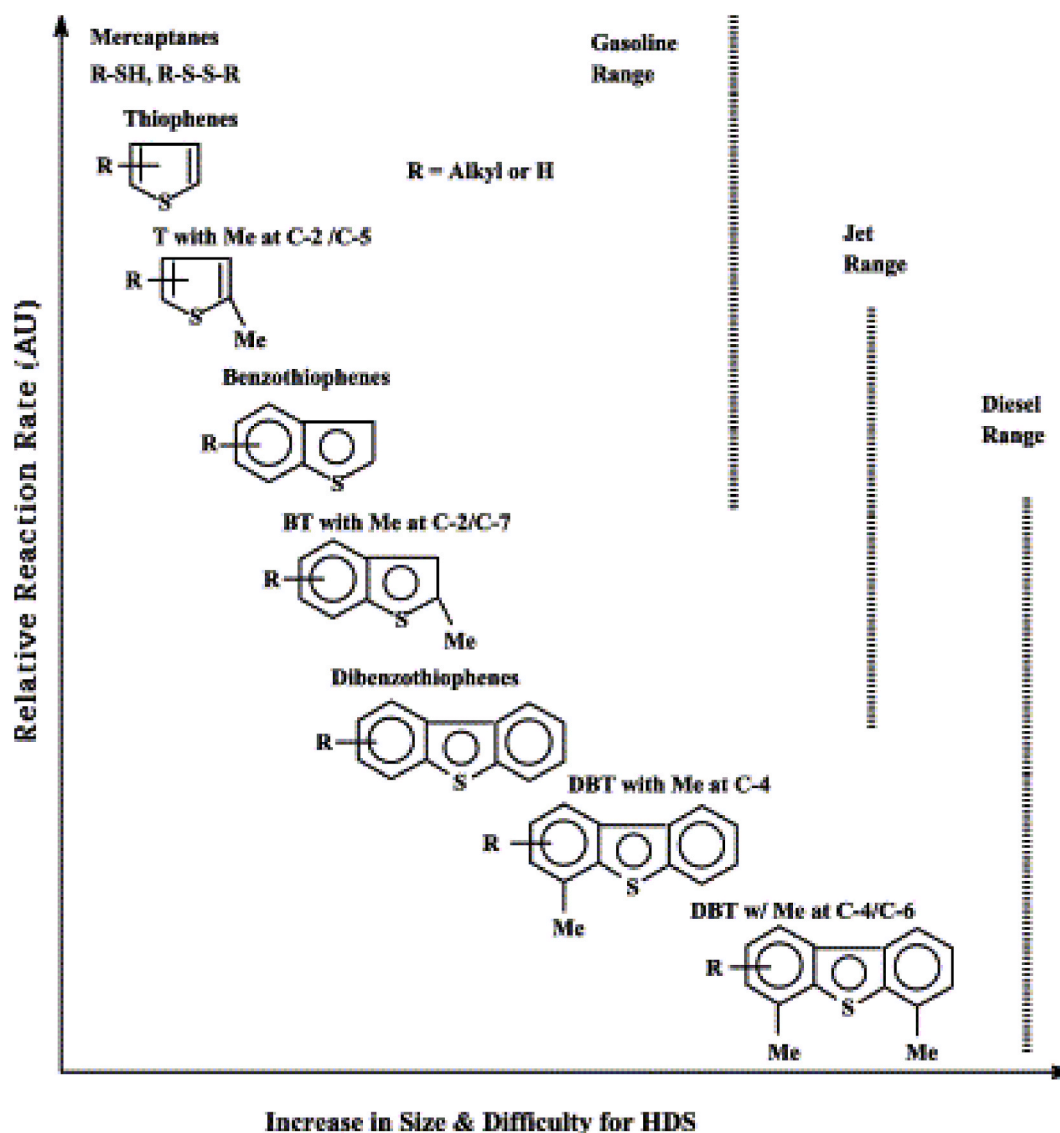


Fig. 2. The dependence of HDS reactivity on the structure of different organic sulfur compounds [128].

complementary desulfurization technologies—including oxidative desulfurization (ODS) [161,162], adsorptive desulfurization (ADS) [163], extractive desulfurization (EDS) [164], and biodesulfurization (BDS) [165]—have also been developed. Each technology exhibits distinct advantages and limitations with respect to sulfur removal efficiency, operating conditions, scalability, and industrial applicability [166].

HDS is currently the only mature technology capable of treating large refinery throughput while simultaneously removing sulfur, nitrogen, oxygen, and, to some extent, metallic contaminants [167]. However, its operation requires elevated temperatures (typically 300–400 °C), high hydrogen pressures (3–15 MPa), and sulfided transition-metal catalysts, resulting in considerable hydrogen consumption and operating costs [139,168]. Furthermore, sterically hindered sulfur compounds, particularly 4,6-dimethyldibenzothiophene, remain difficult to convert completely because of diffusion limitations and steric effects around the sulfur atom. Compared with HDS, the main concerns associated with these alternative desulfurization techniques are lower liquid yields due to hydrocarbon losses during solvent extraction [169], the generation of sulfur-rich by-products such as sulfonic waste and sulfone-laden solvents that require additional treatment [169,170], and—particularly for biodesulfurization—slower overall

reaction kinetics that limit throughput [171].

Alternative desulfurization technologies have therefore attracted increasing attention as complementary rather than replacement processes. ODS oxidizes organosulfur compounds into highly polar sulfones that can subsequently be removed by extraction or adsorption under relatively mild conditions [172–174]. This approach is particularly effective for refractory sulfur compounds and generally operates without hydrogen; however, it requires oxidizing agents, catalyst regeneration, and downstream separation of oxidation products [175–177]. ADS removes sulfur compounds through selective adsorption on porous materials such as activated carbon, zeolites, metal oxides, or metal–organic frameworks (MOFs), offering operation at ambient or moderately elevated conditions with minimal hydrogen consumption [178]. Nevertheless, adsorption capacity, adsorbent regeneration, and competitive adsorption by aromatic hydrocarbons remain significant challenges for large-scale implementation [179]. Similarly, EDS employs selective solvents, including ionic liquids and deep eutectic solvents, to extract sulfur-containing molecules from fuel [180]. Although EDS operates under mild conditions and offers relatively simple process integration, solvent recovery, extraction efficiency, and operating costs continue to limit widespread industrial deployment [181]. BDS utilizes sulfur-metabolizing microorganisms under environmentally benign

conditions and exhibits excellent selectivity toward refractory sulfur compounds while preserving fuel hydrocarbon structures [182,183]. However, its slow reaction kinetics, microbial stability, and scale-up challenges currently restrict its industrial application [165,184]. A critical comparison of major desulfurization technologies is shown in Table 3.

Consequently, rather than competing directly with HDS, these technologies are increasingly viewed as complementary polishing processes capable of achieving ultra-deep desulfurization after conventional hydrotreating. Hybrid strategies, such as HDS-ODS [185,186] or HDS-ADS [187], have attracted growing attention because they combine the high throughput and industrial maturity of HDS with the superior removal efficiency of alternative methods toward refractory sulfur species. Such integrated approaches are particularly attractive for processing increasingly complex heavy feedstocks, biomass-derived oils, and waste-derived pyrolysis oils, where sulfur speciation, catalyst deactivation, and hydrogen consumption become increasingly important.

4. Hydrodesulfurization mechanisms

Hydrodesulfurization is a key catalytic process for removing sulfur from petroleum and alternative heavy feedstocks through hydrogen-assisted cleavage of C–S bonds. Despite decades of industrial application and extensive research, the HDS mechanism remains only known as a complex interplay of surface reactions, adsorption phenomena, and catalyst structural dynamics. The overall process involves adsorption of sulfur-containing molecules onto active sites, followed by hydrogenation and/or direct sulfur removal pathways, ultimately producing hydrogen sulfide (H₂S) and desulfurized hydrocarbons. The efficiency and selectivity of these pathways are strongly governed by the nature of the catalyst, which determines how reactant molecules are adsorbed, activated, and transformed. Therefore, a fundamental understanding of the structure and function of these active sites is essential for elucidating HDS reaction mechanisms and for designing more effective catalysts.

4.1. The structure of active site

The active phase of industrial HDS catalysts is typically based on transition metal sulfides, most commonly cobalt- or nickel-promoted molybdenum disulfide supported on high-surface-area alumina (CoMo/Al₂O₃ or NiMo/Al₂O₃) [188–190]. Extensive experimental and theoretical studies have established that the catalytically active phase is not the bulk metal oxide precursor, but rather the sulfided form, where molybdenum disulfide (MoS₂) forms layered structures composed of S–Mo–S slabs [191]. These slabs expose different types of edge and basal

plane sites, among which the edge sites are widely recognized as the primary active centers for hydrodesulfurization reactions.

The most widely used model for HDS active site was proposed by Daage M. and Chianelli R.R. [191] in 1994, as presented in Fig. 3a. Specifically, the catalyst particle is assumed to be a stacked disc with several layers. The upper and lower discs correspond to the rim sites, while the discs positioned between them represent the edge sites. The basal plane does not have any catalytic activity. Sulfur hydrogenolysis takes place at both rim and edge sites, but reactant hydrogenation occurs solely at the rim sites [192]. The reason for this activity difference is due to the steric hindrance effect where the coordination formed as six-member rings inside cannot absorb any reagent with the η^6 coordination [194]. Therefore, an MoS₂ catalyst with the smallest lateral size and a stacking layer number of 2 exposes the greatest number of edge sites on the top and bottom S–Mo–S atomic layers, resulting in the most favorable catalytic activity for PAH hydrogenation [195].

The Rim–Edge model has its drawbacks, including challenges in accounting for catalyst behavior in systems involving multiple metals [196]. Moreover, because the model emphasizes macroscopic characteristics, it may not adequately reflect how atomic-scale variations in catalyst structure influence performance [197]. J. V. Lauritsen and co-workers developed a more recent model that identifies different catalytic active sites on the surface through atomic-level imaging [198]. In this framework (Fig. 3b), the CUS (corner) sites [193]—created by missing sulfur atoms at edge or corner positions—behave as Lewis acid sites that attract reactants. In contrast, Brim sites do not depend on the presence of unsaturated sulfur and instead exhibit metallic behavior, enabling formation of an R–S thiolate intermediate. This intermediate is highly reactive and can be rapidly hydrogenated. Smaller sulfur-containing molecules such as thiophene and benzothiophenes tend to react mainly at Brim sites, whereas larger sulfide species involve cooperation between Brim and CUS sites: hydrogenation is associated with Brim, while C–S bond cleavage is linked to CUS activity [199].

Atomic-scale investigations have significantly advanced the understanding of promoter site formation in conventional sulfide hydro-treating catalysts. Using scanning tunneling microscopy (STM) combined with density functional theory (DFT), Lauritsen et al. [200] demonstrated that Co and Ni promoter atoms preferentially substitute Mo atoms at the edges of MoS₂ nanoclusters, forming the well-known CoMoS and NiMoS active phases rather than existing as separate sulfide particles. These promoter atoms modify the local sulfur coverage and electronic structure at the edge sites, generating metallic edge states that facilitate hydrogen activation, sulfur vacancy formation, and the adsorption and transformation of sulfur-containing molecules, thereby substantially enhancing hydrodesulfurization activity. The distinct edge structures of CoMoS and NiMoS also contribute to their different

Table 3
Critical comparison of major desulfurization technologies.

Tech-nology	Operating conditions	Sulfur removal efficiency	Industrial maturity	Advantages	Major limitations	Typical application
HDS	High temperature (300–400 °C), high H ₂ pressure (3–15 MPa)	Excellent for most sulfur compounds; limited for refractory DBTs	Commercial	Large throughput; simultaneous HDS/HDN/HDO; refinery integration.	High hydrogen consumption, catalyst deactivation, refractory sulfur compounds.	Primary refinery desulfurization.
ODS	Mild temperature (<100 °C), atmospheric pressure	Excellent for refractory sulfur compounds	Pilot/Demonstration	No hydrogen required; Removes organosulfur compounds without destroying the carbon skeletal backbone. Mild operation.	Selectivity of reaction, safety concerns associated with the handling and storage of oxidizing agents, expensive cost of equipment, separation cost, installation of facility for generation of oxidant sources.	Post-HDS polishing.
ADS	Mild conditions	Moderate–High	Pilot	Low energy consumption; simple operation.	Limited adsorption capacity; adsorbent regeneration.	Ultra-low sulfur polishing.
EDS	Ambient–moderate temperature	Moderate	Pilot	Mild operation; good selectivity.	Solvent recovery; multiple extraction stages.	Complementary sulfur removal.
BDS	Ambient conditions	High selectivity	Laboratory/Pilot	Environmentally friendly; preserves fuel quality.	Slow kinetics; microbial stability; difficult scale-up.	Specialized deep desulfurization.

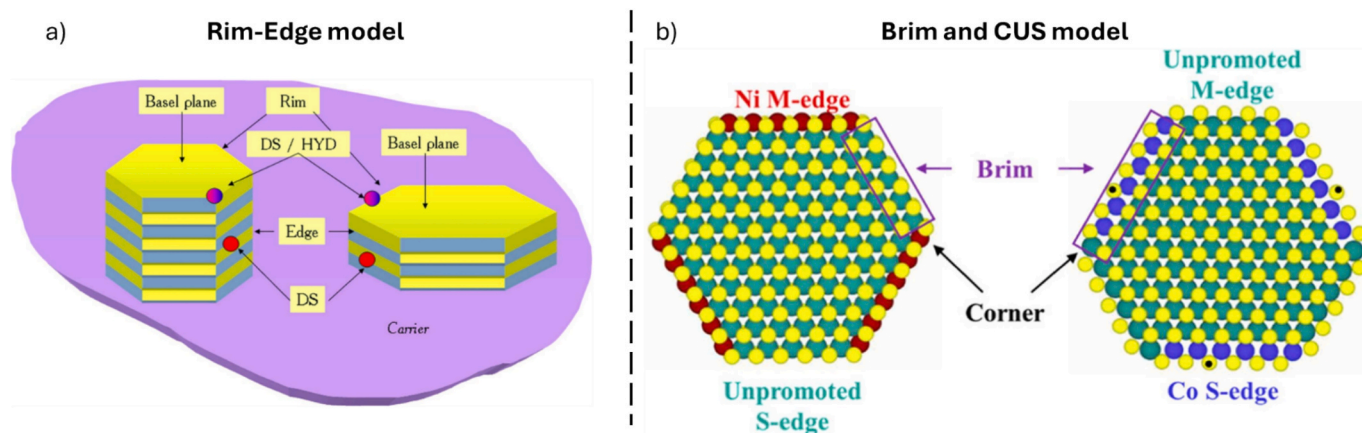


Fig. 3. The Rim-Edge (a) [192] and Brim-CUS [193] models elucidating HDS active sites.

hydrogenation and direct desulfurization selectivities. Similar promoter-site concepts have been proposed for Ni- or Co-promoted WS₂ catalysts (NiWS and CoWS), where promoter atoms occupy edge sites of WS₂ slabs and modify the electronic properties of the active edges, although tungsten-based catalysts are more frequently employed in applications requiring enhanced hydrogenation and hydrodenitrogenation than in conventional hydrodesulfurization [201,202].

4.2. HDS over aliphatic sulfur

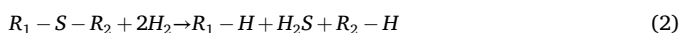
Aliphatic sulfur compounds represent the most reactive class of sulfur species in hydrodesulfurization and are generally removed under relatively mild hydrotreating conditions compared with aromatic sulfur compounds [128,203]. These species include thiols (mercaptans), sulfides, and disulfides, which are commonly found in lighter petroleum fractions and, to a lesser extent, in certain waste- and biomass-derived oils. Their relatively high reactivity is primarily attributed to the weaker C–S bonds and the absence of aromatic stabilization, making them more susceptible to hydrogenolysis over sulfided transition metal catalysts. As a result, aliphatic sulfur compounds are typically the first to be converted during hydrotreating processes and rarely persist in deeply hydrotreated products [204,205].

The hydrodesulfurization of aliphatic sulfur compounds proceeds predominantly via direct hydrogenolysis pathways, in which the C–S bond is cleaved with the assistance of activated hydrogen species on the catalyst surface. For thiols (R–SH), desulfurization typically occurs through adsorption at coordinatively unsaturated sites, followed by S–H bond activation and subsequent C–S bond cleavage to produce the corresponding hydrocarbon (R–H) and hydrogen sulfide (H₂S). Similarly, sulfides (R–S–R') undergo cleavage of the C–S bond to yield two hydrocarbon fragments, while disulfides (R–S–S–R') are readily reduced to thiols or directly converted to hydrocarbons and H₂S under hydrogen-rich conditions. These reactions (Eqs. (1)–(3)) are generally fast and exhibit low activation barriers compared with those of thiophenic compounds.

Thiols:



Sulfides:



Disulfides:



Despite their relative ease of removal, the presence of aliphatic sulfur compounds can still influence overall HDS performance, particularly in

complex feedstocks. For example, the rapid conversion of thiols and sulfides can lead to early generation of H₂S which reduces the H₂/H₂S ratio in the recycled gas and thereby results in decreased overall HDS efficiency [206]. Moreover, H₂S may also participate in secondary reactions under specific hydroprocessing conditions. In selective hydrotreating of cracked gasoline and other olefin-rich feedstocks, H₂S can react with olefins to form alkyl mercaptans, thereby regenerating sulfur-containing species and complicating the achievement of ultra-low sulfur specifications [207,208]. Consequently, careful control of reaction severity and H₂S partial pressure is required to minimize mercaptan reformation while preserving desirable olefin content. Nevertheless, under typical refining conditions, aliphatic sulfur compounds are efficiently removed in the initial stages of hydrotreating, and their contribution to residual sulfur in final products is generally minimal.

4.3. HDS over thiophenic sulfur

Thiophenic sulfur compounds represent the most important and challenging class of sulfur species in hydrodesulfurization, particularly in heavy petroleum fractions and waste-derived oils. These compounds include thiophene, benzothiophene (BT), dibenzothiophene (DBT), and their alkylated derivatives, which are characterized by sulfur atoms incorporated into aromatic heterocyclic ring systems. The aromatic stabilization of these structures significantly increases the strength of the C–S bond and reduces their reactivity toward direct hydrogenolysis [128]. As a result, thiophenic sulfur compounds are considerably more refractory than aliphatic sulfur species and are often responsible for the residual sulfur content in hydrotreated fuels.

