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Reaction–Transport Regime Analysis for Desulfurization of Gas and Petroleum Streams: An Engineering Diagnostic Framework

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Abstract

Sulfur removal from natural gas, light hydrocarbons, diesel-range fuels, and heavy petroleum fractions is governed not only by intrinsic reaction chemistry but also by adsorption and catalytic surface phenomena, interphase mass transfer, internal diffusion, hydrodynamics, downstream separation, and energy input. This paper develops a diagnostic reaction–transport–separation framework for interpreting desulfurization performance across gas- and liquid-phase systems. Rather than providing an exhaustive review of all desulfurization technologies, representative routes are used to illustrate controlling regimes, including hydrodesulfurization, oxidative desulfurization, catalytic oxidation/sweetening, adsorption/reactive adsorption, and radical-assisted oxidation. Systems are classified as reaction-controlled, external-mass-transfer-limited, internal-diffusion-limited, separation-limited, energy/intensification-limited, or mixed using apparent kinetic constants, volumetric mass-transfer coefficients, effectiveness factors, Thiele moduli, and Damköhler-type ratios. Hydrodynamic cavitation is treated as an intensification layer that may improve interfacial renewal, oxidant activation, and apparent rates only when these benefits exceed energy, erosion, emulsion, and separation penalties. A dimensionless cavitation enhancement factor is proposed to relate apparent rate improvement to measurable cavitation intensity while avoiding double-counting of physical and chemical effects. Illustrative ODS and HDS calculations show how regime analysis prevents overinterpretation of apparent rate constants. The framework provides an engineering basis for selecting hybrid reactors and defining validation requirements for scale-up, including sulfur speciation, closed sulfur balances, independent mass-transfer measurements, catalyst or adsorbent durability, oxidant utilization, and energy-normalized sulfur removal.

Keywords: desulfurization; hydrodesulfurization; oxidative desulfurization; adsorption; hydrodynamic cavitation; mass transfer; reaction engineering; sulfur removal; process intensification; kinetic modeling

1. Introduction

Sulfur compounds in natural gas, refinery streams, and petroleum-derived fuels create environmental, operational, and economic challenges. During combustion, sulfur-containing fuels produce sulfur oxides, which contribute to acid rain, particulate formation, catalyst poisoning in downstream emission-control devices, and air-quality deterioration. In natural gas and industrial gas streams, hydrogen sulfide is toxic, corrosive, and hazardous, while mercaptans produce severe odor problems and can cause corrosion and product-quality issues. In petroleum refining, thiophenes, benzothiophenes, dibenzothiophenes, and alkylated dibenzothiophenes are particularly important because their aromatic structure and steric hindrance make them difficult to remove under mild conditions [1-6,10-14,29].

Industrial desulfurization has therefore become a central part of gas processing and petroleum refining. For natural gas, common technologies include amine absorption, physical solvents, chemical scavengers, adsorption, catalytic oxidation, and sulfur recovery through Claus-type processes. For refinery liquid fuels, hydrodesulfurization remains the benchmark technology. It converts sulfur-containing hydrocarbons into hydrogen sulfide through catalytic hydrogenolysis and hydrogenation reactions, usually over sulfided Co–Mo/Al_2O_3 or Ni–Mo/Al_2O_3 catalysts [1–4,34,40]. Although hydrodesulfurization is reliable and industrially mature, its effectiveness decreases for refractory aromatic sulfur compounds, especially sterically hindered molecules such as 4,6-dimethyldibenzothiophene [34,41,42]. Achieving ultra-low sulfur levels may require severe temperature and pressure, high hydrogen consumption, and large reactor volumes [1-4,10-12].

Alternative and complementary desulfurization methods have therefore received sustained attention. Oxidative desulfurization can transform sulfur compounds into more polar sulfoxides and sulfones under relatively mild conditions, followed by extraction or adsorption. Adsorptive desulfurization can remove sulfur compounds selectively at low temperature, but it is often limited by capacity, regeneration, competitive adsorption, and slow diffusion in microporous structures. Catalytic oxidation and sweetening processes can convert mercaptans into disulfides or hydrogen sulfide into elemental sulfur, although these transformations do not always represent complete sulfur removal unless products are separated. Electrochemical and photocatalytic methods provide low-severity oxidation routes but face limitations associated with electrode fouling, photon penetration, catalyst recovery, and scale-up. Radical-assisted processes can be very fast at the molecular level but are frequently controlled by mass transfer, oxidant activation, and scavenging reactions [5-9,15-20,31,32,37,38].