The hydrodesulfurization of thiophenic compounds proceeds through two primary reaction pathways: the direct desulfurization (DDS) pathway and the hydrogenation (HYD) pathway. In the DDS pathway, the sulfur atom is removed directly from the aromatic ring without prior hydrogenation, producing desulfurized aromatic hydrocarbons such as biphenyl (from DBT) and hydrogen sulfide [131,209]. This pathway typically occurs on coordinatively unsaturated sites located at the edges of sulfided catalysts, promoting DDS-pathway selectivity at high S-edge/Mo-edge ratios [210,211]. In contrast, the HYD pathway involves initial hydrogenation of one or more aromatic rings to form partially or fully saturated intermediates, followed by C–S bond cleavage to produce cycloalkane derivatives and H₂S. This pathway is generally associated with brim or hydrogenation sites [199]. Among the thiophenic compounds, the sulfur removal efficiency follows the order of thiophene > benzothiophenes > dibenzothiophene > polycyclic aromatic thiophene. Generally, aromaticity and steric hindrance effect prevent adsorption and activation over the catalytic active site [128].

The relative contribution of the direct desulfurization (DDS) and hydrogenation (HYD) pathways in hydrodesulfurization is

fundamentally controlled by the molecular structure of thiophenic sulfur compounds, particularly steric hindrance and aromaticity. For relatively simple molecules such as thiophene, both HDS and HYD occur in parallel. An investigation of HDS of thiophene on the Mo_3S_9 model catalyst was performed [212], and the free-energy barriers for each reaction pathway are presented in Fig. 4. The most favorable route was the pathway with the lowest activation free energy, 89.6 kJ mol^{-1} , which yields butadiene as the major product. Overall, these results suggest that intramolecular elimination is the dominant mechanism in the HDS of thiophene.

With increasing aromaticity and molecular size, the HDS of benzo-thiophenes required an HDY step prior to C–S bond cleavage. In particular, it was necessary to first convert it into DHBT before subsequent removal reactions. The potential reaction steps and corresponding activation energies for the HDS of BT over Brim and CUS sites are illustrated in Fig. 5.

The DBT molecule, which contains two benzene rings, exhibits relatively low HDS activity [213]. Recent work indicates that sulfur removal in DBT can proceed through two distinct pathways: DDS and HDY [214]. On CoMoS-based catalysts, HDS occurs at both CUS and Brim sites [199]. Hydrogenation is favored at Brim sites, with an activation energy of $32.20 \text{ kcal mol}^{-1}$, whereas C–S bond cleavage is more favorable at CUS sites, with an activation energy of $34.61 \text{ kcal mol}^{-1}$. It is also worth noting that under identical operating conditions (4 MPa H_2 and 650 K), the activation energy for HDY increases in the order of thiophene < BT < DBT. In contrast, the activation energy for DDS does not follow the same sequence; it follows thiophene < DBT $\approx$ BT. The reduced ease of HDY for high-aromaticity sulfur compounds confirmed the steric hindrance effect, which limits their adsorption on the active sites [215]. By comparison, DDS appears to be less sensitive to this effect. The proposed HDS reaction schemes for DBT conversion via Brim and CUS sites are shown in Fig. 6 [199].

For highly refractory compounds such as 4,6-dimethyldibenzothiophene, the presence of adjacent methyl groups effectively blocks direct interaction between the sulfur atom and catalytic active sites, making DDS kinetically unfavorable. Instead, these molecules preferentially undergo π -type adsorption on the aromatic ring, followed by partial hydrogenation that reduces molecular planarity and steric constraints, thereby enabling subsequent C–S bond cleavage [216]. As a result, the HYD pathway becomes dominant for sterically hindered and highly condensed thiophenic species (Fig. 7). Additionally, increasing aromatic ring condensation further stabilizes the C–S bond and enhances π -interactions with the catalyst surface, reinforcing the dependence on

hydrogenation-assisted desulfurization [199]. Overall, these structure–reactivity relationships highlight that the transition from DDS- to HYD-dominated mechanisms is driven by increasing steric hindrance and aromatic complexity, which are key characteristics of refractory sulfur compounds in heavy feedstocks.

Although the intrinsic structure of sulfur compounds dominantly determines their preferred hydrodesulfurization pathway, the actual extent to which the DDS and HYD mechanisms contribute under practical conditions is also highly sensitive to operating parameters. Variables such as temperature, hydrogen pressure, liquid hourly space velocity (LHSV), hydrogen-to-oil ratio, and hydrogen sulfide partial pressure can significantly alter adsorption equilibria, reaction kinetics, catalyst sulfidity, and the availability of active sites. In the next section, the effect of operating parameters on HDS efficiency is discussed.

5. Effect of operating parameters on HDS efficiency

The efficiency of hydrodesulfurization (HDS) is governed not only by sulfur speciation, but also by the operating conditions under which the reaction is conducted. Because HDS involves coupled phenomena including liquid–gas mass transfer, adsorption of sulfur compounds, hydrogen activation, C–S bond cleavage, hydrogenation, and catalyst surface regeneration, process variables can significantly alter sulfur conversion, selectivity between the direct desulfurization (DDS) and hydrogenation (HYD) pathways, hydrogen consumption, and catalyst stability. Industrial hydrotreating units therefore rely on careful optimization of operating parameters to achieve target sulfur specifications while maintaining throughput and minimizing cost. Previous studies consistently report that temperature, hydrogen pressure, liquid hourly space velocity (LHSV), and feed composition are among the most influential variables affecting HDS performance (Table 4).

It is important to distinguish the intrinsic kinetic effects of operating parameters from indirect effects associated with transport phenomena and catalyst deactivation. Temperature primarily influences the intrinsic kinetics of hydrodesulfurization by increasing the reaction rates of C–S bond cleavage and hydrogenation pathways in accordance with established HDS kinetic models [227,228]. In contrast, hydrogen pressure mainly affects hydrogen availability by increasing hydrogen partial pressure and hydrogen solubility in the liquid phase, thereby improving hydrogen transfer to the catalyst surface, enhancing hydrogenation reactions, and suppressing coke formation and catalyst deactivation [229–231]. Likewise, although decreasing the liquid hourly space velocity (LHSV) generally increases reactant residence time and promotes

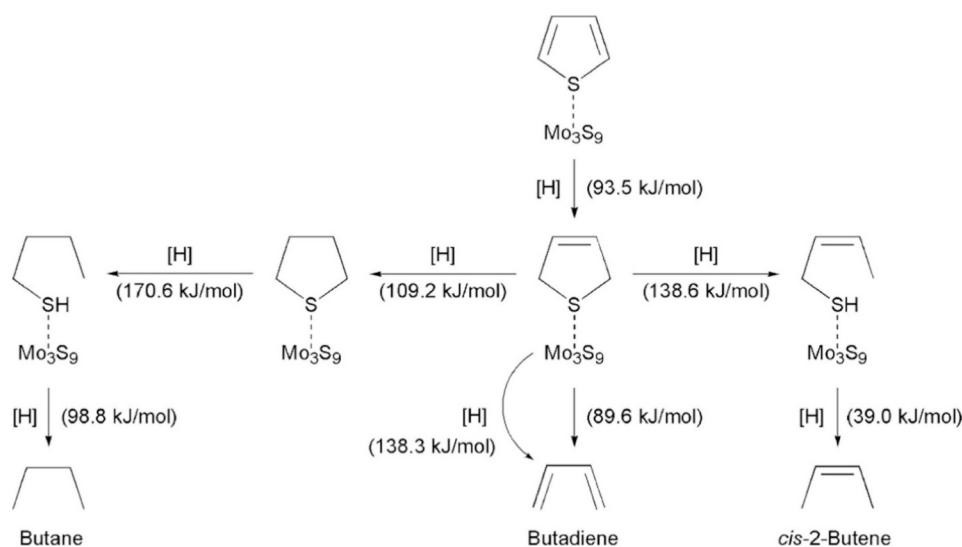


Fig. 4. The thiophene HDS mechanism via Mo_3S_9 model catalyst [212].

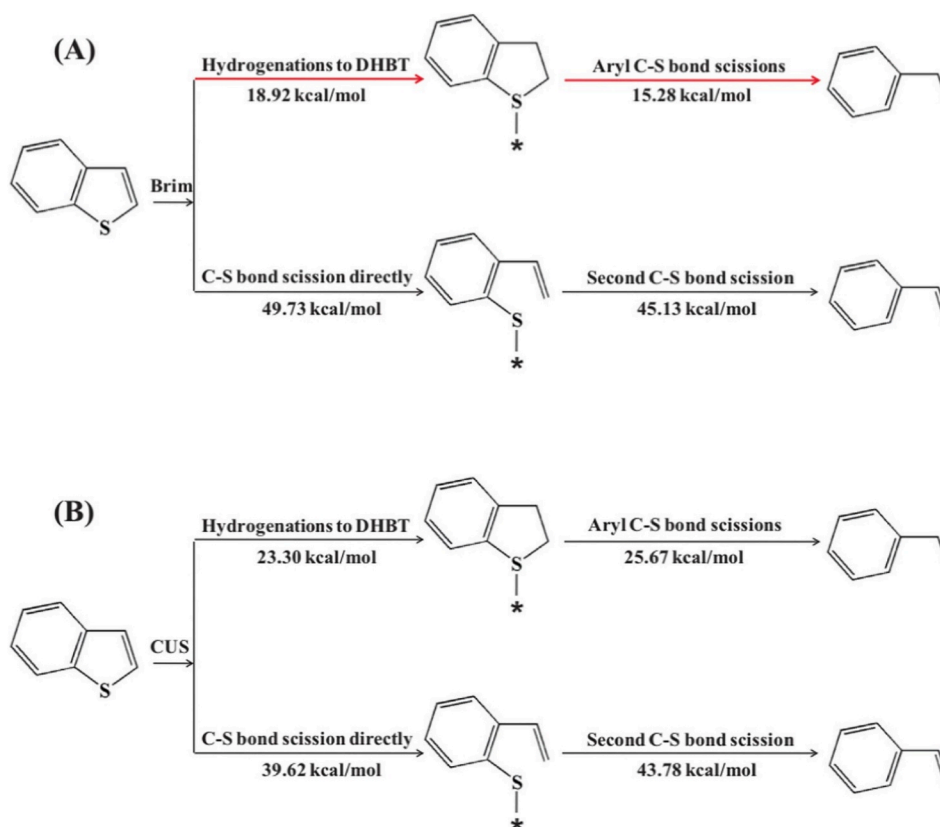


Fig. 5. HDS mechanism of benzothiophenes conversion via Brim (a) and CUS (b) active sites [199].

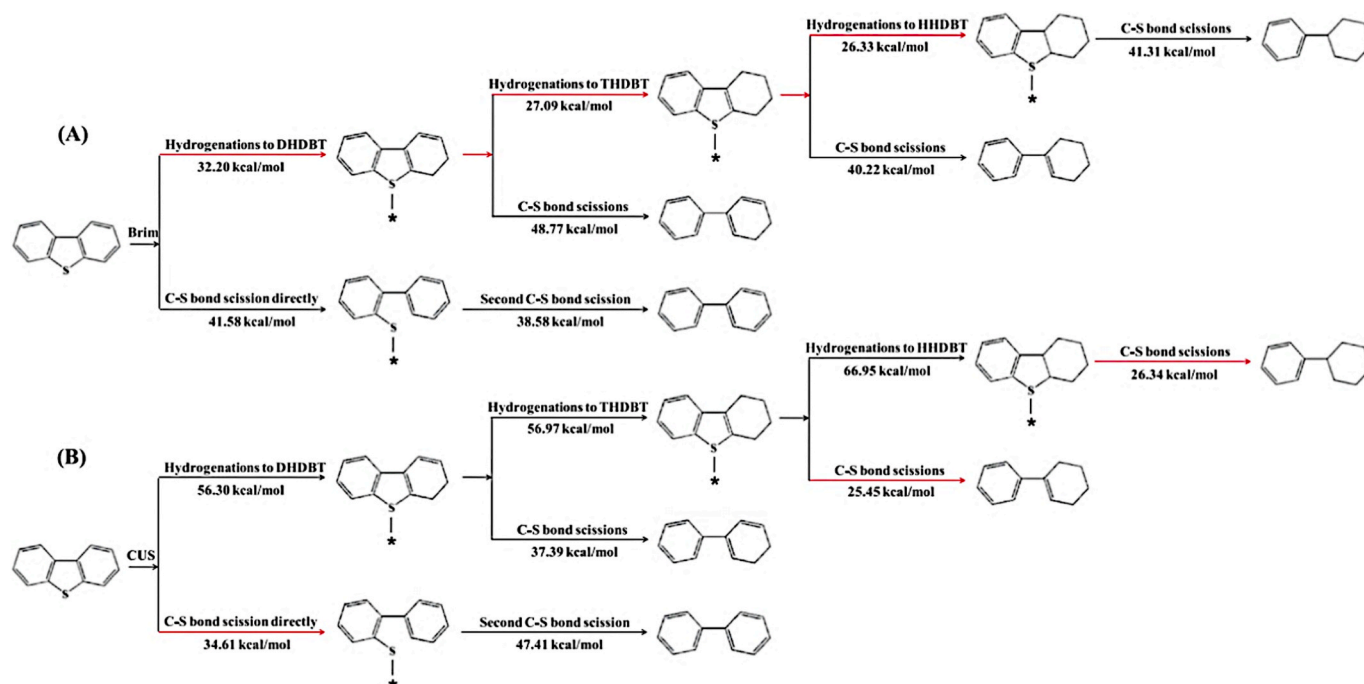


Fig. 6. The HDS mechanism of dibenzothiophenes conversion via Brim (a) and CUS (b) active sites [199].

sulfur conversion, the observed improvement cannot always be attributed solely to intrinsic reaction kinetics [188,232,233]. Changes in LHSV may also modify external and internal mass-transfer resistance, hydrogen distribution within catalyst pores and beds, and the extent of catalyst deactivation during prolonged operation, particularly when

processing heavy feedstocks containing refractory sulfur compounds, resins, and asphaltenes [234]. Consequently, the hydrodesulfurization performance observed in practical reactors reflects the combined influence of intrinsic catalytic kinetics, hydrogen transport, and catalyst stability rather than the isolated effect of a single operating parameter.

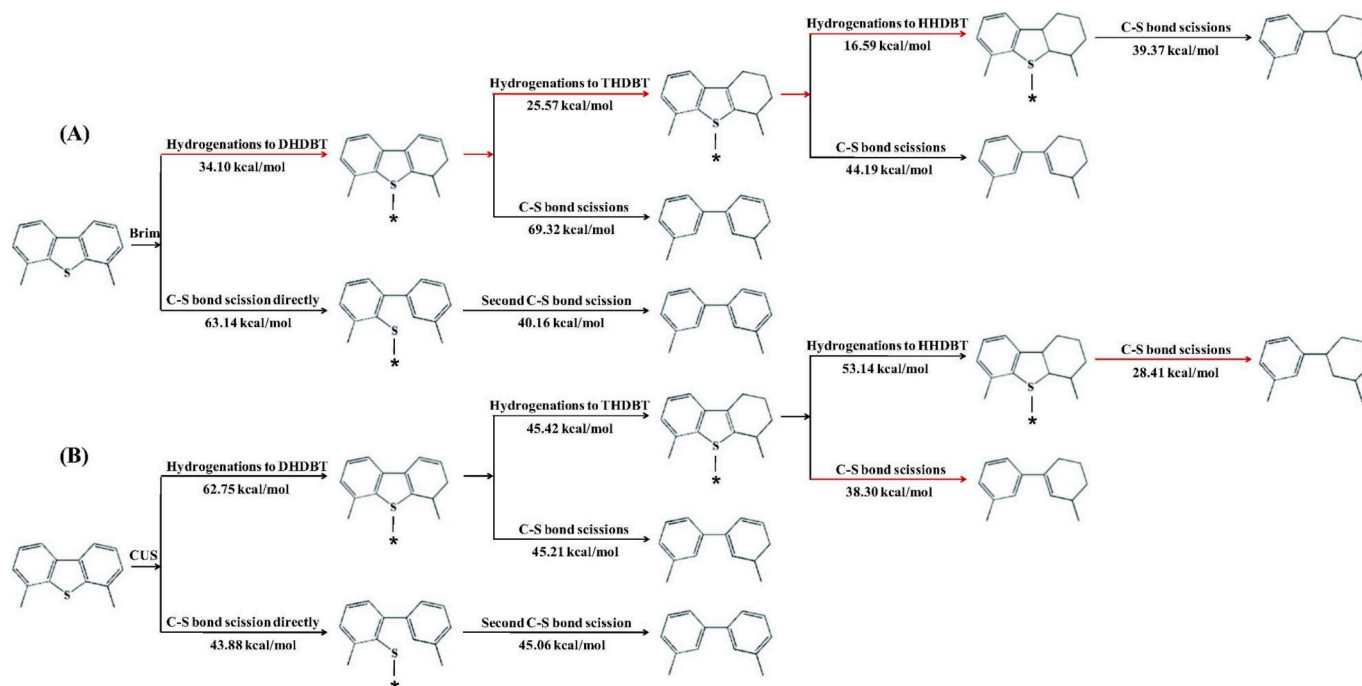


Fig. 7. The HDS mechanism of 4,6-dimethyldibenzothiophene (4,6-DMDBT) conversion via the brim and CUS sites [199].

Table 4

Quantitative comparison of representative HDS operating conditions reported for different feedstocks.

Feedstock	Sulfur content	Catalyst	Temperature (°C)	H ₂ Pressure (bar)	LHSV (h ⁻¹)	HDS (%)	Ref
Diesel	500 ppm of 4,6-DMDBT in dodecane (model feed)	NiFeMo/Al ₂ O ₃	340	40	2.5	98.5	[217]
	500 ppm of 4,6-DMDBT in dodecane (model feed)	Ni ₂ P/GaAlO _x -0.50	340	34	4.8	70.1	[218]
	12.100 ppm	Phosphorus, boron and fluorine modified NiMo/Al ₂ O ₃ catalysts	350	45	1.1	81	[219]
Heavy gas oil	120 ppm	Aluminum-nickel-molybdenum oxide catalyst	400	35	1.2	98	[220]
	12,700 ppm	NiMo/Al ₂ O ₃	360	45	1.5	98.0	[188]
	58,000 ppm	Oil-soluble NiMo catalyst	425	70	–	72.6	[221]
Vacuum residue	12,700 ppm	Ni-Mo bimetallic	350	40	2	99.9	[222]
Tire pyrolysis oil	9000 ppm	NiMo/Al ₂ O ₃	392	140	–	96.0	[223]
	4600 ppm	3Co-10Mo/NBC	330	60	–	99.6	[224]
	1650 ppm	NiMo/Al ₂ O ₃	320	40	10	90.0	[225]
Plastic pyrolysis oil	42.9 ppm	NiMo/Al ₂ O ₃	350	80	1	71.8	[226]

5.1. Effect of operating temperature

Among the operating variables, reaction temperature is one of the most influential parameters because it directly governs intrinsic reaction kinetics, adsorption-desorption equilibria, hydrogenation activity, and the rate of C–S bond cleavage. In general, increasing temperature enhances hydrodesulfurization (HDS) rates by accelerating surface reactions and promoting the conversion of sulfur-containing compounds [235], particularly relatively refractory thiophenic species [236]. Elevated temperature can also improve hydrogen availability in heavy feeds by increasing the solubility and diffusivity of H₂ in the liquid phase [237,238], thereby facilitating hydrogenation and sulfur removal.

Although increasing temperature generally accelerates hydrodesulfurization kinetics, aromatic hydrogenation is an exothermic reaction that becomes progressively less favorable thermodynamically at elevated temperatures [239]. Consequently, excessively high reaction temperatures may reduce aromatic saturation despite enhancing intrinsic reaction rates, particularly during diesel hydrotreating where aromatic hydrogenation contributes to cetane improvement and

facilitates the conversion of refractory sulfur compounds through the HYD pathway [240]. Industrial operating temperatures are therefore selected as a compromise between reaction kinetics, aromatic hydrogenation thermodynamics, catalyst stability, and hydrogen consumption.

Besides, excessively high temperatures may adversely affect catalyst performance and product selectivity. Under severe hydroprocessing conditions, thermal cracking reactions become more pronounced, generating reactive radicals and unstable intermediates that can undergo condensation and polymerization. In feeds rich in polyaromatic hydrocarbons, resins, or asphaltenes, these reactions often lead to the formation of coke precursors and ultimately carbonaceous deposits on the catalyst surface [241]. Such deposits block pore structures, cover active sites, and accelerate catalyst deactivation. In some cases, refractory sulfur compounds may become incorporated into the coke matrix rather than being converted into desulfurized liquid products, thereby lowering carbon utilization efficiency. Therefore, temperature optimization requires a careful balance between maximizing sulfur conversion and minimizing hydrogen consumption, coke formation, and

catalyst aging.

Because of the competing effects of temperature on hydrogenation and cracking reactions, industrial hydroprocessing of complex heavy feeds is frequently carried out in multistage reactor configurations operated at progressively higher temperatures [158]. In the first stage, moderate temperatures—typically below 380 °C—are employed to promote hydrogenation of aromatic rings, olefins, and other unstable unsaturated species, while achieving preliminary sulfur removal [242]. Several studies have shown that effective pre-hydrogenation improves feedstock stability and suppresses subsequent coke formation [243]. This is particularly important for feeds such as crude shale oil, which often contain high concentrations of reactive olefinic compounds [244]. Hydrogenation of these species is essential to prevent polymerization and condensation reactions that generate heavier molecules or coke during downstream processing [245]. After stabilization and partial upgrading in the first stage, deep desulfurization is commonly performed in a second-stage reactor operated at higher temperatures, often above 400 °C, where the conversion of refractory sulfur species becomes more favorable. This staged temperature strategy allows refiners to exploit the benefits of both low-temperature hydrogenation and high-temperature sulfur removal while reducing the risk of excessive coke formation and catalyst deactivation. The general effect of varying operating temperature is shown in Fig. 8.

5.2. Effect of hydrogen pressure

Hydrogen pressure is a critical operating variable in the hydrodesulfurization (HDS) of heavy feeds because it directly determines hydrogen availability for catalytic reactions, gas–liquid mass transfer, catalyst surface sulfidity, and suppression of coke-forming side reactions [246–248]. In contrast to lighter distillates, heavy feeds such as vacuum gas oils (VGO), atmospheric and vacuum residues, bitumen-derived fractions, shale oils, and waste-derived heavy liquids contain larger aromatic molecules, higher sulfur concentrations, and greater amounts of resins, asphaltenes, nitrogen compounds, and metals. These

characteristics substantially increase hydrogen demand during upgrading. Industrial HDS units therefore operate at elevated pressures—commonly several MPa and, for residue hydrotreating, often up to 10 MPa—to achieve appreciable sulfur removal and maintain catalyst performance [249].

One of the primary benefits of increasing hydrogen pressure is the enhancement of hydrogen solubility and diffusivity in the liquid feed. Heavy oils are highly viscous and compositionally complex, which can limit hydrogen dissolution and transport to catalyst pores and active sites. Raising pressure increases the concentration of dissolved hydrogen, improves gas–liquid mass transfer, and reduces local hydrogen starvation within the catalyst bed [250]. This effect is particularly important in trickle-bed and fixed-bed reactors processing heavy feeds, where diffusion limitations may already restrict the conversion of bulky sulfur-containing molecules. Studies on vacuum residue hydrotreatment have shown that pressure improves sulfur removal partly by overcoming transport constraints and improving utilization of catalyst active sites [230].

Hydrogen pressure also strongly affects the balance between the direct desulfurization (DDS) and hydrogenation (HYD) pathways [251]. At higher pressure, increased hydrogen surface coverage favors aromatic ring hydrogenation and thus promotes the HYD route, which is especially beneficial for sterically hindered refractory sulfur compounds such as alkylated dibenzothiophenes. Hydrogenation of adjacent aromatic rings reduces steric hindrance and weakens the C–S bond, facilitating subsequent sulfur removal. Consequently, increasing pressure is often associated with lower residual sulfur levels and improved desulfurization performance [230,252].

Another major advantage of elevated hydrogen pressure is the suppression of coke formation and catalyst deactivation [252]. Under hydrogen-deficient conditions, thermally cracked fragments, olefins, and radical intermediates generated from heavy molecules may undergo condensation and polyaromatization, producing carbonaceous deposits on catalyst surfaces. High hydrogen pressure stabilizes these reactive intermediates through rapid hydrogenation, thereby reducing coke

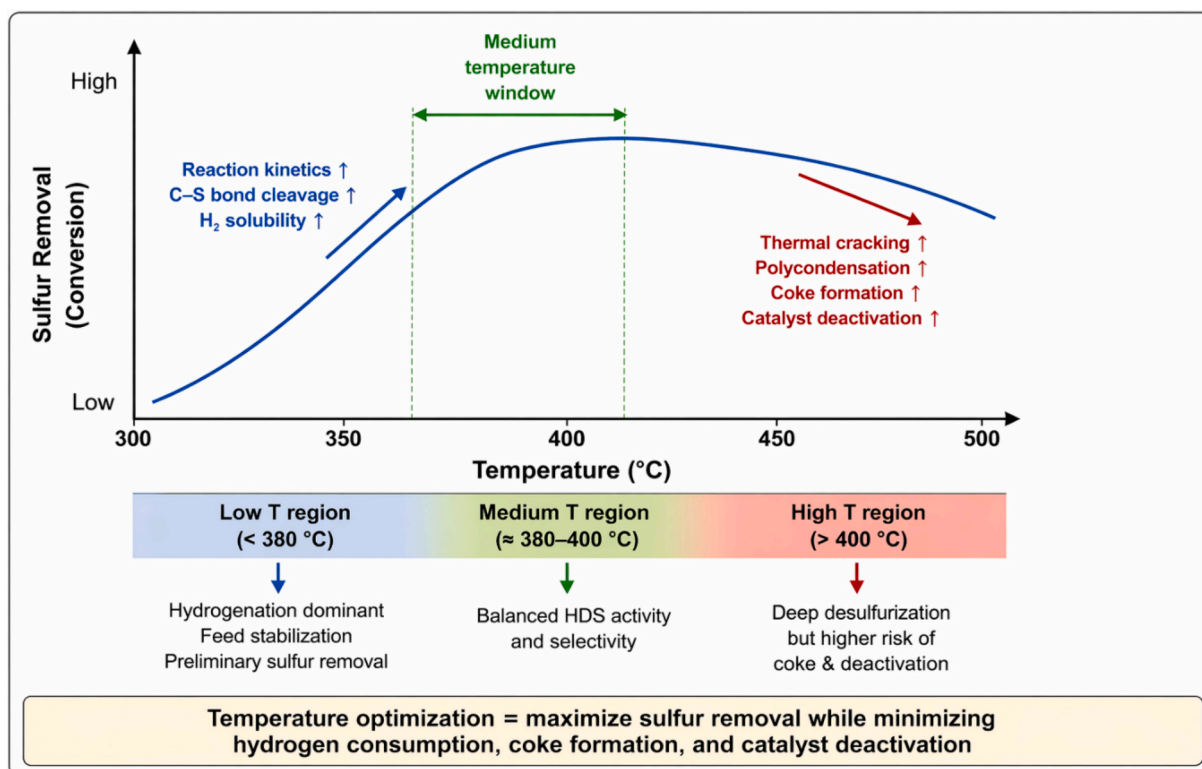


Fig. 8. Effect of operating temperature on HDS efficiency.

deposition, preserving pore accessibility, and extending catalyst cycle duration. This effect is especially valuable for feeds rich in asphaltenes, pyrolysis oils containing unsaturated species, and shale-derived feeds with high olefin content [253]. Industrial residue hydroprocessing technologies therefore frequently combine high pressure with staged catalyst systems to improve both desulfurization and runtime. The general influence of varying hydrogen pressure on HDS efficiency of heavy feed is displayed in Fig. 9.

Despite these technical benefits, increasing hydrogen pressure is associated with substantial economic penalties. Higher pressure requires greater hydrogen compression duty, thicker reactor walls, more stringent materials-of-construction requirements, and increased capital and operating costs. In many cases, sulfur removal gains become incremental beyond a certain pressure threshold, particularly when catalyst activity or mass transfer becomes the dominant limitation [230].

Besides enhancing hydrodesulfurization, elevated hydrogen pressure also promotes hydrodenitrogenation (HDN) and aromatic hydrogenation (HDA) [147], both of which facilitate the conversion of refractory sulfur compounds in complex feedstocks. Removal of nitrogen-containing compounds reduces competitive adsorption on active sites, while aromatic hydrogenation improves the accessibility of sterically hindered sulfur atoms to subsequent C–S bond cleavage [254]. Consequently, relatively high hydrogen pressures are generally preferred in the hydrotreating of diesel-range feedstocks, vacuum gas oils, and heavier residues. In contrast, selective hydrodesulfurization of FCC cracked naphtha requires a careful balance between sulfur removal and olefin preservation. Excessively high hydrogen pressure accelerates

olefin hydrogenation, leading to octane loss despite improved sulfur conversion [255]. Therefore, operating pressure in cracked gasoline hydrotreating is optimized to achieve ultra-low sulfur specifications while minimizing undesirable olefin saturation.

Therefore, commercial operation seeks an optimum pressure window that balances sulfur conversion, hydrogen consumption, catalyst stability, and profitability. For increasingly complex future feedstocks—including co-processing of petroleum residues with waste- or biomass-derived heavy oils—optimization of hydrogen pressure will remain a central challenge and a key target for process simulation and data-driven control strategies [256].

5.3. Effect of liquid hourly space velocity

The Liquid hourly space velocity (LHSV) is a key operating parameter in hydrodesulfurization (HDS), defined as the volumetric feed flow rate per unit volume of catalyst bed (h^{-1}). It is inversely related to the average residence time of the liquid feed in the reactor and therefore strongly influences catalyst contact time, sulfur conversion, hydrogen utilization, and product quality. From an industrial perspective, LHSV is not an independent variable chosen solely for kinetic optimization. Rather, it represents a complex compromise among reaction temperature, hydrogen partial pressure, reactor volume (capital investment), catalyst cycle length, and the additional catalyst volume required to handle feed contaminants such as metals and asphaltenes [257,258]. Thus, the selected LHSV reflects both kinetic and economic considerations, balancing desulfurization performance against throughput,

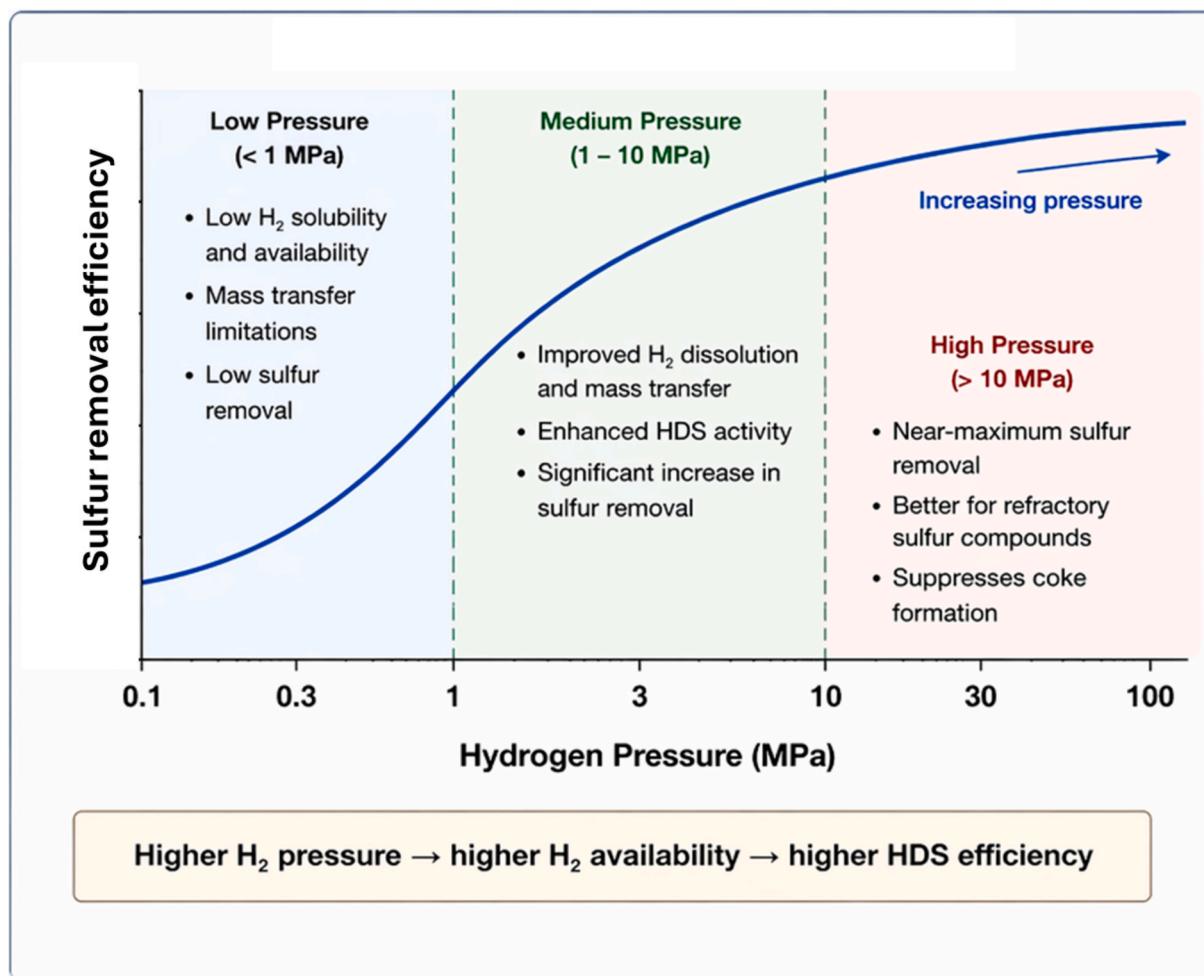


Fig. 9. Effect of hydrogen pressure on HDS efficiency of heavy feedstocks.

catalyst life, and capital cost [258].

For heavy feeds, the effect of LHSV extends beyond intrinsic kinetics because the residence time available for intraparticle diffusion becomes a critical factor. Large sulfur-containing molecules must diffuse through the liquid film surrounding catalyst particles and then through catalyst pore networks before reaching active sites [259]. At high LHSV (short residence time), bulky sulfur compounds—particularly refractory species such as alkylated dibenzothiophenes and asphaltene-associated sulfur—may exit the reactor before they have sufficient time to diffuse into the pore network and undergo conversion [243]. This is not because LHSV changes the molecular diffusivity, but because the available time for diffusion and reaction is constrained by the high throughput.

Numerous studies have shown that decreasing LHSV generally improves sulfur removal, especially for feeds rich in dibenzothiophenic sulfur species and high-boiling fractions [260,261]. From a kinetic perspective, lowering LHSV increases the time available for sequential HDS reactions, including adsorption of sulfur compounds, hydrogenation of aromatic rings, C–S bond cleavage, and desorption of products. This is especially important for refractory sulfur compounds such as alkylated dibenzothiophenes, which often require multistep conversion through the hydrogenation (HYD) route before sulfur removal can occur. Experimental work on vacuum gas oil hydrotreating in trickle-bed reactors demonstrated that sulfur removal increased significantly as LHSV decreased, confirming the beneficial effect of longer residence time on overall HDS conversion [261].

For heavy feeds containing viscous hydrocarbons, asphaltenes, or highly aromatic molecules, the time required for diffusion-limited species to reach active sites is further extended. Reactor modeling studies for industrial VGO hydrotreaters have shown that the coupling between residence time, hydrodynamic behavior, and diffusion resistance becomes increasingly important when processing heavy fractions at elevated throughput [158]. However, the underlying limitation remains the residence time available for diffusion-limited species to access the catalyst active sites.

In an existing unit with fixed reactor volume and catalyst loading, LHSV is effectively determined by the feed rate [262]. The trade-off between throughput and product quality therefore becomes relevant primarily when processing a different or more refractory feedstock, where reducing capacity (i.e., lowering LHSV) may be a strategy to achieve the required sulfur removal [257]. Conversely, for a unit designed for a specific feed and product slate, LHSV is set at the design stage and remains relatively constant during normal operation unless catalyst deactivation or a change in feed quality necessitates adjustment.

When feedstock quality deteriorates or catalyst activity declines, LHSV may be reduced to maintain product specifications, albeit at the expense of throughput. However, it is generally considered a less favorable strategy because it requires lowering refinery throughput or increasing reactor capacity, both of which have significant economic implications. Instead, reactor temperature is commonly increased during the catalyst cycle to compensate for catalyst deactivation and maintain product sulfur specifications while preserving the designed processing capacity [263,264]. Only when temperature limits or catalyst activity become insufficient may throughput reduction (lower effective LHSV) be adopted as a temporary operational strategy for processing more refractory feedstocks or extending catalyst cycle length.

Nevertheless, as feedstocks become heavier and more diverse, the selection of optimum LHSV—whether at the design stage or as an operational adjustment—is increasingly addressed through reactor modeling, statistical optimization, and machine learning methods that integrate sulfur conversion, hydrogen consumption, catalyst life, and economic objectives [255,262]. Therefore, LHSV remains one of the most powerful variables—both in design and operation—for balancing desulfurization efficiency and refinery productivity in heavy-feed hydroprocessing systems.