A common limitation across these approaches is that desulfurization is often discussed primarily from the perspective of intrinsic chemistry, while reactor-scale performance is governed by coupled chemical and physical phenomena. A high intrinsic rate constant does not guarantee high overall sulfur removal if oxidant transfer is slow, if sulfur compounds cannot access catalyst pores, if the feed contains competitive adsorbates, if emulsions complicate separation, or if energy input is excessive. Conversely, a process with moderate intrinsic kinetics may perform well when mass transfer, phase contact, adsorption, and reactor hydrodynamics are optimized [21-28,34,39].

This paper presents a focused regime-based kinetic-process framework that connects chemistry, transport, hydrodynamics and separation in advanced desulfurization. The aim is to provide a diagnostic engineering structure for deciding whether observed sulfur removal is controlled by intrinsic reaction kinetics, adsorption or surface reaction, external mass transfer, internal diffusion, hydrodynamic contacting, downstream separation or energy efficiency [21-28].

The specific novelty is the integration of desulfurization chemistry with regime diagnosis and reactor selection. Rather than treating catalysts, oxidants, adsorbents or cavitation devices as isolated solutions, the framework links measurable quantities such as apparent kinetic constants, k_{La}, effectiveness factors, Thiele moduli, Damköhler ratios, cavitation intensity and energy-normalized sulfur removal to the controlling process regime [21-28].

Hydrodynamic cavitation is treated as a representative intensification layer rather than a universal solution. Its contribution is separated into possible improvements in interfacial transfer, oxidant activation, apparent kinetic enhancement and surface renewal, while recognizing the penalties of energy input, erosion, emulsion formation, heat generation and downstream phase separation [21-25,34,39].

Accordingly, the objectives are to:

1. Classify the dominant sulfur species and treatment routes for natural gas, light petroleum fractions, middle distillates, and heavy petroleum fractions;
2. Summarize representative reaction pathways and kinetic forms for hydrodesulfurization, oxidative desulfurization, catalytic oxidation, adsorption, radical-assisted oxidation, and briefly contextualize electrochemical and photocatalytic routes as additional regime examples;
3. Develop a unified kinetic–process framework linking intrinsic reaction rates, catalytic surface effects, mass transfer, internal diffusion, adsorption, and hydrodynamic intensification;
4. Introduce a dimensionless hydrodynamic-cavitation enhancement factor that can be experimentally estimated from apparent rate constants or measurable cavitation intensity;
5. Identify major reactor-design implications, scale-up challenges, and validation requirements.

The framework is intended to guide model development, experimental design, and reactor selection. It is not presented as a final predictive model; rather, it provides a structured basis for developing validated kinetic and process models for different feed types and desulfurization pathways.

2. Sulfur Species, Feed Classification, and Process Context

Desulfurization strategy depends strongly on the type of feed, the chemical form of sulfur, the required product specification, and the downstream treatment route. Natural gas and petroleum liquids should not be treated as identical systems because they differ in phase behavior, sulfur speciation, concentration range, operating pressure, downstream separation requirements, and safety constraints [1-12,29].

2.1 Sulfur species in natural gas and gas-treatment systems

Natural gas and acid-gas streams may contain H_2S, mercaptans, COS, CS_2, sulfides, and disulfides, depending on gas source, processing history, and upstream treatment. In such gas systems, important limitations include gas–liquid mass transfer, solvent selectivity, regeneration energy, sulfur handling, corrosion control, and catalyst or adsorbent deactivation. In aqueous alkaline oxidation systems, the chemical form of sulfur depends strongly on pH, redox potential, oxygen supply, and residence time [10-12,33].

For natural-gas desulfurization, especially H_2S absorption into amine, alkaline, or physical-solvent systems, the observed removal rate is often controlled by gas–liquid mass transfer, liquid-phase reaction, or a combination of both. A simplified gas-side flux expression may be written as [26–28]:

$$N_{H_2S} = k_G a(P_{H_2S} - P^*_{H_2S})$$

where N_{H_2S} is the volumetric absorption rate of hydrogen sulfide, $k_G a$ is the volumetric gas-side mass-transfer coefficient, P_{H_2S} is the bulk gas-phase partial pressure of hydrogen sulfide, and $P^*_{H_2S}$ is the equilibrium partial pressure corresponding to the liquid-phase concentration. This expression shows that removal depends not only on solvent chemistry, but also on interfacial area, gas velocity, liquid circulation rate, contactor geometry, solvent loading, temperature, and pressure.