5.4. Effect of feedstock composition

The initial sulfur content of heavy feedstocks is one of the most important variables influencing HDS performance because it determines the required reaction severity, hydrogen demand, catalyst loading, and achievable product sulfur specifications. Heavy feeds such as vacuum gas oils (VGO), atmospheric and vacuum residues, bitumen-derived oils, shale oils, and waste pyrolysis oils can contain sulfur levels ranging from below 1 wt% to more than 5 wt% depending on origin and prior upgrading history. In general, feeds with higher sulfur concentrations require more severe operating conditions—higher temperature, higher hydrogen pressure, lower liquid hourly space velocity (LHSV), or multistage reactor operation—to reach the same final sulfur target as lower-sulfur feeds. Reviews of heavy-oil upgrading consistently note that high-sulfur heavy feeds are substantially more difficult and expensive to desulfurize than lighter or sweeter feedstocks [139,167,265].

Besides, it is important to recognize that hydrodesulfurization performance reported in the literature is expressed using several related but not identical metrics. Sulfur removal efficiency or desulfurization percentage is generally calculated from the reduction in total sulfur concentration between the feed and product streams according to:

$$\eta_{\text{HDS}} = \frac{S_{\text{feed}} - S_{\text{product}}}{S_{\text{feed}}} \times 100\%$$

where S_{feed} and S_{product} denote the sulfur concentrations of the feed and treated products, respectively. Sulfur concentration is commonly determined using standardized analytical methods, including ultraviolet fluorescence (ASTM D5453), energy-dispersive X-ray fluorescence (ASTM D4294), wavelength-dispersive X-ray fluorescence (ASTM D2622), or CHNS elemental analysis for solid samples and catalysts. In some research studies, sulfur may also be quantified after sample digestion or combustion using ion chromatography (IC) or inductively coupled plasma (ICP)-based techniques, although these methods are less frequently employed for routine petroleum sulfur analysis. In contrast, sulfur conversion is more commonly reported for studies using model sulfur compounds and is calculated from the conversion of an individual sulfur-containing molecule, such as thiophene, benzothiophene, or dibenzothiophene, based on reactant consumption or product formation. Consequently, although sulfur removal efficiency, desulfurization percentage, and sulfur conversion all reflect hydrodesulfurization performance, they are not directly interchangeable because they may refer to different sulfur species, analytical methods, feed compositions, and experimental protocols. Therefore, quantitative comparisons among different studies should be interpreted with caution, particularly when evaluating catalyst performance across model compounds, petroleum-derived heavy feeds, and chemically diverse alternative feedstocks.

From a stoichiometric perspective, increasing sulfur content directly raises hydrogen consumption, since sulfur is removed primarily through hydrogen-assisted cleavage of C–S bonds to form hydrogen sulfide. However, the actual hydrogen requirement is usually much greater than the theoretical sulfur-removal demand because high-sulfur heavy feeds are commonly rich in aromatics, resins, olefins, nitrogen compounds, and asphaltenes that also undergo hydrogenation, hydrodenitrogenation, and stabilization reactions [160]. Therefore, sulfur-rich heavy feeds impose a compounded hydrogen penalty that affects refinery hydrogen-network capacity and operating cost. Modern process reviews of HDS emphasize hydrogen partial pressure and hydrogen availability as central variables when treating high-sulfur gas oils and residues [266].

The effect of sulfur content is also closely linked to sulfur speciation, which is often more important than bulk sulfur concentration alone. As sulfur concentration increases in heavier fractions, sulfur tends to be concentrated in more refractory molecular forms such as benzothiophenes, dibenzothiophenes, alkylated DBTs, and sulfur species associated with resin/asphaltene matrices [121]. These compounds are

significantly less reactive than aliphatic sulfides or mercaptans and often require multistep hydrogenation (HYD pathway) before C–S bond cleavage can occur. Consequently, two feeds with similar total sulfur levels may exhibit very different HDS efficiencies depending on the proportion of sterically hindered thiophenic sulfur species. High-sulfur heavy oils are widely described as containing bulky sulfur structures that are difficult to remove under conventional HDS conditions (Fig. 10) [267].

Higher feed sulfur content also increases the in-situ formation of H_2S , which can influence catalyst performance. Moderate H_2S partial pressure is beneficial because it helps maintain the sulfided active phase of CoMo or NiMo catalysts [268]. However, excessive H_2S concentrations may inhibit sulfur removal by competitive adsorption on active sites, suppress hydrogenation reactions, and reduce conversion of refractory sulfur compounds [269]. Experimental kinetic studies on dibenzothiophene and 4,6-dimethyldibenzothiophene HDS have shown that increasing H_2S partial pressure can significantly reduce overall conversion, with the direct desulfurization (DDS) route often more strongly inhibited than the HYD route [270].

In practical operation, high-sulfur feeds are also frequently associated with faster catalyst deactivation. Although sulfur itself is necessary to preserve catalyst sulfidity, sulfur-rich heavy feeds often contain larger concentrations of metals, Conradson carbon precursors, and poly-aromatic compounds that promote coke formation, pore blockage, and metals deposition [271,272]. As catalyst activity declines with runtime, refiners commonly compensate by increasing temperature, reducing LHSV, or raising hydrogen pressure to maintain product sulfur specifications. This progressive increase in operating severity is particularly common in residue hydrotreating service. From an economic standpoint, sulfur-rich heavy crudes and residues are often discounted relative to sweeter crudes, creating a trade-off between lower feedstock cost and higher upgrading expense. As global crude slates become heavier and sourer, the ability to efficiently process sulfur-rich feeds has become a strategic advantage for complex refineries. Accordingly, recent developments increasingly combine kinetic modeling, catalyst optimization, and machine learning tools to predict HDS performance as a function of total sulfur content, sulfur speciation, and operating conditions.

Moreover, even though it is not within the scope of this reviewer, it is worth noting that the nitrogen containing compound in the feedstock is also a critical factor governing hydroprocessing severity. As discussed

before, nitrogen-containing heterocyclic compounds, particularly basic species such as quinoline and acridine, adsorb strongly on coordinatively unsaturated sites of sulfided catalysts, thereby competing with sulfur-containing molecules for active sites and suppressing hydrogen activation. As a result, nitrogen compounds inhibit the hydrogenation (HYD) pathway of hydrodesulfurization more strongly than the direct desulfurization (DDS) pathway, leading to lower overall sulfur conversion for refractory sulfur compounds. Furthermore, hydrodenitrogenation generally requires more severe operating conditions than hydrodesulfurization because C–N bond cleavage typically proceeds only after extensive hydrogenation of aromatic rings [273,274]. Consequently, HDS and HDN are closely coupled in industrial hydroprocessing, and catalyst selection and operating conditions must be optimized by considering both reactions simultaneously rather than independently.

5.5. Sustainability and techno-economic considerations

Although higher temperatures, elevated hydrogen pressures, and longer residence times generally improve sulfur removal, these benefits are accompanied by increased hydrogen consumption and energy demand, creating an important trade-off between hydrodesulfurization performance and process sustainability. In commercial refineries, hydrogen is one of the most expensive operating utilities and is primarily produced by steam methane reforming (SMR), a process responsible for significant CO_2 emissions [275]. Consequently, the environmental footprint of hydrodesulfurization is governed not only by the sulfur content of the treated fuel but also by the efficiency with which hydrogen is utilized. This issue becomes increasingly critical for processing heavy petroleum residues and alternative feedstocks, because their high concentrations of sulfur, nitrogen, oxygen, aromatics, and heavy molecules demand huge hydrogen supply for hydrotreating reactions. Therefore, maximizing sulfur conversion by simply increasing reaction severity may not necessarily represent the most sustainable or economically favorable operating strategy [139]. Instead, hydrogen utilization efficiency has emerged as an equally important performance indicator alongside sulfur removal efficiency [276].

From a techno-economic perspective, future optimization of industrial hydrodesulfurization should therefore focus on balancing sulfur conversion, hydrogen consumption, catalyst lifetime, and refinery throughput rather than maximizing a single performance metric. The

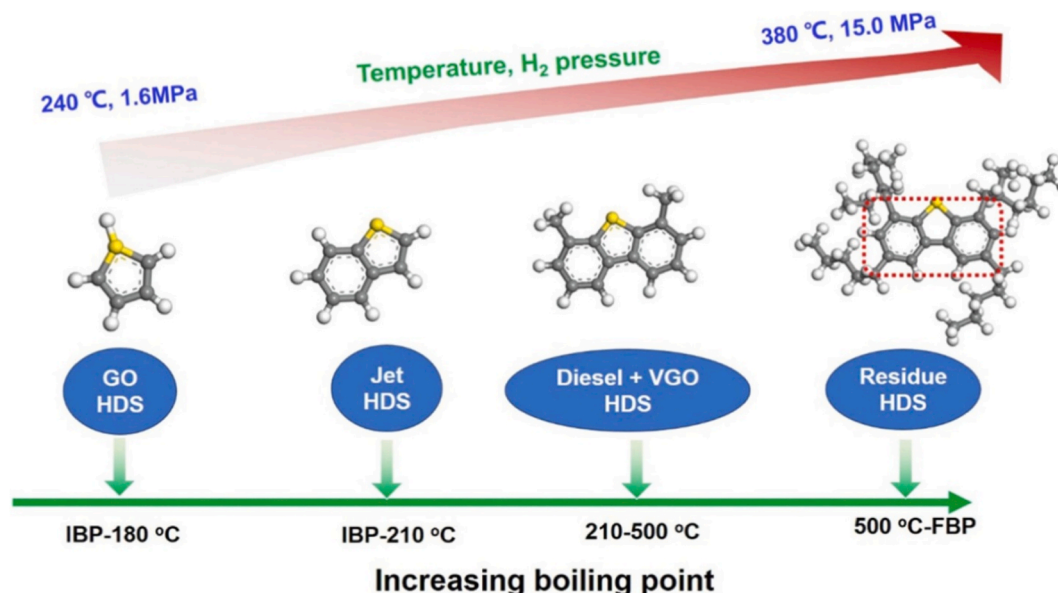


Fig. 10. The dependence of HDS operating conditions on the structure of refractory sulfur compounds [267].

developments in advanced catalyst design, process intensification, hydrogen-recycle strategies, and machine-learning-assisted process optimization provide new opportunities to simultaneously improve desulfurization efficiency while reducing hydrogen consumption and operating costs. In particular, data-driven optimization enables simultaneous evaluation of multiple objectives—including product sulfur concentration, hydrogen consumption, product yield, and greenhouse-gas emissions—allowing refinery operation to move beyond conventional trial-and-error optimization toward more sustainable and economically efficient decision-making. Such multi-objective optimization is expected to become increasingly important as refineries process heavier crude oils and integrate renewable and waste-derived feedstocks into existing hydroprocessing infrastructure [277,278].

6. Catalyst deactivation and regeneration under industrial hydrosulfurization

6.1. Catalyst deactivation

Hydrosulfurization (HDS) catalysts are expected to operate continuously for several months or even years under severe hydroprocessing conditions while maintaining high sulfur conversion and product quality. However, catalyst deactivation remains one of the primary factors limiting process efficiency, refinery profitability, and operational flexibility [167,279]. It has been estimated that catalyst replacement and regeneration account for a substantial fraction of the operating cost of commercial hydrotreating units, while catalyst deactivation also increases hydrogen consumption, reactor pressure drop, and energy demand due to the progressive increase in reactor temperature required to maintain product sulfur specifications [280]. Consequently, catalyst lifetime is often considered one of the most important performance indicators in industrial hydroprocessing, alongside sulfur conversion and product yield.

Although catalyst deactivation has been extensively investigated using model sulfur compounds such as thiophene, benzothiophene, and dibenzothiophene [281,282], these simplified systems do not adequately represent the complexity of industrial feedstocks. As discussed in the previous sections, commercial gas oils, vacuum gas oils (VGOs), atmospheric and vacuum residues, as well as emerging alternative feedstocks including biomass-derived oils, waste tire pyrolysis oils, and waste plastic pyrolysis oils, contain a broad spectrum of sulfur-, nitrogen-, oxygen-, and metal-containing compounds together with large quantities of resins and asphaltenes. These heavy fractions not only contain the most refractory sulfur species but also act as precursors for coke formation and metal deposition, making catalyst deactivation a coupled physicochemical process rather than the consequence of a single poisoning mechanism.

A major limitation of many previous HDS studies is the tendency to investigate individual deactivation mechanisms independently. Coke deposition, metal poisoning, nitrogen inhibition, and thermal sintering are often discussed as isolated phenomena. In industrial reactors, however, these mechanisms evolve simultaneously and strongly influence one another [283–285]. For example, coke deposition narrows catalyst pores, thereby increasing diffusion resistance for hydrogen [286]. The resulting reduction in hydrogenation efficiency promotes the formation of unsaturated intermediates, which further accelerates coke deposition. Likewise, deposited nickel and vanadium species block catalyst pores but also poison of active sites [287,288]. Consequently, catalyst deactivation should be regarded as a dynamic feedback process rather than the linear accumulation of independent deactivation events. This coupled behavior explains why catalyst performance often deteriorates much more rapidly than predicted from laboratory experiments performed using model compounds. A critical comparison of catalyst deactivation mechanisms during industrial hydrosulfurization is presented in Table 5.

Another important distinction between laboratory and industrial

Table 5
Critical comparison of catalyst deactivation mechanisms during industrial hydrosulfurization.

Deactivation mechanism	Primary origin	Dominant stage of catalyst life	Primary impact on catalyst	Reversibility	Typical industrial indicators	Main mitigation strategies	Critical remarks
Coke deposition	Polycondensation of radicals derived from resins, asphaltenes, and heavy aromatics	Early → Middle cycle	Active-site coverage, pore blockage, increased diffusion resistance	High (soft coke); Moderate (hard coke)	Increasing reactor temperature, declining HDS activity, pressure drop, higher hydrogen consumption	Increase H ₂ partial pressure, improve hydrogenation activity, hierarchical catalysts, aromatic solvents, asphaltene dispersants	Most important <i>short-term</i> deactivation mechanism; governed more by type of heavy hydrocarbon structure than total heavy compound content
Metal deposition (Ni, V, Fe)	Hydrodemetalization of porphyrins and organometallic species	Middle → Late cycle	Pore-mouth blockage, diffusion limitation, loss of accessible active sites	Irreversible	Progressive loss of activity despite regeneration; increased pressure drop; high metal concentration in spent catalyst	Guard-bed catalysts, feed pretreatment, hierarchical pore structures	Determines ultimate catalyst lifetime because deposited metals cannot be removed by conventional regeneration
Nitrogen inhibition	Nitrogen compounds (quinolines, acridines, carbazoles)	Entire catalyst cycle	Competitive adsorption on coordinatively unsaturated sites; suppression of hydrogenation pathway	Reversible	Reduced HDS activity for refractory sulfur compounds, especially alkyl-dibenzothiophenes	H ₂ N pretreatment, catalysts with improved resistance to nitrogen adsorption	Frequently underestimated; becomes increasingly important for feeds rich in refractory sulfur species
Sulfur phase transformation / loss of sulfidation	Oxidation during regeneration, insufficient sulfur activity	Mainly after regeneration	Decrease in active CoMoS/NiMoS phase density	Partially reversible	Lower intrinsic HDS activity after regeneration	Controlled sulfiding procedures, optimized regeneration atmosphere	Often coupled with metal sintering during repeated regeneration cycles
Active phase sintering	High regeneration temperature, local hot spots, prolonged thermal exposure	Late cycle / Regeneration	Loss of metal dispersion, shorter MoS ₂ slabs, reduced edge sites	Irreversible	Permanent activity loss after regeneration, lower metal dispersion (TEM/XRD)	Controlled oxidation, plasma-assisted regeneration, chemical reactivation	Main reason regenerated catalyst rarely recover fresh catalyst activity
Support degradation	Hydrothermal aging, repeated regeneration, steam exposure	Late cycle	Collapse of pore structure, lower surface area, weaker metal-support interaction	Irreversible	Reduced BET surface area, lower pore volume	Thermally stable supports, optimized regeneration temperature	Increasingly important for long catalyst cycles and renewable-feed co-processing

hydrodesulfurization lies in the evolution of the dominant deactivation mechanism throughout the catalyst life cycle. During the initial stage of operation, catalyst activity is primarily limited by reversible coke deposition and competitive adsorption of heteroatom-containing molecules [66,284,289]. These phenomena mainly reduce the number of accessible active sites without causing significant structural damage to the catalyst. As operation continues, heavy metals such as nickel and vanadium gradually accumulate within the pore network through hydrometallization reactions [290]. Metal deposition progressively shifts the controlling mechanism from intrinsic reaction kinetics toward internal diffusion limitation because bulky sulfur-containing molecules can no longer effectively access the active sulfide phase [291]. Finally, repeated regeneration cycles and prolonged exposure to severe operating conditions induce irreversible structural degradation, including active metal sintering, collapse of the pore structure, and loss of active CoMoS or NiMoS phases. At this stage, catalyst replacement rather than regeneration becomes the only practical solution. This continuous transition from reversible to irreversible deactivation has received considerably less attention than individual deactivation mechanisms but is critical for understanding industrial catalyst lifetime. The evolution of catalyst deactivation during industrial HDS cycle is shown in Fig. 11.

Feedstock composition further complicates catalyst deactivation because different hydroprocessing feeds exhibit fundamentally different deactivation pathways. For middle distillates and light gas oils, catalyst deactivation is generally dominated by coke formation and competitive adsorption of nitrogen compounds [280]. In contrast, vacuum residues and other heavy feedstocks contain high concentrations of asphaltenes, organometallic compounds, and Conradson carbon precursors, making metal deposition and pore blockage equally important [99,279]. Emerging alternative feedstocks present additional challenges. Biomass-derived oils contain large amounts of oxygenated compounds that consume hydrogen through hydrodeoxygenation reactions and accelerate catalyst deactivation via active site oxidation and coke deposition [292], whereas waste-derived pyrolysis oils often contain chlorine, alkali metals, and unstable oxygenates that introduce new poisoning pathways not encountered in conventional petroleum refining [293]. These observations suggest that catalyst lifetime cannot be generalized using a single deactivation model but should instead be interpreted in relation to feedstock chemistry and reaction environment. This issue becomes increasingly important as modern refineries transition toward co-processing renewable and waste-derived feedstocks together with conventional petroleum streams.

Equally important is the trade-off between catalyst activity and catalyst stability. Strategies that maximize hydrodesulfurization activity do not necessarily maximize catalyst lifetime. Increasing reaction temperature, for example, enhances sulfur conversion by accelerating C–S bond cleavage but simultaneously promotes thermal cracking, radical

formation, and coke deposition [294]. Similarly, catalysts possessing stronger acidity generally improve hydrocracking activity but also facilitate polycondensation reactions that increase coke yield [295]. Conversely, increasing hydrogen partial pressure suppresses coke formation by stabilizing reactive intermediates but substantially increases hydrogen consumption, compressor duty, and capital investment [18]. Therefore, industrial catalyst design should not focus exclusively on maximizing intrinsic activity but rather on achieving an appropriate balance between sulfur removal efficiency, hydrogen utilization, resistance to deactivation, and regeneration capability. This multi-objective optimization remains one of the major challenges in modern hydroprocessing and highlights the need for integrated catalyst and process design.

6.2. Catalyst regeneration

Catalyst regeneration has become an indispensable component of industrial hydrodesulfurization (HDS), as catalyst replacement represents one of the largest operating costs in refinery hydrotreating units. In commercial practice, HDS catalysts are rarely discarded after a single operating cycle. Instead, they typically undergo several regeneration and reactivation cycles before permanent deactivation necessitates replacement. Consequently, catalyst regeneration should not be viewed simply as a method for recovering catalytic activity, but rather as a strategy for maximizing catalyst lifetime and minimizing refinery operating costs. The effectiveness of regeneration, however, depends strongly on the dominant deactivation mechanism. While carbonaceous deposits can generally be removed efficiently, irreversible changes such as metal deposition, active phase sintering, and support degradation cannot be fully reversed.

Conventional oxidative regeneration

Controlled oxidative combustion remains the most widely adopted regeneration technology in commercial HDS units because of its simplicity, relatively low operating cost, and high efficiency in removing carbonaceous deposits [296,297]. During regeneration, deposited coke is oxidized to CO and CO₂ under carefully controlled oxygen concentrations [298,299], restoring catalyst pore accessibility and exposing previously blocked active sites. Depending on catalyst type and operating history [300], oxidative regeneration can recover approximately 70–100% of the catalytic activity after the first regeneration cycle [67,301,302], particularly when deactivation is dominated by coke deposition. However, the degree of recovery potentially decreases after repeated regeneration because irreversible structural changes accumulate throughout successive operating cycles.

The principal challenge associated with oxidative regeneration is thermal management. Coke combustion is highly exothermic, and local temperature excursions (“hot spots”) may exceed the thermal stability of

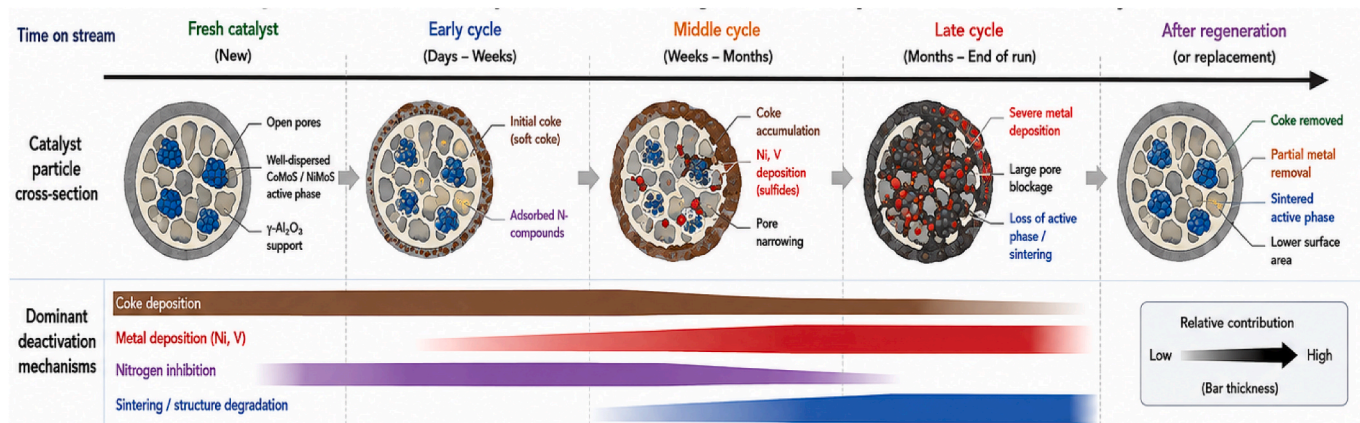


Fig. 11. Evolution of catalyst deactivation during industrial hydrodesulfurization.

the sulfided active phase. Excessive temperatures accelerate sintering of molybdenum sites, weaken promoter-metal interactions, and promote the formation of inactive oxide and spinel phases such as MoO_3 , NiAl_2O_4 and CoAl_2O_4 [303,304]. Consequently, oxidatively regenerated catalysts typically require a subsequent re-sulfidation step (e.g., using activation mixtures such as $\text{H}_2\text{S}/\text{H}_2$ or DMDS/H_2 at elevated temperatures) to restore the active form of catalyst prior to reuse. Consequently, although coke is effectively removed, oxidatively regenerated catalysts frequently suffer from a lower active-site density, reduced sulfur vacancy concentrations, and diminished hydrogenation activity relative to fresh catalysts. This degradation accounts for why catalytic activity recovery remains incomplete despite nearly total removal of carbonaceous deposits.

Recent microscopic characterization further demonstrates that regeneration modifies the morphology of the active phase [305]. Fresh catalysts generally possess highly dispersed Type II NiMoS or CoMoS structures with abundant edge sites that promote hydrodesulfurization. After prolonged operation and regeneration, however, MoS_2 slabs become shorter and less uniformly distributed, while promoter atoms are redistributed or partially incorporated into inactive phases. These structural changes reduce the number of coordinatively unsaturated sites responsible for sulfur-vacancy formation, thereby decreasing intrinsic HDS activity even when pore accessibility has been restored. Thus, regeneration primarily recovers physical accessibility, whereas complete recovery of intrinsic catalytic activity remains fundamentally limited by irreversible structural evolution.

Alternative regeneration technologies.

To overcome the shortcomings of conventional oxidative regeneration, several alternative regeneration technologies have been investigated. Steam gasification and CO_2 -assisted regeneration remove coke through gasification reactions rather than complete oxidation, thereby reducing the risk of localized overheating and simultaneously generating synthesis gas (H_2 and CO) as valuable by-products [306–308]. These methods are particularly attractive from a sustainability perspective because they reduce direct CO_2 emissions associated with conventional combustion. Nevertheless, gasification reactions are kinetically much slower than oxidation and generally require temperatures above 700°C , where support degradation [309,310] and active-phase sintering [311] become increasingly significant. Consequently, their industrial application remains limited despite attractive environmental benefits.

More recently, plasma-assisted regeneration has emerged as a promising low-temperature alternative [312]. Non-thermal plasma generates highly reactive oxygen species capable of oxidizing coke at significantly lower bulk temperatures than conventional combustion, thereby reducing thermal damage to the catalyst. However, plasma

treatment introduces new challenges, including non-uniform plasma distribution, limited penetration into catalyst beds, and high equipment costs [313]. At present, plasma regeneration remains primarily at the laboratory scale, and its long-term industrial feasibility has yet to be demonstrated.

Chemical reactivation strategies represent another promising approach because they aim not only to remove coke but also to reconstruct the active sulfide phase. Chelating agents and controlled re-sulfidation treatments can partially redispersed sintered active metals and restore promoter-metal interactions that are lost during operation [314]. Commercial reactivation technologies, such as the REACT process, have demonstrated recovery of more than 90% of fresh catalyst activity under favorable conditions by combining controlled decoking with reconstruction of the active sulfide phase [279].

Nevertheless, these technologies require multiple processing steps and specialized facilities, increasing operational complexity and regeneration costs. Consequently, their economic viability depends strongly on catalyst value, metal loading, and refinery operating strategy. The critical comparison of catalyst regeneration techniques for industrial HDS is shown on Table 6.

Selection of catalyst regeneration techniques.

An important limitation of many previous studies is the implicit assumption that a single regeneration technology is universally applicable. Regeneration efficiency depends strongly on the dominant deactivation mechanism. Coke deposition, which mainly blocks active sites and catalyst pores, can usually be removed effectively through oxidation or gasification. In contrast, metal deposition resulting from hydrodemetallization of Ni- and V-containing porphyrins is essentially irreversible because deposited metals remain strongly bound within the catalyst pore network. Likewise, thermal sintering and support collapse permanently reduce active-site density and pore accessibility, rendering catalyst regeneration progressively less effective with increasing catalyst age.

This distinction has important industrial implications. During the early stages of catalyst operation, regeneration can substantially extend catalyst lifetime because deactivation is largely governed by reversible coke deposition. However, as irreversible metal accumulation and structural degradation become dominant, the benefit of regeneration diminishes, and catalyst replacement eventually becomes more economical than repeated regeneration. Therefore, refinery catalyst management should optimize the timing of regeneration rather than simply maximizing the number of regeneration cycles. Delayed regeneration may allow irreversible structural damage to accumulate, whereas excessively frequent regeneration increases operational costs and accelerates thermal aging through repeated oxidation–sulfidation cycles. This trade-off highlights the need for optimized regeneration

Table 6

Critical comparison of catalyst regeneration technologies for industrial hydrodesulfurization.

Regeneration technology	Primary regeneration mechanism	Effective for	Activity recovery	Main advantages	Major limitations	Industrial maturity
Air oxidation	Coke combustion (CO/CO_2 formation).	Coke deposition.	High (70–95% after first cycle).	Mature, simple, relatively low cost.	Hot spots, active phase oxidation, metal sintering, incomplete recovery after repeated cycles.	Commercial
Steam gasification	$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	Coke deposition.	Moderate.	Lower direct CO_2 emissions; syngas generation.	High temperature ($>700^\circ\text{C}$), support degradation, slow kinetics.	Pilot
CO_2 gasification	$\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$	Coke deposition.	Moderate.	Carbon utilization, reduced oxidation severity.	High energy demand, slow regeneration rate.	Pilot
Plasma-assisted regeneration	Reactive oxygen species remove coke.	Coke deposition.	High (laboratory).	Low bulk temperature, reduced thermal damage.	Equipment complexity, scale-up challenges, high cost.	Laboratory/Pilot
Chemical reactivation (e.g., REACT)	Coke removal + active phase reconstruction.	Coke + partial active phase degradation.	Very high ($>90\%$ under favorable conditions).	Restores dispersion and promoter interactions.	Multi-step process, higher cost, specialized facilities.	Commercial (specialized)

scheduling rather than routine periodic regeneration.

Beyond the dominant deactivation mechanism, the practical recovery of catalytic activity is also governed by several factors. First, the presence of metal contaminants—including nickel, vanadium, and iron deposited during hydrometallization, as well as silicon and sodium—can significantly limit regeneration effectiveness [315,316]. These contaminants cause irreversible pore blockage, active-site poisoning, and structural degradation that cannot be removed by oxidative methods. Vogelaar et al. [280] demonstrated that contaminant metals can penetrate into the catalyst pellet, with vanadium and sodium diffusing into the pore network while iron deposits forming a layer on the exterior surface, catalyzing coke formation and rapid pore mouth plugging. Dufresne [317] reported that various contaminants originate either from the feed (e.g., vanadium, nickel, arsenic, sodium) or from additives used during refining operations (e.g., silicon) or corrosion (e.g., iron). When contamination levels are excessive, catalytic activity becomes seriously affected, and catalyst replacement often becomes more economical than regeneration.

Second, the catalyst type strongly influences regeneration effectiveness. It is well established that Co–Mo–S structures can exist as either Type I or Type II, which possess different catalytic properties and sensitivities to oxidation [318,319]. Type I catalysts (characterized by strong metal-support interactions via Mo–O linkages to alumina) are more tolerant to air oxidation and can recover significant activity after conventional regeneration. In contrast, Type II catalysts (which exhibit weaker support interactions and higher intrinsic activity) are more sensitive to oxidation. Studies have shown that high-temperature regeneration can induce a transition from Type II to Type I Co–Mo–S, resulting in significantly lower hydrodesulfurization activity. For Type II catalysts, simple air oxidation typically recovers only a fraction of the original activity because the oxidation process induces sintering of MoS₂ slabs and loss of promoter-metal interactions. Advanced chemical rejuvenation technologies are specifically designed for high-activity Type II catalysts, redistributing active metals and re-establishing active catalytic sites in a Type II configuration [320].

Third, most industrial catalyst regeneration is now performed ex-situ by specialized companies rather than in-situ. Dufresne [317] noted that ex situ regeneration is “the rule nowadays for a better performance recovery” due to precise temperature control and optimized carbon and sulfur removal. This practice is preferred for several reasons, including improved safety (controlled temperature management to avoid hot spots and thermal excursions), better quality control through standardized regeneration protocols, and superior activity recovery. The ex-situ approach involves catalyst unloading, packaging, transportation to a regeneration facility, regeneration or rejuvenation, and reloading.

Fourth, regardless of the regeneration method employed, all procedures require subsequent sulfidation to convert the oxide phase back to the active CoMoS/NiMoS phase [305,321]. The re-sulfidation step is essential because the oxidation process converts the active sulfide structures to oxides, which are catalytically inactive. Studies have shown that air exposure (passivation) and subsequent resulfidation can substantially increase thiophene hydrodesulfurization activity of sulfided Co–Mo/Al₂O₃ catalysts, with the activity increase stemming from a decrease in Mo-support interactions. Bremmer et al. [305] demonstrated that after oxidation and resulfidation treatment, catalysts exhibited more than 20% higher activity than after resulfidation alone, ascribed to a redistribution of the (Ni/Co)MoS₂ slabs during the second sulfidation treatment. The sulfidation procedure, including the temperature program and conditions, significantly influences the final activity recovery.

Future perspectives: from catalyst regeneration to predictive catalyst lifetime management.

Current industrial practice largely relies on fixed operating cycles and empirical experience to determine regeneration timing. However, this approach does not account for variations in feedstock composition, catalyst aging rate, or operating severity. The increasing availability of

online process measurements and digital refinery technologies provides new opportunities for transitioning from reactive catalyst regeneration toward predictive catalyst lifetime management.

Machine learning models coupled with soft sensors and digital twins can continuously estimate catalyst activity, coke accumulation, hydrogen consumption, sulfur conversion, and remaining useful life (RUL) using real-time process data [288,322]. Instead of initiating regeneration after significant activity loss has occurred, predictive models enable regeneration to be scheduled at the optimal point where catalyst recovery is maximized while irreversible deactivation remains limited. Such predictive maintenance strategies have the potential to reduce hydrogen consumption, minimize unplanned shutdowns, extend catalyst service life, and improve refinery profitability [323]. Consequently, future catalyst management is expected to integrate catalyst design, online monitoring, and artificial intelligence into a unified framework for lifetime optimization rather than focusing solely on catalyst regeneration efficiency.

7. Transition from experimental to Data-Driven approaches

7.1. Limitations of conventional experimental approaches in HDS

Hydrodesulfurization has historically relied on experimental trial-and-error approaches for catalyst development and process optimization. While this paradigm has been effective for relatively simple petroleum-derived feedstocks, it becomes increasingly inadequate when applied to more complex systems, including heavy oils, biomass-derived liquids, and waste or pyrolysis oils. These feedstocks differ significantly in composition, yet they share a common characteristic: a high degree of chemical complexity that leads to nonlinear and interdependent reaction behavior. In heavy oil fractions, this complexity arises from the presence of refractory sulfur compounds, including sterically hindered species such as alkylated dibenzothiophenes, which exhibit complex reactivity and diffusion limitations. As a result, HDS performance is governed by a combination of factors, including catalyst composition, support properties, reaction conditions, and feed characteristics, all of which interact in a highly nonlinear and interdependent manner [324]. This complexity makes it difficult to isolate the influence of individual variables using conventional experimental methods.

A major limitation of traditional approaches is the large experimental burden required to explore the multidimensional parameter space. The development of new HDS catalysts typically involves systematic variation of metal loadings, promoters, support materials, and preparation methods, followed by extensive testing under different operating conditions. Such experimental campaigns are both time-consuming and resource-intensive, requiring significant consumption of materials and energy [324]. Moreover, the optimization of process parameters, such as temperature, pressure, and hydrogen flow rate, further increases the number of required experiments. This challenge is further amplified when dealing with alternative feedstocks such as biomass-derived oils and pyrolysis liquids, which contain a broad spectrum of oxygenated compounds (e.g., phenolics, acids, ketones) in addition to sulfur species. These compounds introduce additional reaction pathways, including hydrodeoxygenation and hydrogenation, which compete with desulfurization reactions and further complicate catalyst evaluation. As a result, the number of variables increases substantially, making experimental campaigns even more time-consuming and resource-intensive.

In practice, it is often infeasible to explore all possible combinations, leading to incomplete optimization and potentially suboptimal catalyst formulations or operating conditions [325]. This limitation is particularly critical for waste-derived and pyrolysis oils, where feedstock variability is high due to differences in source materials and processing conditions. Unlike conventional petroleum streams, these alternative feeds can vary widely in composition, including sulfur, nitrogen, oxygen, and metal impurities, which significantly influence catalytic

behavior. The variability makes it difficult to establish generalized experimental correlations, as results obtained for one feedstock may not be directly transferable to another.

Another key challenge lies in the limited scalability and transferability of laboratory findings to industrial systems. Experimental studies are often conducted using model compounds or simplified feeds under controlled conditions, which do not fully capture the complexity of real feedstocks. Industrial feeds exhibit significant variability in composition, including the presence of metals, asphaltenes, and other contaminants that influence catalyst performance and deactivation behavior. This issue is particularly pronounced for biomass-derived and waste oils, where the presence of unstable and reactive species can lead to polymerization, coke formation, and rapid catalyst deactivation under industrial conditions. Consequently, catalysts and conditions optimized at the laboratory scale may not perform as expected in refinery environments, highlighting a persistent gap between experimental studies and practical implementation.

In addition, conventional mechanistic modeling approaches face significant limitations in describing these systems. The reaction networks of involved in hydroprocessing of heavy oils and alternative feedstocks are highly complex, comprising of multiple parallel and sequential pathways, such as direct desulfurization, hydrogenation, hydrodeoxygenation, and cracking, each route influenced by catalyst structure and operating conditions. Developing detailed kinetic models for such systems is challenging due to the large number of species and reactions involved, as well as the lack of comprehensive experimental data. This complexity is further compounded by uncertainties in experimental measurements and variability in feed composition, introducing additional challenges in developing reliable and predictive mechanistic models.