For reactive absorption, the liquid-phase reaction can enhance absorption by consuming dissolved H_2S or HS^- near the interface. A practical diagnostic comparison can be made between the characteristic reaction rate and mass-transfer rate. For a pseudo-first-order liquid-phase reaction, a gas-treatment Damköhler-type ratio may be written as [26–28]:

$$Da_{abs} = \frac{k_{rxn}}{k_L a}$$

where k_{rxn} is the apparent liquid-phase reaction constant and $k_L a$ is the volumetric liquid-side mass-transfer coefficient. When $Da_{abs} \ll 1$, liquid-phase reaction is slow relative to transfer and solvent chemistry or reaction kinetics may control. When $Da_{abs} \approx 1$, absorption and reaction are coupled. When $Da_{abs} \gg 1$, the reaction is fast and the observed removal may become controlled mainly by gas–liquid contacting, interfacial area, solvent circulation, or diffusion through the liquid film.

This regime distinction is important because increasing solvent reactivity or alkalinity will not necessarily improve H_2S removal if the absorber is already gas–liquid-transfer-limited. In that case, improvements should focus on contactor design, packing efficiency, gas/liquid distribution, pressure drop, solvent circulation, foaming control, and regeneration capacity. Conversely, if the process is reaction- or equilibrium-limited, changing solvent formulation, pH, redox chemistry, or operating temperature may be more effective. Therefore, natural-gas desulfurization should be evaluated using H_2S partial pressure, solvent loading, $k_G a$or $k_L a$, equilibrium driving force, reaction enhancement, regeneration energy, corrosion tendency, and sulfur recovery performance.

2.2 Sulfur species in liquid petroleum fractions

Liquid petroleum fractions contain a broader distribution of organosulfur compounds. Light fractions may contain thiols, sulfides, and disulfides, whereas diesel and heavier fractions contain thiophenes, benzothiophenes, dibenzothiophenes, alkylated dibenzothiophenes, and complex polyaromatic sulfur species. Reactivity generally decreases as aromaticity, molecular size, and steric hindrance increase [1-4,29].

A typical qualitative reactivity order is:

$$\mathrm{H_2S} > \mathrm{RSH} > \mathrm{RSR'} > \text{thiophenes} > \text{benzothiophenes} > \text{dibenzothiophenes} > \text{alkylated dibenzothiophenes}$$

This order is approximate and depends on process route. In hydrodesulfurization, the C–S bond environment, aromatic-ring hydrogenation, and steric accessibility strongly influence reactivity. In oxidative desulfurization, electron density on sulfur and accessibility of the oxidant to the sulfur atom are important. In adsorption, molecular size, polarity, π-interactions, and competitive adsorption determine uptake and selectivity [1-4,15,16].

2.3 Classification of feeds and dominant treatment routes

Desulfurization strategies must be selected according to feed composition, sulfur speciation, phase behavior, product-quality requirements, and downstream processing constraints. Natural gas, light hydrocarbons, gasoline, diesel, and heavy petroleum fractions contain different dominant sulfur compounds and therefore require different treatment routes. For example, gas streams are often governed by acid-gas removal, corrosion control, and sulfur recovery, whereas liquid fuels require catalytic, oxidative, adsorptive, or hybrid approaches depending on sulfur molecular structure and required sulfur specification. Table 1 summarizes representative feed categories, major sulfur species, established industrial treatments, emerging or complementary routes, and the main limitations that influence process selection.

Table 1. Classification of feed types, dominant sulfur species, treatment routes, and practical limitations.