Finally, experimental approaches are inherently limited in their ability to handle uncertainty and data variability. Measurements in HDS systems are often affected by sensor inaccuracies, sampling inconsistencies, environmental fluctuations, and variations in feed composition particularly for biomass and waste-derived oils. Traditional analysis methods typically assume consistent data, which may not reflect real-world conditions. As a result, the predictive capability of experimentally derived correlations is often limited, especially when extrapolated beyond the studied conditions [326].

Taken together, these limitations underscore the need for alternative approaches that can efficiently handle the complexity, high dimensionality, and uncertainty inherent in hydrodesulfurization. The transition toward data-driven methodologies, particularly ML, offers a promising pathway to overcome these challenges by enabling more comprehensive modeling, efficient optimization, and improved predictive capability across a wide range of feedstocks, including heavy oils, biomass-derived liquids, and waste or pyrolysis oils.

7.2. Need for Data-Driven methods

The increasing complexity of hydrodesulfurization (HDS) systems, particularly for heavy feeds and emerging alternative feedstocks such as biomass-derived liquids and waste or pyrolysis oils, has driven a transition toward data-driven methodologies. Machine learning (ML) has emerged as a powerful tool for modeling and optimization in these systems. Unlike conventional mechanistic or empirical approaches, ML methods can capture highly nonlinear relationships without requiring explicit assumptions about the underlying reaction mechanisms [327]. This capability is especially important in HDS, where process performance depends on the intricate interplay of multiple variables, including temperature, pressure, catalyst composition, hydrogen availability, and feedstock properties.

Traditional modeling approaches often struggle to represent the high-dimensional interactions among feedstock composition, catalyst properties, and operating conditions, whereas data-driven models can effectively learn complex nonlinear relationships directly from experimental and

industrial datasets without requiring explicit kinetic assumptions [325]. Recent studies have also demonstrated the practical advantages of machine learning in hydrodesulfurization-related applications. For example, support vector regression (SVR) combined with hybrid parameter optimization achieved excellent prediction accuracy for industrial ultra-low sulfur diesel production, with an average absolute relative error (AARE) of 0.0745, a coefficient of determination ($R^2 = 0.997$), and a computation time of only 56 s during model optimization, while additional vector quantization further reduced training time and improved predictive performance [328]. Likewise, Random Forest, Lasso, and Ridge regression models have successfully identified the key structural descriptors governing dibenzothiophene hydrodesulfurization and accurately predicted catalyst activity and selectivity, demonstrating the capability of ML algorithms to extract structure–performance relationships that are difficult to formulate explicitly using conventional kinetic expressions [329].

Nevertheless, purely data-driven models often suffer from limited extrapolation capability and may violate fundamental physicochemical principles when applied outside the training domain. To overcome these limitations, increasing attention has been devoted to hybrid approaches that integrate first-principles reaction kinetics with machine learning. Wang et al. [330] incorporated the Langmuir–Hinshelwood reaction mechanism directly into an artificial neural network, enabling the model to preserve known HDS reaction pathways while substantially reducing the amount of training data required compared with conventional black-box ANN models. More recently, Physics-Informed Neural Networks (PINNs) have emerged as a promising framework for refinery reaction kinetics by embedding ordinary differential equations derived from Langmuir–Hinshelwood–Hougen–Watson kinetic models into the neural network loss function. This strategy simultaneously preserves physical consistency, estimates kinetic parameters, and improves generalization under varying operating conditions, offering a practical bridge between mechanistic and data-driven modeling for complex hydrotreating systems [331]. Consequently, rather than replacing mechanistic models, current research increasingly favors hybrid physics-informed machine learning frameworks that combine the interpretability of reaction kinetics with the predictive capability and computational efficiency of modern machine learning algorithms.

The need for data-driven approaches becomes even more pronounced when considering biomass-derived and waste-based feedstocks. Unlike conventional petroleum streams, these feeds contain a wide range of oxygenated compounds, nitrogen-containing species, and unstable intermediates, in addition to sulfur compounds. As a result, hydroprocessing of such feedstocks involves not only hydrodesulfurization but also simultaneous hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), and hydrogenation reactions. These competing and overlapping reaction pathways significantly increase system complexity and make it difficult to isolate individual reaction effects through conventional experimental approaches. Data-driven models offer a practical solution by capturing the collective behavior of these interconnected reactions, enabling more accurate prediction of overall process performance across diverse feed compositions.

In addition to handling complexity, data-driven approaches significantly reduce the experimental burden associated with catalyst and process development. The upgrading of biomass and waste oils often requires extensive screening of catalysts capable of simultaneously removing sulfur, oxygen, and nitrogen while maintaining fuel quality and stability. Traditional experimental methods would require a vast number of experiments to explore the combinatorial space of catalyst formulations and operating conditions. By contrast, ML models can predict performance metrics such as sulfur removal efficiency, oxygen reduction, product distribution, and hydrogen consumption, thereby narrowing the search space and guiding experimental efforts toward the most promising conditions. This leads to faster development cycles and more efficient use of resources, which is particularly important for emerging feedstocks where experimental data are often limited. This leads to faster development cycles and more efficient use of resources,

which is particularly important for emerging feedstocks where experimental data are often limited.

Another key advantage of data-driven methods is their ability to address the inherently multi-objective nature of industrial HDS processes. In practice, HDS optimization involves balancing several competing objectives, such as maximizing heteroatom (S, O, N) removal while minimizing hydrogen consumption, process cost, and emissions (e.g., SO_2). These challenges are further amplified in biomass and waste upgrading, where excessive hydrogenation can lead to undesired saturation of valuable compounds or excessive coke formation. Conventional approaches often focus on a single objective, which can result in suboptimal overall performance. In contrast, ML-based models can simultaneously predict and optimize multiple outputs, enabling a more comprehensive understanding of trade-offs and facilitating better decision-making in process design and operation.

Furthermore, data-driven models offer a robust framework for handling uncertainty and variability in real-world systems [326]. HDS datasets are often affected by measurement errors, sensor inaccuracies, and variability in feedstock composition, all of which can complicate modeling efforts. Biomass-derived and pyrolysis oils are particularly challenging due to their highly variable composition, which depends on feedstock origin, processing conditions, and storage stability. This variability introduces significant uncertainty into experimental and industrial datasets, making it difficult to develop generalized models using traditional approaches. Advanced ML techniques, such as fuzzy logic and probabilistic learning methods, explicitly account for such uncertainties, improving the reliability and generalizability of predictions across different feedstocks and operating conditions.

Finally, data-driven approaches provide a critical bridge between laboratory-scale studies and industrial applications. By integrating data from multiple sources, including laboratory experiments, pilot-scale studies, and refinery operations, ML models can support the

development of soft sensors and real-time predictive tools. This capability is particularly valuable for mixed-feed systems, where conventional and alternative feedstocks are co-processed, resulting in dynamic and evolving process conditions. Real-time predictive models enable adaptive process control, improved operational stability, and enhanced efficiency, thereby facilitating the transition toward more flexible and sustainable refinery operations.

Overall, the integration of data-driven methodologies into hydrodesulfurization and broader hydroprocessing systems represents a critical step toward addressing the challenges posed by increasingly complex feedstocks. By enabling efficient modeling, optimization, and prediction across conventional and alternative feeds, machine learning provides a unifying framework that supports the development of next-generation catalysts and processes for cleaner and more sustainable fuel production.

7.3. Workflow for Data-Driven HDS research

The development of machine learning (ML) models for hydrodesulfurization (HDS) extends beyond algorithm selection and follows a structured workflow encompassing data acquisition, feature engineering, model development, validation, optimization, and industrial deployment. Each stage influences the reliability and practical applicability of the final model, and deficiencies in any step may propagate throughout the workflow. For example, inaccurate catalyst characterization or inconsistent feedstock analysis cannot be compensated for by more sophisticated ML algorithms, whereas inadequate validation may lead to overly optimistic performance estimates that fail under industrial conditions. Therefore, successful implementation of ML in HDS requires the integration of high-quality experimental and refinery data, physically meaningful descriptors, robust validation strategies, and continuous interaction with process engineering and catalyst science. Fig. 12

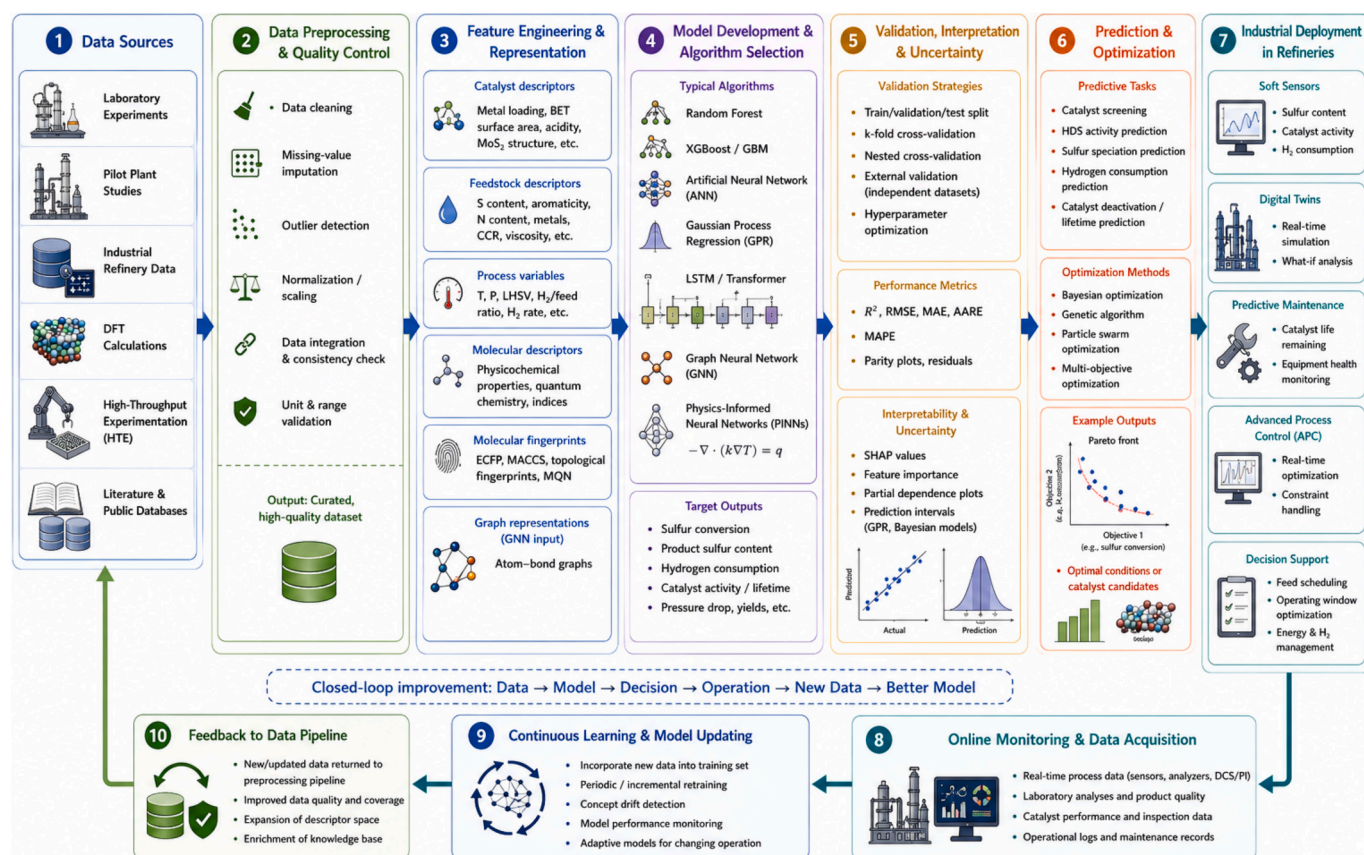


Fig. 12. The simplified workflow for data-driven HDS research.

summarizes the proposed workflow for data-driven HDS research, while Table 7 highlights the objectives, commonly used techniques, and expected outputs at each stage.

The process begins with data generation and collection, where training datasets are obtained from laboratory experiments, high-throughput catalyst screening, or industrial refinery operations, including hydroprocessing systems involving petroleum fractions, bio-oils, and mixed or co-processed feedstocks. These datasets typically include input variables such as operating conditions (e.g., temperature and pressure), catalyst characteristics (e.g., composition, loading, and support properties), and feedstock properties (e.g., sulfur, oxygen, and nitrogen content, molecular composition, and polarity or acidity of the feedstock) [332]. Corresponding outputs may include sulfur content in the product, conversion efficiency, emissions, and process cost, as well as oxygen and nitrogen removal efficiency, product stability, and hydrogen consumption, particularly in biomass and waste oil upgrading. The quality and representativeness of the training dataset largely determine the reliability and generalizability of machine-learning models. However, HDS datasets are often fragmented across laboratory studies and industrial sources, resulting in inconsistent data quality and limited transferability. These broader challenges associated with data availability and industrial deployment are discussed in Section 8.5.

The performance of machine learning (ML) models depends not only on the selected algorithm but also on how catalysts, feedstocks, and operating conditions are represented as numerical inputs. This process, known as feature engineering, converts raw experimental or computational data into descriptors that capture the physicochemical characteristics governing hydrodesulfurization (HDS). Appropriate feature selection improves prediction accuracy, model robustness, and interpretability, and is often more influential than the choice of ML algorithm itself.

Depending on the prediction objective, different descriptor categories can be employed (Table 8). Catalyst descriptors (e.g., metal loading, BET surface area, pore volume, and MoS₂ slab morphology) are commonly used for catalyst activity prediction [329], whereas process descriptors (e.g., temperature, hydrogen pressure, and liquid hourly space velocity) are more suitable for process optimization and soft-sensing applications [333]. Feedstock descriptors, including sulfur content, aromaticity, API gravity, and asphaltene content, are frequently incorporated to account for product quality prediction and catalyst deactivation [332,334].

At the molecular level, conventional physicochemical descriptors (e.g., molecular weight, HOMO–LUMO energies, dipole moment, polarizability, and C–S bond dissociation energies) have been widely employed for structure–activity relationship studies because they provide physically interpretable information related to molecular stability and reactivity [255]. However, these descriptors generally characterize global molecular properties and often fail to distinguish subtle local structural differences responsible for the markedly different reactivities of

refractory sulfur compounds, such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). More recently, molecular representations have evolved from handcrafted descriptors toward data-driven encodings that preserve molecular topology and local chemical environments [335]. SMILES (Simplified Molecular Input Line Entry System) provides a standardized string representation of molecular structures and serves as the basis for generating many cheminformatics descriptors and sequence-based deep learning models [336]. Molecular fingerprints, particularly Extended-Connectivity Fingerprints (ECFPs, also known as Morgan fingerprints), encode local atomic neighborhoods into fixed-length binary vectors that efficiently capture functional groups and substructural motifs, making them well suited for quantitative structure–activity relationship (QSAR) analysis, virtual screening, and molecular property prediction [337,338]. In contrast, graph-based representations model molecules as atom–bond graphs, allowing Graph Neural Networks (GNNs) to automatically learn hierarchical structural features directly from molecular topology without predefined descriptors [339]. Compared with conventional fingerprints, graph representations are better able to preserve connectivity patterns, steric environments, and heteroatom distributions that govern adsorption and reaction pathways on catalyst surfaces. Consequently, GNNs have shown considerable promise for catalyst discovery and molecular property prediction, particularly for chemically diverse systems where complex structural relationships are difficult to describe using manually engineered descriptors [340]. Although GNNs have not yet been widely applied to hydrodesulfurization, they represent a promising direction for future data-driven catalyst design involving refractory thiophenic compounds and chemically complex heavy-feed molecules.

The next stage involves model development, where various machine learning (ML) algorithms are trained to establish relationships between input variables and target outputs. Because HDS-related prediction tasks differ substantially in terms of data characteristics, prediction objectives, and interpretability requirements, no single algorithm is universally optimal. Instead, the selection of an appropriate ML model should be guided by the nature of the problem, the size and quality of the available dataset, computational cost, and the desired balance between predictive accuracy and model interpretability. Tree-based ensemble methods, such as Random Forest (RF) and Extreme Gradient Boosting (XGBoost), are particularly suitable for catalyst screening, feedstock characterization, and process optimization because they effectively capture nonlinear relationships, are relatively robust to noisy and heterogeneous datasets, and provide quantitative measures of feature importance that facilitate interpretation of catalyst properties, feed composition, and operating variables. In contrast, regression-based methods, including Gaussian Process Regression (GPR) and Artificial Neural Networks (ANNs), are often preferred for kinetic prediction and process modeling because of their superior ability to approximate highly nonlinear reaction behavior. In particular, GPR is advantageous for small experimental datasets owing to its capability for uncertainty

Table 7
Typical workflow for machine learning-assisted hydrodesulfurization.

Workflow stage	Main objective	Typical methods	Representative outputs	Industrial relevance
Data acquisition	Collect catalyst, feedstock, process, and simulation data	Laboratory experiments, pilot plants, refinery historians, DFT, HTE	Raw datasets	Foundation for ML development
Data preprocessing	Improve data consistency and quality	Cleaning, normalization, outlier detection, missing-value imputation	Curated datasets	Reduces bias and improves model robustness
Feature engineering	Transform raw data into machine-readable descriptors	Catalyst descriptors, molecular descriptors, fingerprints, graph representations	Feature matrix	Improves predictive performance and interpretability
Model development	Learn relationships between inputs and outputs	RF, XGBoost, ANN, GPR, LSTM, GNN, PINNs	Predictive models	Catalyst design, process optimization
Validation & interpretation	Assess reliability and explain predictions	k-fold CV, nested CV, external validation, SHAP, uncertainty quantification	Validated and interpretable models	Improves industrial confidence
Optimization	Identify optimal catalyst or operating conditions	Bayesian optimization, genetic algorithms, multi-objective optimization	Optimal process windows	Reduced hydrogen consumption and improved sulfur conversion
Industrial deployment	Integrate ML into refinery operation	Soft sensors, digital twins, APC, predictive maintenance	Real-time decision support	Intelligent refinery operation

Table 8
Common descriptors and data representations used for machine learning in hydrosulfurization.