Feed category	Major sulfur species	Common industrial treatment	Emerging or complementary routes	Main limitations
Natural gas and acid gas streams	H_2S, COS, CS_2, mercaptans	Amine treating, physical solvents, scavengers, Claus sulfur recovery, tail-gas treatment	adsorption, catalytic oxidation, electrochemical oxidation, membrane-assisted treatment	gas–liquid transfer, solvent regeneration, corrosion, sulfur handling, selectivity
LPG and light hydrocarbons	mercaptans, sulfides, disulfides	caustic extraction, Merox-type sweetening, adsorption	catalytic oxidation, reactive adsorption, electrochemical oxidation	product separation, spent caustic, disulfide management, odor control
Gasoline fractions	thiophenes, mercaptans, sulfides	selective hydrodesulfurization, sweetening	oxidative desulfurization, adsorption, reactive extraction	octane loss during deep HDS, olefin hydrogenation, selectivity
Diesel and middle distillates	benzothiophene, dibenzothiophene, alkylated DBTs	hydrodesulfurization	oxidative desulfurization, adsorptive desulfurization, hybrid oxidation–adsorption	refractory sulfur compounds, hydrogen demand, catalyst diffusion limitations
Heavy petroleum fractions	alkylated DBTs, thiophenic structures, sulfides, asphaltenic sulfur	severe HDS, hydrocracking, residue upgrading	catalytic oxidation, reactive adsorption, intensified hybrid reactors	high viscosity, internal diffusion resistance, catalyst deactivation, metals/asphaltenes

This classification shows why a unified but flexible kinetic–process framework is required. A single kinetic expression or reactor model cannot describe all desulfurization systems because the controlling phenomena vary with feed type and sulfur chemistry. Gas-treatment systems may be dominated by gas–liquid transfer, solvent regeneration, corrosion, and sulfur recovery, while liquid-fuel systems may be limited by refractory organosulfur chemistry, catalyst diffusion resistance, oxidant transfer, adsorption capacity, or downstream separation. Therefore, the model structure must be adapted to the dominant sulfur species, phase system, catalyst or adsorbent, transport regime, and reactor configuration [1-12,26-28].

3. Representative Reaction Pathways and Kinetic Characteristics

3.1 Hydrodesulfurization

Hydrodesulfurization converts organosulfur compounds into hydrocarbons and hydrogen sulfide using hydrogen over sulfided transition-metal catalysts. For a simplified sulfide, the overall reaction may be written as [1-4,30,40]:

$$\mathrm{R-S-R' + 2H_2 \rightarrow RH + R'H + H_2S}$$

For dibenzothiophene-type molecules, two major pathways are typically considered: direct desulfurization and hydrogenation [40–42]. In the direct desulfurization route, C–S bond cleavage produces biphenyl-type hydrocarbons and hydrogen sulfide:

$$\mathrm{DBT + 2H_2 \rightarrow biphenyl + H_2S}$$

In the hydrogenation route, the aromatic rings are first partially hydrogenated, which facilitates subsequent C–S bond cleavage:

Hydrodesulfurization kinetics are often described by Langmuir–Hinshelwood or Hougen–Watson expressions because reactants and inhibitors adsorb competitively on catalytic sites. A simplified surface-rate expression may be written as [1-4,26,27,40]:

$$r_{HDS} = \frac{kK_S C_S K_H C_{H_2}}{1 + K_S C_S + K_H C_{H_2} + K_P C_{H_2S} + \sum K_i C_i}$$

where C_S is the concentration of the sulfur compound, C_{H_2} is the dissolved or available hydrogen concentration, C_{H_2S} is the hydrogen sulfide concentration, C_i represents competing hydrocarbons or inhibitors, K_j are adsorption constants, and k is the surface reaction constant. In many practical reactor models, especially when hydrogen is in large excess, the rate is simplified to pseudo-first-order form:

$$-r_S = k_{obs} C_S$$

where k_{obs} includes effects of temperature, hydrogen pressure, catalyst loading, and inhibition.

The temperature dependence is commonly represented by the Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

where A is the pre-exponential factor, E_a is apparent activation energy, R is the gas constant, and T is absolute temperature. Apparent activation energies depend on compound structure and whether the measured rate is intrinsic or affected by diffusion. If measured activation energies are unusually low, mass-transfer or diffusion limitations may be present [26,27,40].

Typical HDS operating conditions for refinery streams are feed- and severity-dependent but generally involve elevated temperature, hydrogen pressure, and sulfided transition-metal catalysts:

- Temperature: approximately 300–400 °C;
- Pressure: several MPa;
- Hydrogen-to-oil ratio: feed- and unit-dependent;
- Catalysts: $Co–Mo/Al_2O_3$, $Ni–Mo/Al_2O_3$, $Ni–W/Al_2O_3$, and modified supports [1–4,34,40].