Descriptor Category	Typical Descriptors / Representations	Typical Applications	Advantages	Limitations	Data Source
Catalyst descriptors	Metal loading, Co/Mo or Ni/Mo ratio, BET surface area, pore volume, acidity, MoS ₂ slab length (TEM), metal dispersion (CO chemisorption)	Catalyst activity, selectivity, stability prediction	Physically interpretable and directly related to catalyst performance	Requires extensive ex-situ characterization; expensive and time-consuming	Lab characterization (XRD, BET, TEM, TPD, Chemisorption)
Process descriptors	Temperature, H ₂ pressure, LHSV (liquid hourly space velocity), H ₂ /oil ratio, feed flow rate, reaction time, WABT (weighted average bed temperature)	Process optimization, soft sensors, yield prediction	Easily obtained from laboratory and industrial operations (DCS)	Limited transferability across different operating conditions; ignores catalyst age	DCS / Plant historian (real-time sensors)
Feedstock descriptors	Total sulfur content, total nitrogen content, aromaticity (e.g., total aromatics %), API gravity, density, viscosity, CCR (Conradson carbon residue), asphaltene content (n-C ₇ insolubles)	Feed characterization, catalyst deactivation, process optimization	Captures gross feedstock variability at the bulk level	Poor representation of molecular complexity (e.g., sulfur speciation is lost)	ASTM lab assays (D4294, D5453, D4683, D189, D6560)
Molecular descriptors (2D/3D)	Molecular weight, normal boiling point, dipole moment, HOMO/LUMO energies, C–S bond dissociation energy, logP, polarizability	Structure-activity relationships (SAR), reactivity prediction	Physically meaningful; quantum-chemically interpretable	Limited to individual molecules; does not capture mixture interactions	DFT / Computational chemistry or PubChem/ ZINC databases
Molecular fingerprints	Morgan fingerprints (ECFP), MACCS keys, Topological fingerprints (RDKit), Atom-pair fingerprints	Molecular property prediction, virtual screening, QSAR modeling	Encodes molecular substructures with high predictive performance; fast to compute	Reduced interpretability (bit vectors are abstract); loss of 3D conformation	RDKit / OpenBabel (generated from SMILES strings)
Graph representations	Atom-bond graphs (nodes = atoms; edges = bonds); optionally with atomic features (element, hybridization, charge, chirality)	Graph Neural Networks (GNNs), catalyst discovery, reaction prediction	Preserves complete molecular topology; automatic feature extraction; captures steric effects	Requires large datasets; high computational cost; difficult to deploy in real-time	RDKit / PyTorch Geometric / DGL (generated from SMILES)
Computational descriptors	DFT-derived adsorption energy, Bader charge density, d-band center (Norskov), sulfur vacancy formation energy, work function	Catalyst screening (e.g., volcano plots); hybrid ML models (PINN inputs)	Strong physical significance; improves model extrapolation and interpretability	Computationally expensive (scales with system size); limited to simplified surface models	DFT calculations (VASP, Quantum ESPRESSO, Gaussian)

quantification, whereas ANNs generally require larger datasets but offer greater flexibility for modeling complex multivariable systems. Hybrid approaches that integrate predictive ML models with optimization algorithms or mechanistic models provide additional opportunities for multi-objective optimization and improved process understanding. Overall, these models are particularly advantageous in HDS systems because they capture nonlinear interactions that are difficult to describe using conventional mechanistic models and can simultaneously account for the coupled effects of hydrosulfurization, hydrodeoxygenation, and hydrodenitrogenation reactions. The strengths, limitations, industrial readiness, and representative HDS applications of the most widely used machine learning algorithms are summarized in Table 9.

Once developed, ML models must undergo rigorous validation to ensure their robustness, generalizability, and reliability for catalyst design and process optimization. Model performance is commonly evaluated using statistical metrics such as the coefficient of determination (R^2), root mean square error (RMSE), mean absolute error (MAE), and average absolute relative error (AARE), which quantify the agreement between predicted and experimental values. However, high prediction accuracy alone does not necessarily indicate good model generalization, particularly for HDS datasets that are often limited in size and highly heterogeneous. Consequently, appropriate validation strategies are essential to assess model transferability and minimize overfitting. Hold-out validation is computationally efficient but can yield biased performance estimates for small datasets due to its dependence on a single data partition. Therefore, k-fold cross-validation has become the preferred validation strategy in many HDS studies [328,341], as it repeatedly trains and evaluates the model using different subsets of the available data, providing a more robust estimate of predictive performance. For model comparison and hyperparameter optimization, nested cross-validation further reduces model selection bias by separating hyperparameter tuning from model evaluation, although it requires significantly greater computational effort [342]. In addition, external validation using independent experimental or industrial datasets provides the most rigorous assessment of model transferability, yet it remains relatively uncommon because of the limited availability of publicly accessible refinery data. Hyperparameter optimization, typically performed using grid search, random search, Bayesian optimization, genetic algorithms, or other metaheuristic approaches, is employed to determine the optimal model architecture while balancing predictive accuracy and model complexity. Beyond deterministic validation, recent studies have emphasized uncertainty quantification through approaches such as Gaussian Process Regression (GPR), Bayesian Neural Networks, and ensemble learning, which estimate prediction confidence alongside prediction accuracy. Such probabilistic models are particularly valuable for industrial HDS applications, where uncertainty information supports risk-aware decision-making, catalyst screening, and process optimization under varying feedstock compositions and operating conditions.

Beyond prediction, an important aspect of the workflow is interpretation and knowledge extraction. ML models can provide insights into the relative importance of input variables and reveal key factors governing HDS performance across both conventional and alternative feedstocks. For instance, feature importance analysis can identify dominant parameters such as reaction temperature, catalyst dosage, or structural characteristics, thereby offering valuable guidance for catalyst design and process optimization. This step transforms data-driven models from purely predictive tools into instruments for scientific understanding. In particular, such analysis can help distinguish the roles of catalyst structure versus feed composition in governing competing reaction pathways in mixed or non-conventional feeds.

Finally, the developed models are deployed for practical applications, including process optimization, catalyst screening, and real-time monitoring in both refinery and emerging biorefinery contexts. In industrial settings, ML models can function as soft sensors, enabling the prediction of sulfur content or other key performance indicators in real

Table 9
Machine Learning Algorithms for HDS Applications.

Algorithm	Strength	Weakness	Best Application	Industrial Readiness
PLS (Partial Least Squares)	Industry standard; handles collinearity; fast	Linear latent variables only; no dynamics	Soft sensor backbone (baseline)	Very High
Linear regression	Highly interpretable; minimal training	Limited to linear relationships	Initial data screening / Benchmark baseline	High
Random Forest	Robust to outliers & non-linear; feature importance	Poor extrapolation beyond training range	Catalyst formulation screening	High
XGBoost	Excellent accuracy; handles missing data natively	Extensive hyperparameter tuning; black-box-ish	Process optimization (steady-state)	High
Gaussian Process	Excellent with small datasets; provides uncertainty (UQ)	Poor scalability (>10 k points); slow inference	Bayesian optimization in lab-scale kinetics	Medium
ANN (MLP)	Captures complex nonlinearities	Black box; requires large datasets	Yield prediction (well-defined feed stocks)	Medium
LSTM	Models temporal dynamics & time delays	Very data-hungry; prone to overfitting	Catalyst deactivation trajectory prediction	Medium
GNN (Graph Neural Network)	Molecular structure-aware; learns from 2D/3D molecular graphs	Computationally expensive; requires molecular descriptors	Structure-activity relationships (SAR); molecular design	Emerging / Lab
PINN	Physics-constrained; extrapolates well; interpretable	Complex architecture; high compute; immature deployment	Reactor simulation / Digital Twin development	Emerging / Lab

time, even when direct measurements are unavailable or costly. This is particularly valuable in co-processing systems, where petroleum and renewable feedstocks are blended, resulting in dynamic process behavior that is difficult to monitor using conventional methods. By supporting data-driven decision-making, these tools facilitate improved operational efficiency, reduced costs, and enhanced environmental performance. Overall, this workflow highlights the integration of experimental and computational approaches, forming a closed-loop system in which data continuously informs model development and optimization, ultimately accelerating innovation in HDS research and application across increasingly diverse and complex feedstock landscapes.

8. Machine learning applications in heavy feedstock hydrodesulfurization

8.1. Machine learning for catalyst design

Machine learning (ML) has emerged as a powerful tool for accelerating catalyst design in hydrodesulfurization (HDS), particularly in systems involving heavy feeds where traditional approaches are limited by the complexity of structure–activity relationships and the high dimensionality of catalyst and process variables. Conventional catalyst development relies heavily on empirical correlations and iterative experimentation, which are often insufficient to capture the nonlinear interactions among catalyst composition, morphology, and reaction conditions, and typically result in locally optimized rather than globally optimal solutions. In contrast, ML models can efficiently extract patterns from multidimensional datasets and establish quantitative relationships between catalyst descriptors and performance metrics, thereby supporting data-guided catalyst design, although not fully replacing mechanistic understanding.

A key application of ML in catalyst design lies in uncovering structure–activity relationships that are difficult to resolve using conventional regression or mechanistic approaches. Recent studies have demonstrated that ML algorithms can identify critical catalyst features governing activity and selectivity, such as pore size, slab length, and surface area, which are directly linked to the availability of active sites [329], although the interpretability of these relationships remains dependent on descriptor quality and dataset representativeness. By analyzing these descriptors, ML models provide insights consistent with experimental observations while offering a more systematic framework for catalyst optimization, but their predictive reliability may deteriorate when extrapolated beyond the training domain. Similarly, in gasoline HDS systems, ML has been used to decode complex synthesis-

structure–activity relationships, identifying key parameters such as promoter ratios and sulfidation conditions that control catalytic performance [255], although such models are often system-specific and may not generalize across different catalyst families.

Beyond interpretation, ML enables the rapid screening and discovery of new catalyst materials by prioritizing candidates within large compositional spaces. For example, ML-assisted analysis of electronic structure descriptors, such as metal-sulfur bond characteristics and crystal orbital Hamilton populations, has been used to identify promising transition metal sulfides with activity comparable to conventional Co-Mo-S catalysts [343]. This approach significantly reduces the need for computationally expensive first-principles calculations and accelerates the identification of cost-effective alternatives, although it typically depends on prior computational or experimental data for training. Furthermore, the integration of ML with high-throughput experimentation provides a scalable pathway for catalyst discovery, where large datasets generated from automated experiments are used to train predictive models that guide subsequent experiments in an iterative loop [344]. Careful experimental design is required to ensure data consistency and coverage of the chemical space.

Despite these advances, challenges remain in ML-driven catalyst design, particularly related to data availability and transferability. Catalyst datasets are often limited in size and lack consistency due to variations in experimental conditions and reporting standards. Additionally, ML models trained on specific systems may not generalize well to new catalysts or feedstocks, highlighting the need for improved descriptor design and integration of mechanistic knowledge. Nevertheless, ML has already demonstrated significant potential in transforming catalyst development from a trial-and-error process into a data-guided, predictive framework.

8.2. Machine learning for process optimization

In addition to catalyst design, machine learning has been widely applied to the optimization of HDS process conditions, where conventional optimization methods are often constrained by model simplifications. The HDS process is inherently complex, involving nonlinear interactions among temperature, pressure, hydrogen partial pressure, catalyst dosage, and feed composition, as well as dynamic variations in feedstock quality in industrial systems. Traditional optimization methods, which often rely on simplified models or single-variable analyses, are insufficient to capture these interactions and may lead to suboptimal operating conditions.

ML-based models offer a robust alternative by enabling accurate prediction and optimization of process performance across multiple

objectives without requiring explicit kinetic formulations. For instance, tree-based ensemble methods such as random forests, gradient boosting, and extreme gradient boosting have been successfully applied to model HDS processes, achieving high predictive accuracy for key outputs such as sulfur concentration, gas emissions, and process cost [327]. These models can simultaneously account for multiple input variables and their interactions, allowing for more comprehensive optimization compared to traditional approaches, but their performance remains highly dependent on the quality and representativeness of training data.

A major advantage of ML in process optimization is its ability to handle multi-objective problems through integration with optimization algorithms such as genetic algorithms or Bayesian optimization. In industrial HDS operations, optimizing sulfur removal must be balanced against minimizing hydrogen consumption, operational cost, and environmental impact. ML models can be integrated with optimization algorithms, such as genetic algorithms, to identify optimal operating conditions that satisfy multiple performance criteria simultaneously. This approach has been shown to significantly improve process efficiency while reducing emissions and operational costs.

Recent developments have extended machine-learning-assisted process optimization beyond conventional performance indicators, such as sulfur conversion and product yield, toward broader sustainability objectives. Rather than optimizing process performance alone, ML surrogate models are increasingly integrated with Techno-Economic Analysis (TEA) and Life Cycle Assessment (LCA) to evaluate economic feasibility together with environmental impacts throughout process development [345–347]. Because surrogate models can rapidly predict process performance, they enable repeated evaluation of large design spaces and can be coupled with multi-objective optimization algorithms to identify operating conditions [346] that simultaneously balance sulfur removal, hydrogen consumption, energy demand, operating cost, and environmental impacts. Such integrated frameworks provide a more comprehensive basis for decision-making than single-objective optimization and are particularly valuable for heavy-feed upgrading, where increasing reaction severity often improves desulfurization at the expense of higher hydrogen consumption and energy use. Consequently, integrating ML with TEA and LCA is emerging as an important strategy for developing economically viable and environmentally sustainable hydroprocessing technologies [348].

Furthermore, ML enables the development of data-driven soft sensors for real-time process monitoring and control, which can compensate for the limited availability or high cost of direct measurements in refinery environments. In many refinery systems, direct measurement of key variables such as sulfur content is challenging due to time delays or high costs. ML models trained on historical process data can predict these variables in real time, enabling more responsive and adaptive process control. This capability is particularly valuable for heavy oil HDS, where feed variability and operational disturbances are common. However, soft sensor performance may degrade under changing operating regimes or feedstock compositions, necessitating periodic model retraining and validation.

Despite these advantages, the application of ML to process optimization also faces challenges. The quality of predictions depends heavily on the availability of representative and high-quality data, and models may require periodic retraining to account for changes in feedstock or operating conditions. In addition, purely data-driven models may fail to capture fundamental process constraints, highlighting the importance of hybrid approaches that combine ML with mechanistic knowledge. Nonetheless, ML-based optimization represents a significant advancement over conventional methods, offering improved efficiency, flexibility, and scalability for industrial HDS processes.

8.3. Machine learning for catalyst deactivation and lifetime prediction

Catalyst deactivation is a critical issue in heavy oil hydrodesulfurization, as the presence of metals, asphaltenes, and coke

precursors in heavy feeds accelerates catalyst aging and reduces process efficiency often in a non-linear and time-dependent manner. Understanding and predicting catalyst deactivation and lifetime remain challenging due to the complex interplay of chemical, physical, and operational factors involved.

ML models can be trained based on historical operational and experimental data to identify patterns associated with catalyst deactivation and to predict performance decay trajectories over time, such as changes in catalyst activity, selectivity, and reactor pressure drop. Unlike conventional regression models that treat observations as independent samples, catalyst deactivation is inherently a sequential process in which the catalyst state depends on its cumulative operating history. Progressive coke formation, metal deposition, and structural changes evolve continuously during operation, resulting in strong temporal correlations [349,350] that are difficult to capture using static machine learning models [47,322]. Consequently, temporal machine-learning architectures, particularly Recurrent Neural Networks (RNNs) and Long Short-Term Memory (LSTM) networks, are well suited for modeling catalyst aging because they explicitly learn long-term dependencies from sequential process data. By utilizing historical operating variables—including feed composition, reactor temperature, hydrogen partial pressure, catalyst age, and pressure drop—these models can better describe the progressive evolution of catalyst activity loss and improve predictions of deactivation trajectories and remaining catalyst lifetime. Recent studies on refinery hydrodesulfurization soft sensors have demonstrated the application of LSTM- and GRU-based models for capturing temporal process dynamics and predicting sulfur-related process variables from continuously measured industrial data, highlighting the potential of these architectures for catalyst health monitoring and predictive maintenance [351]. This predictive capability enables proactive maintenance and catalyst replacement strategies, reducing unplanned shutdowns and improving overall process reliability, although its effectiveness depends on the availability of long-term, high-quality datasets.

In addition, ML can contribute to a deeper understanding of deactivation mechanisms by identifying correlations between operating conditions and degradation trends, even when mechanistic pathways are not fully resolved. For example, feature importance analysis can reveal the relative impact of parameters such as temperature, sulfur concentration, and metal deposition on catalyst stability. Such insights can guide the design of more robust catalysts and optimized operating conditions that mitigate deactivation effects. However, ML models may struggle to distinguish causation from correlation, particularly in complex systems where multiple deactivation mechanisms coexist.

The integration of ML with real-time process data further enhances its applicability for catalyst health monitoring. By continuously analyzing process variables, ML-based systems can detect early signs of catalyst deactivation and provide actionable recommendations for process adjustment. This approach aligns with the broader trend toward digitalization and smart refinery operations, where data-driven tools are used to enhance efficiency and sustainability [352].

However, accurate prediction of catalyst lifetime remains challenging due to limited availability of long-term datasets and the variability of industrial operating conditions. Furthermore, the extrapolation of short-term experimental data to long-term catalyst behavior introduces significant uncertainty. Combining ML with mechanistic understanding and multiscale modeling may provide a more comprehensive solution. Despite these challenges, ML-based approaches are increasingly recognized as valuable tools for managing catalyst performance and extending catalyst lifetime in heavy oil HDS systems.

8.4. Summary of ML applications in HDS

Machine learning (ML) has emerged as a powerful tool for accelerating catalyst development, optimizing operating conditions, predicting

catalyst deactivation, and enabling real-time process monitoring in hydrodesulfurization (HDS). Compared with conventional trial-and-error experimentation and mechanistic modeling, ML is capable of extracting nonlinear relationships among catalyst properties, feedstock characteristics, and operating conditions from multidimensional datasets, thereby reducing experimental effort and facilitating multi-objective optimization. Nevertheless, the successful deployment of ML in refinery-scale HDS depends not only on algorithm selection but also on data quality, feature representation, model reliability, and industrial applicability.

The predictive capability of ML models is fundamentally constrained by the quality and representativeness of the underlying datasets. Current HDS datasets are generally characterized by limited sample size, heterogeneous experimental protocols, inconsistent reporting standards, and restricted access to industrial operating data. Such limitations reduce model transferability and increase the risk of overfitting, particularly when the number of catalysts, feedstock, and process descriptors exceeds the number of available observations. Consequently, improving data quality through standardized experimental protocols, comprehensive catalyst characterization, and FAIR (Findable, Accessible, Interoperable, and Reusable) data practices are likely to have a greater impact on prediction accuracy than simply adopting increasingly sophisticated ML algorithms. Table 10 summarized the characteristics of data sources used for machine learning in hydrodesulfurization.

An additional challenge arises from the lack of standardized reporting of hydrodesulfurization performance across the literature. Depending on the study, model outputs are reported as sulfur conversion, sulfur removal efficiency, desulfurization percentage, residual sulfur concentration, or conversion of individual sulfur compounds (e.g., dibenzothiophene), which are not always calculated using identical definitions or analytical methods. Consequently, datasets compiled from multiple literature sources may contain inconsistent response variables (labels) together with variations in feed characterization, reactor configuration, and sulfur analysis. Without careful harmonization during data preprocessing, these inconsistencies can introduce label noise, reduce model generalizability, and complicate feature engineering by obscuring the true relationships between catalyst descriptors, feedstock characteristics, operating conditions, and HDS performance. Therefore, standardizing performance metrics and ensuring consistent data curation should be considered an essential prerequisite for developing reliable and transferable machine-learning models.

Another critical challenge concerns model reliability and generalization. Although many published studies report high coefficients of determination ($R^2 > 0.95$), these values are frequently obtained using random train-test splitting and may therefore overestimate predictive capability. Performance metrics reported for training datasets primarily reflect goodness-of-fit and should not be interpreted as indicators of model generalization. Validation datasets are commonly used for model selection and hyperparameter tuning, whereas independent test datasets—or preferably external datasets collected from different studies or operating conditions—provide the most reliable assessment of predictive performance on unseen data. Reliable assessment requires

rigorous validation strategies, including k-fold or nested cross-validation together with external validation using independent datasets whenever possible. Furthermore, uncertainty quantification remains largely absent from current HDS studies despite its importance for industrial decision-making. Probabilistic approaches, such as Gaussian Process Regression, Bayesian learning, and ensemble models, provide prediction intervals in addition to point estimates, allowing engineers to evaluate the confidence associated with catalyst screening and process optimization.

The effectiveness of ML is also strongly influenced by feature engineering and descriptor selection. Catalyst descriptors (e.g., metal loading, BET surface area, acidity, and MoS_2 slab morphology), feedstock properties (e.g., sulfur speciation, aromaticity, and asphaltene content), and operating parameters must adequately represent the physicochemical factors governing HDS performance. More recently, graph-based molecular representations and Graph Neural Networks (GNNs) have emerged as promising alternatives to conventional molecular descriptors by automatically learning structural features directly from molecular topology. Although these methods remain largely unexplored for HDS, they offer considerable potential for catalyst discovery and molecular reactivity prediction when larger and more standardized datasets become available.

Despite their excellent predictive performance, many ML models remain difficult to interpret, limiting their acceptance in industrial environments. Explainable artificial intelligence (XAI) techniques, including SHAP (Shapley Additive Explanations), permutation feature importance, and partial dependence analysis, provide valuable insights into the relative influence of catalyst properties, feed composition, and operating conditions on model predictions. Such approaches bridge the gap between purely empirical predictions and mechanistic understanding, thereby improving scientific interpretability and increasing confidence in ML-assisted catalyst design.

Finally, industrial implementation remains one of the most significant challenges for ML-assisted hydrodesulfurization. Industrial HDS units operate under continuously changing feed compositions, catalyst aging, equipment fouling, and process disturbances, whereas most published ML models are developed using static laboratory datasets. Future developments should therefore focus on dynamic learning architectures capable of handling time-dependent process behavior, integration with first-principles reactor models through hybrid physics-informed frameworks, continuous model updating using online process data, and deployment within refinery digital twins and advanced process control systems. Such developments will enable ML to evolve from an offline predictive tool into an active decision-support technology for intelligent refinery operation.

Fig. 13 summarizes the current applications of machine learning throughout the HDS workflow together with the major technical challenges that must be addressed before widespread industrial implementation can be achieved.

Table 10
Characteristics of data sources used for machine learning in hydrodesulfurization.

Data source	Typical size	Strengths	Limitations	Typical applications
Laboratory experiments	10–500 samples	High accuracy; well-controlled conditions	Small datasets; limited operating window	Catalyst screening, kinetic studies
Pilot-scale experiments	100–1000 samples	More representative of industrial operation	Expensive and time-consuming	Process optimization, scale-up
Industrial refinery data	10^3 – 10^6 samples	Large datasets; real operating conditions	Proprietary, noisy, missing values, catalyst aging, feed changes	Soft sensors, predictive maintenance, digital twins
DFT simulations	10^2 – 10^4 calculations	Electronic descriptors; mechanistic insight	Simplified models; high computational cost	Catalyst design, descriptor generation
High-throughput experimentation (HTE)	10^3 – 10^5 samples	Large, standardized datasets	Specialized equipment required	ML-assisted catalyst discovery

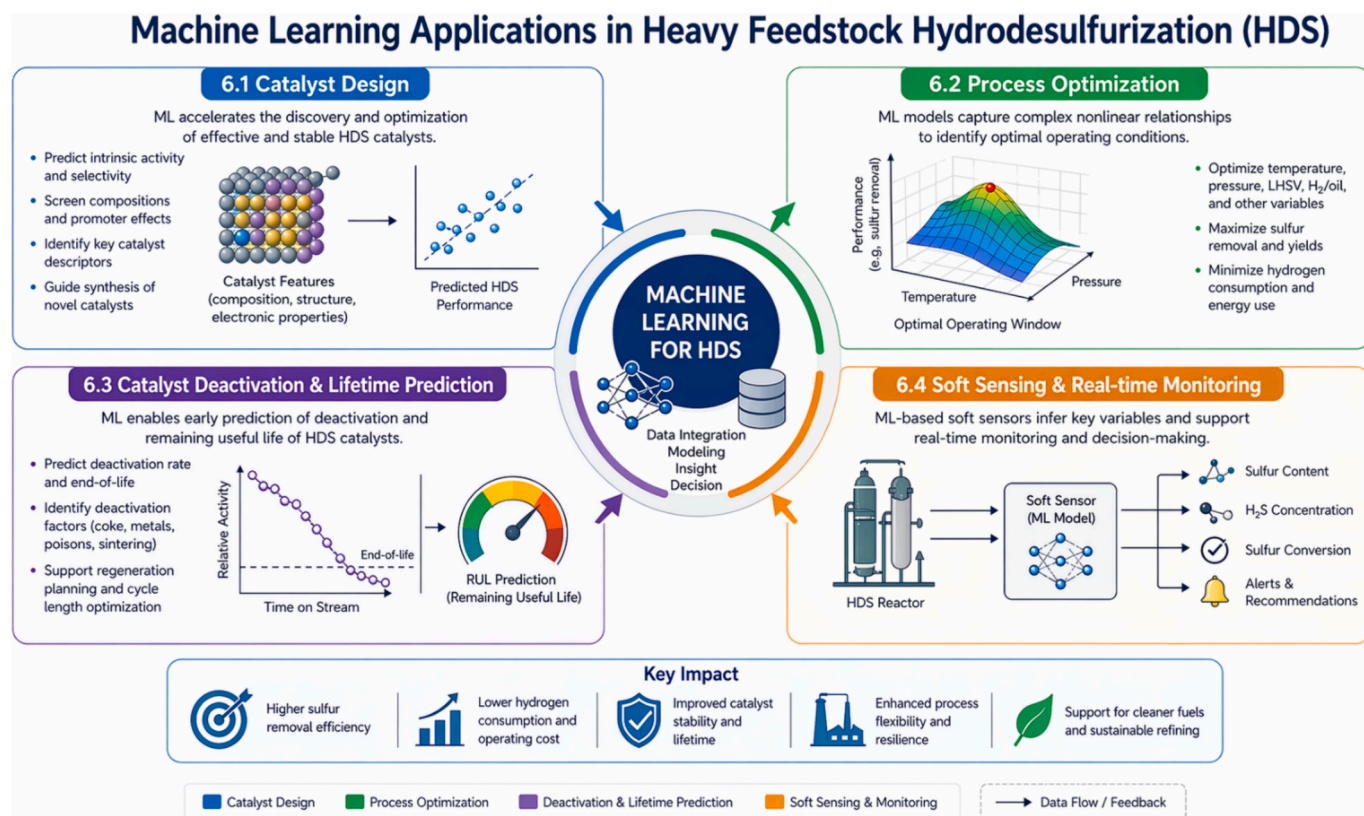


Fig. 13. Machine learning applications in heavy feedstock hydrodesulfurization.

8.5. Industrial deployment: Challenges and opportunities

Despite the rapid development of machine learning (ML) models for catalyst design, process optimization, and product property prediction, their industrial implementation in hydrodesulfurization (HDS) remains limited. Most published ML studies are developed using laboratory-scale datasets obtained under well-controlled operating conditions, whereas industrial HDS units operate under continuously changing feedstock compositions, catalyst aging, equipment fouling, and process disturbances. Consequently, models that exhibit excellent predictive performance under laboratory conditions often experience significant performance degradation when applied to refinery operations. This discrepancy highlights that industrial deployment requires not only accurate prediction models but also robust, transferable, and continuously adaptive learning frameworks.

One of the primary challenges is distribution shift, where the statistical characteristics of industrial data differ substantially from those used during model training. Laboratory datasets generally involve a limited number of catalysts, model sulfur compounds, or fixed operating conditions, whereas refinery feedstocks continuously vary in sulfur speciation, aromaticity, nitrogen content, metal contaminants, and asphaltene concentration. Furthermore, catalyst properties evolve throughout the operating cycle due to coke deposition, metal accumulation, and structural degradation, causing the input–output relationships learned during model training to gradually become invalid. Consequently, periodic model retraining or online adaptive learning becomes necessary to maintain prediction accuracy.

Another limitation concerns the quality of industrial process data. Refinery measurements are collected from hundreds of online sensors operating under harsh environments and are frequently affected by measurement uncertainty, missing values, sensor drift, communication failures, and maintenance interruptions. Unlike laboratory measurements, industrial datasets therefore require extensive preprocessing,

including outlier detection, missing-value imputation, signal filtering, normalization, and synchronization of variables collected at different sampling frequencies. Failure to adequately address these issues often introduces systematic errors that cannot be compensated for by increasingly sophisticated ML algorithms.

Besides, it should be recognized that commercial hydroprocessing is already supported by extensive proprietary databases, pilot-plant studies, reactor models, and digital twins developed by process licensors, catalyst suppliers, and refinery operators. These resources are routinely used for catalyst evaluation, reactor design, process optimization, and performance monitoring using real industrial feedstocks. However, because such models are generally calibrated for specific catalyst systems and feedstocks with similar boiling ranges and compositional characteristics, their predictive capability is often limited when extrapolated to substantially different feedstocks, such as unconventional crudes, biomass-derived oils, waste-plastic pyrolysis oils, or highly aromatic residues. Consequently, improving the transferability and adaptability of data-driven models across chemically diverse feedstocks remains one of the major challenges for future ML-assisted hydroprocessing.

A related challenge is the absence of comprehensive public benchmark datasets for hydrodesulfurization. Unlike several other fields of catalysis and materials informatics, there is currently no open-source HDS database that systematically integrates catalyst composition, feedstock characteristics, operating conditions, catalyst deactivation behavior, and product quality across multiple studies. Most publicly available datasets originate from individual laboratory investigations employing model compounds or specific feedstocks, whereas industrial refinery datasets remain largely inaccessible because they contain commercially sensitive information on catalyst formulations, feedstock composition, operating strategies, and process economics. Consequently, although extensive industrial data exist, the limited availability of standardized and publicly accessible datasets restricts model

reproducibility, benchmarking, and the development of transferable machine-learning models. High-throughput experimentation (HTE) offers a promising strategy to complement existing industrial knowledge by rapidly generating large, internally consistent datasets through automated catalyst synthesis and parallel catalyst evaluation. Together with standardized reporting protocols, FAIR data principles, anonymized industrial datasets, and collaborative data-sharing initiatives among academia, catalyst suppliers, and refineries, these developments could substantially accelerate the establishment of reliable benchmark datasets and improve the generalizability of next-generation machine-learning models for hydroprocessing.

Model interpretability also remains an important barrier to industrial adoption. Although deep learning models frequently achieve superior predictive accuracy, their “black-box” nature limits operator confidence, particularly for safety-critical decisions involving reactor temperature, hydrogen consumption, or catalyst replacement schedules. Consequently, explainable artificial intelligence (XAI) techniques, including SHAP, permutation feature importance, and partial dependence analysis, are increasingly incorporated into refinery applications to identify the catalyst, feedstock, and operating variables that most strongly influence model predictions. Such approaches facilitate model verification, improve engineering confidence, and support process optimization while maintaining compliance with industrial safety requirements.

In addition, machine learning models applied to hydrodesulfurization can generally be categorized as either purely correlation-based or mechanistically constrained approaches. Correlation-based models learn statistical relationships directly from historical experimental or operational data and often achieve high predictive accuracy within the range of the training dataset. However, their predictive reliability may deteriorate when extrapolated to new catalysts, feedstocks, or operating conditions that differ substantially from those represented during model development. In contrast, mechanistically constrained or physics-informed models integrate reaction kinetics, reactor models, conservation laws, or first-principles simulations into the learning process. By embedding physical knowledge, these hybrid approaches improve model interpretability, reduce physically unrealistic predictions, and provide greater robustness for refinery-scale applications where operating conditions continuously evolve.

A further challenge is the integration of ML with existing refinery operation. Most current applications remain offline decision-support tools, where predictions are generated after experimental data have been collected. Future developments should instead focus on online learning and hybrid digital refinery frameworks, where ML models continuously receive real-time sensor data, update their predictions, and communicate with process control systems. Combining ML with first-principles reactor models, process simulators, and digital twins can improve model extrapolation beyond the range of historical operating conditions while preserving physical consistency. Such hybrid approaches are expected to be particularly valuable for catalyst lifetime

prediction, hydrogen management, predictive maintenance, and autonomous process optimization. The major barriers to industrial deployment of machine learning in hydrodesulfurization are summarized on Table 11.

Hence, the future success of ML-assisted HDS will depend less on developing increasingly complex algorithms than on improving data quality, model transferability, interpretability, and seamless integration with industrial process control systems [353]. Addressing these challenges will enable ML to evolve from an offline predictive tool into an intelligent decision-support system capable of optimizing refinery operation in real time.

9. Conclusions

Hydrodesulfurization (HDS) remains the cornerstone technology for producing ultra-low-sulfur fuels and enabling the processing of increasingly challenging heavy and alternative feedstocks. However, the transition from conventional light crude oils to vacuum gas oils, petroleum residues, biomass-derived oils, waste tire pyrolysis oils, and waste plastic pyrolysis oils has fundamentally increased the complexity of sulfur removal. The high abundance of refractory thiophenic compounds, the coexistence of nitrogen-, oxygen-, and metal-containing species, and the accelerated catalyst deactivation associated with these feeds demand a more comprehensive understanding of sulfur chemistry, catalytic mechanisms, and process interactions than ever before.

This review indicates that successful deep desulfurization depends on the synergistic optimization of catalyst properties, feedstock characteristics, and operating conditions. Advances in catalyst design—including improved active-phase engineering, metal-support interactions, hierarchical pore structures, and defect engineering—have enhanced the conversion of refractory sulfur compounds while mitigating coke formation and metal deposition. Nevertheless, catalyst deactivation remains the main limitation to long-term industrial performance, emphasizing the importance of regeneration strategies, predictive catalyst lifetime management, and hydrogen-efficient process operation. Moreover, because hydrodesulfurization occurs simultaneously with hydrodenitrogenation, hydrodeoxygenation, hydrodemetallization, and hydrocracking, future catalyst and process development must adopt a holistic perspective that balances sulfur removal, hydrogen utilization, product quality, catalyst stability, and overall process economics.

A primary contribution here is of reviewing the integration of catalytic fundamentals with emerging data-driven methodologies. Rather than treating machine learning as an independent research topic, we demonstrate how sulfur speciation, molecular descriptors, catalyst properties, and operating variables can be translated into informative features for predictive modeling. Recent developments in machine learning have shown considerable potential for accelerating catalyst

Table 11
Major barriers to industrial deployment of machine learning in hydrodesulfurization.

Challenge	Cause	Impact on ML performance	Potential solutions
Distribution shift	Changes in feedstock composition, catalyst aging, operating conditions	Reduced prediction accuracy and poor model generalization	Transfer learning, online learning, periodic model retraining
Limited data quality	Sensor drift, missing values, measurement noise, inconsistent sampling	Increased uncertainty and overfitting	Data cleaning, preprocessing, sensor validation, data reconciliation
Small labeled datasets	Limited catalyst testing and proprietary industrial data	Poor robustness of deep learning models	High-throughput experimentation, data sharing, active learning
Model interpretability	Black-box behavior of deep learning models	Low operator confidence and limited industrial acceptance	SHAP, LIME, feature importance analysis, XAI
Model transferability	Models trained under laboratory conditions	Poor performance in refinery operation	Hybrid physics-informed ML, external validation, transfer learning
Dynamic process behavior	Catalyst deactivation, feedstock switching, equipment fouling	Static models become obsolete over time	LSTM, Transformer models, adaptive learning, digital twins
Industrial integration	Difficulty coupling ML with process control systems	Limited real-time optimization capability	Digital twins, soft sensors, advanced process control (APC), model predictive control (MPC)

discovery, enabling soft sensing of product sulfur concentration, predicting catalyst deactivation, optimizing operating conditions, and supporting advanced process control through digital twins and refinery-wide decision-support systems. Compared with conventional trial-and-error experimentation, these approaches provide an efficient framework for navigating the complex, nonlinear relationships governing industrial hydrodesulfurization.

Even with these advances, several important challenges continue to limit industrial deployment. The scarcity of standardized, high-quality datasets, the heterogeneity of heavy feedstocks, distribution shifts between laboratory and refinery conditions, and the limited interpretability of many machine-learning models constrain model reliability and transferability. Future progress will therefore require the development of FAIR data infrastructures, standardized reporting protocols, explainable machine learning models, hybrid mechanistic–data-driven frameworks, and rigorous validation using industrial-scale datasets. Furthermore, next-generation optimization should move beyond maximizing sulfur conversion alone by incorporating hydrogen consumption, catalyst lifetime, energy efficiency, techno-economic performance, and life cycle environmental impacts into multi-objective optimization frameworks.

In summary, the future of hydrodesulfurization lies in the convergence of advanced catalysis, mechanistic understanding, process systems engineering, and artificial intelligence. Integrating these complementary disciplines will enable the transition from empirical process optimization toward intelligent, self-adaptive refinery operations capable of processing increasingly diverse and refractory feedstocks while simultaneously improving energy efficiency, reducing carbon emissions, and enhancing economic sustainability. Such a paradigm shift will be essential for catalyzing the evolving role of hydroprocessing within low-carbon, circular, and digitally enabled refining systems.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process.

During the preparation of this work, the authors used ChatGPT (OpenAI) to assist in generating Figs. 1, 11, 12, and 13. The authors reviewed and edited all generated content as needed and take full responsibility for the content of the article.

CRedit authorship contribution statement

Tung M. Nguyen: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jia Wei Chew:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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