The main limitations of HDS are high hydrogen demand, difficulty removing sterically hindered refractory sulfur compounds, possible octane loss in gasoline due to olefin hydrogenation, catalyst deactivation by coke or metals, and internal diffusion resistance for heavy molecules. HDS remains industrially essential, but its limitations create opportunities for complementary polishing processes such as oxidative or adsorptive desulfurization. [1-4,14]

3.2 Oxidative desulfurization

Oxidative desulfurization converts organosulfur compounds into more polar oxidized species, usually sulfoxides and sulfones. These products are more easily removed from hydrocarbon phases by extraction, adsorption, crystallization, or membrane-based separation. The general oxidation sequence is [5,6,15,16,35-37]:

$$\mathrm{R-S-R'} \overset{[\mathrm{O}]}{\rightarrow} \mathrm{R-S(O)-R'} \overset{[\mathrm{O}]}{\rightarrow} \mathrm{R-S(O)_2-R'}$$

For dibenzothiophene, the simplified transformation is:

$$\mathrm{DBT} \rightarrow \mathrm{DBT\ sulfoxide} \rightarrow \mathrm{DBT\ sulfone}$$

Common oxidants include hydrogen peroxide, organic hydroperoxides, peracids, ozone, molecular oxygen under catalytic conditions, and combinations of oxidants with catalysts or phase-transfer agents [5,6,15,16,43-44].

In ODS, oxidant selection controls both the reaction pathway and the dominant engineering limitation. Hydrogen peroxide is the most common oxidant because it can supply active oxygen under mild conditions when activated by acids, polyoxometalates, titanium catalysts, ionic liquids, phase-transfer agents, or cavitation; however, unactivated H_2O_2 may be kinetically inefficient and excess oxidant can decompose without useful sulfur oxidation. Organic hydroperoxides and peracids provide stronger oxygen-transfer routes but introduce cost, stability, safety, and by-product concerns. Ozone offers high oxidative strength and may operate through direct oxidation and secondary radical pathways, but its performance is often constrained by gas–liquid transfer and utilization efficiency. Molecular oxygen is attractive for cost and atom economy, yet generally requires catalysts or co-oxidants because O_2 activation is slow under mild conditions. Radical-generating systems based on persulfate, Fenton-like chemistry, photocatalysis, electrochemistry, ultrasound, or hydrodynamic cavitation can accelerate oxidation through $\bullet OH$, $SO_4^{\bullet-}$, or related species, but their apparent rates depend strongly on radical generation, scavenging, phase transfer, oxidant efficiency, and energy input. Thus, oxidant choice should be evaluated using selectivity to sulfoxides/sulfones, oxidant utilization, separation compatibility, safety, and energy-normalized sulfur removal rather than sulfur conversion alone. This logic parallels Advanced Oxidation Process (AOP) analysis, where direct molecular oxidation and radical-mediated oxidation are distinguished and k_{app} is treated as an emergent process parameter rather than a purely intrinsic kinetic constant [49].

Catalysts may include heteropolyacids, transition-metal oxides, polyoxometalates, titanium-containing materials, supported metal catalysts, ionic liquids, carbon-based catalysts, and enzyme-inspired systems [5,6,15,16].

The kinetic form depends on oxidant concentration, catalyst type, solvent or extraction phase, and mass transfer. If oxidant is present in large excess and its concentration changes slowly, the rate may be approximated as pseudo-first-order with respect to sulfur compound concentration:

$$-r_S = k_{obs} C_S$$

where k_{obs} includes oxidant concentration, catalyst concentration, interfacial area, temperature, and phase-transfer effects. If both sulfur compound and oxidant concentrations vary significantly, a second-order or generalized power-law form may be used:

$$-r_S = k C_S^n C_{ox}^m$$

where C_{ox} is oxidant concentration and n and m are apparent reaction orders.

For liquid–liquid ODS systems, the observed rate may be limited not by intrinsic oxidation but by transport of oxidant or sulfur species across the interface. This is especially important when a polar oxidant phase contacts a nonpolar hydrocarbon phase. Interfacial area, mixing intensity, phase ratio, viscosity, and emulsification can strongly influence apparent kinetics. Therefore, kinetic constants measured under one mixing condition may not be transferable to another reactor unless mass-transfer effects are quantified [5,6,15,16].

Typical ODS conditons are milder than HDS:

- Temperature: often 30–100 °C depending on oxidant, catalyst, solvent, and feed composition [5,6,15,16,43-44];
- Pressure: usually atmospheric to moderate;
- Oxidant-to-sulfur molar ratio: commonly above stoichiometric requirement;
- Downstream separation: extraction or adsorption is usually required.

ODS has important advantages: it can treat refractory aromatic sulfur compounds under mild conditions and without high pressure. However, it also has limitations: oxidant cost, oxidant decomposition, sulfone separation, solvent recovery, possible hydrocarbon co-oxidation, emulsion formation, and scale-up of multiphase contactors. These limitations make process integration and reactor engineering as important as intrinsic catalyst activity [5,6,15,16,25].

3.3 Catalytic oxidation and sweetening of thiols and hydrogen sulfide [10-12,33]

Catalytic oxidation is widely used for mercaptan sweetening and selective hydrogen sulfide oxidation. For thiols, the common reaction is oxidation to disulfides:

$$2\mathrm{RSH} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{RSSR} + \mathrm{H_2O}$$

This reaction reduces odor and corrosivity but does not necessarily remove sulfur from the hydrocarbon phase unless the resulting disulfides are separated. Therefore, thiol oxidation should be described as sweetening when sulfur remains in the product phase, and as desulfurization only when coupled with product separation.

For hydrogen sulfide, selective oxidation may produce elemental sulfur:

$$\mathrm{H_2S} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{S^0} + \mathrm{H_2O}$$

Under strongly oxidizing conditions, further oxidation can form sulfur dioxide, sulfite, thiosulfate, or sulfate depending on the medium:

$$\mathrm{H_2S} + 2\mathrm{O_2} \rightarrow \mathrm{H_2SO_4}$$

Selective sulfur formation is often desirable because elemental sulfur is recoverable, while over-oxidation can create secondary pollution or downstream treatment burdens.

Catalysts for thiol and H_2S oxidation include cobalt phthalocyanine complexes, activated carbon, metal oxides, supported transition metals, alkaline catalysts, and redox mediators. Kinetic forms may be first-order in sulfur species under excess oxygen [10-12,33]:

$$-r_{RSH} = kC_{RSH}$$

or may include oxygen concentration and catalyst-site coverage:

$$r = \frac{k K_S C_S K_O C_{O_2}}{1 + K_S C_S + K_O C_{O_2} + K_P C_P}$$

In gas–liquid or trickle-bed systems, oxygen transfer and pore diffusion may control the observed rate. Catalyst deactivation by sulfur deposition, carbon fouling, or over-oxidation products can be significant. Thus, catalytic oxidation should be analyzed using both kinetic and transport criteria [10-12,26-28,33].

3.4 Adsorptive and reactive adsorptive desulfurization

Adsorptive desulfurization removes sulfur compounds through physical adsorption, chemisorption, π-complexation, acid–base interactions, metal–sulfur bonding, or reactive adsorption. It is particularly attractive for polishing streams to ultra-low sulfur levels because it can operate under mild conditions and can be selective when adsorbent chemistry is properly designed [7-9,31,32].

Common adsorbents include:

- Activated carbon and modified carbon materials;
- Zeolites exchanged with Cu^+, Ag^+, Zn^{2+}, or other cations;
- Alumina, silica, and metal oxides;
- Metal–organic frameworks;
- Mesoporous materials;
- Supported metal or metal-oxide sorbents;
- Reactive adsorbents that simultaneously oxidize and capture sulfur species.

The basic adsorption step can be written as:

$$\mathrm{S_{bulk}} + * \rightleftharpoons \mathrm{S_{ads}}$$

where $*$ represents an adsorption site. Equilibrium behavior is often described using Langmuir, Freundlich, or Langmuir–Freundlich isotherms. A Langmuir isotherm is:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

where q_e is equilibrium uptake, q_{max} is maximum capacity, K_L is Langmuir affinity constant, and C_e is equilibrium concentration. A Freundlich model is:

$$q_e = K_F C_e^{1/n_F}$$

Kinetic uptake is frequently fitted using the pseudo-second-order model:

$$\frac{dq}{dt} = k_2(q_e - q)^2$$

or in integrated form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

However, this model is empirical and should not be used alone as proof of chemisorption [47,48]. Mechanistic interpretation requires additional evidence such as isotherm shape, adsorption heat, regeneration behavior, spectroscopic analysis, competitive adsorption tests, diffusion modeling, and breakthrough data [7-9,31,32].

For reactive adsorption, adsorption and chemical transformation occur together:

$$\mathrm{S_{ads}} + \mathrm{O_{ads}} \rightarrow \text{oxidized sulfur product}$$

A simplified surface-reaction expression may be:

$$r_{surf} = \frac{k K_S C_S}{(1 + K_S C_S + \sum K_i C_i)^p}$$

where p depends on the assumed mechanism and number of occupied sites involved. For fixed-bed adsorbers, breakthrough modeling is essential. Useful descriptors include breakthrough time, mass-transfer zone length, bed utilization, adsorption capacity at breakthrough, regeneration efficiency, and performance loss over cycles.

Adsorptive desulfurization is limited by competing aromatics, nitrogen compounds, moisture, steric exclusion in micropores, adsorbent regeneration, capacity loss, and pressure drop in fixed beds. These issues should be included in process design rather than evaluated only through equilibrium uptake under idealized model-fuel conditions [7-9,31,32].

3.5 Radical-assisted oxidation

Radical-assisted processes rely on highly reactive species such as hydroxyl radicals, sulfate radicals, superoxide radicals, and other oxygen-centered intermediates. These radicals may be generated through peroxide activation, ozone decomposition, photocatalysis, electrochemistry, ultrasound, hydrodynamic cavitation, Fenton-like chemistry, or plasma-assisted systems [19,20,24].

For liquid-fuel organosulfur compounds, the desired products are generally sulfoxides and sulfones:

$$\mathrm{R-S-R'\rightarrow R-S(O)-R'\rightarrow R-S(O)_2-R'}$$

For H_2S or HS^- in aqueous or gas-treatment systems, oxidation may produce elemental sulfur under selective conditions:

$$\mathrm{H_2S/HS^-\rightarrow S^0}$$

or sulfate under stronger oxidation:

$$\mathrm{H_2S/HS^-\rightarrow SO_4^{2-}}$$

Hydroxyl radical reactions can have very high second-order rate constants, often making intrinsic radical reaction steps extremely fast. However, this does not necessarily imply fast reactor-scale sulfur removal. Radical lifetime, radical scavenging by hydrocarbons or solvents, oxidant decomposition, interfacial transport, and local radical generation strongly influence performance [19,20].

A simplified radical oxidation rate may be written as:

$$-r_S = k_{rad}C_SC_R$$

where C_R is the concentration of reactive radical species. Because C_R is difficult to measure directly, an apparent rate constant is often used:

$$-r_S = k_{obs}C_S$$

where k_{obs} reflects radical generation, radical consumption, mass transfer, and mixing. This reinforces the need for a kinetic–process framework rather than a purely molecular kinetic description [19,20].

Electrochemical and photocatalytic desulfurization routes are not treated here as stand-alone process reviews. In the present framework, they are relevant mainly because they illustrate additional regime limitations: electrode mass transfer, current efficiency, electrode fouling, photon penetration, catalyst recovery, light scattering, oxidant utilization, and scale-up of energy delivery. These routes can therefore be analyzed using the same diagnostic structure proposed for HDS, ODS, adsorption, and catalytic oxidation, but detailed technology-specific optimization is outside the scope of this paper.

4. Transport, Diffusion, and Regime Analysis

4.1 Interphase mass transfer

Many desulfurization systems are multiphase. Examples include gas–liquid absorption of H_2S, liquid–liquid oxidative desulfurization using polar oxidants, gas–liquid oxygen transfer in thiol oxidation, and slurry reactors containing liquid fuel, oxidant, and solid catalyst. In such systems, the observed rate may be controlled by interphase mass transfer.

A common volumetric mass-transfer expression is:

$$r_{mt} = k_La(C^* - C)$$

where k_La is the volumetric liquid-side mass-transfer coefficient, C^* is the equilibrium concentration at the interface, and C is the bulk concentration. Increasing interfacial area, turbulence, gas dispersion, or liquid circulation can increase $k_L a$, but excessive emulsification may complicate downstream separation [26-28].

For ODS, interphase transport is especially important because oxidants such as hydrogen peroxide are commonly in polar phases, while sulfur compounds are in the hydrocarbon phase. If the oxidant or active oxygen species cannot reach the sulfur compound efficiently, intrinsic catalyst activity may not translate into high overall conversion.

4.2 Internal diffusion and catalyst effectiveness

For porous catalysts and adsorbents, internal diffusion can limit observed rates. The effectiveness factor is defined as:

$$\eta = \frac{\text{actual rate inside porous particle}}{\text{rate if entire particle were at external surface concentration}}$$

For a first-order reaction in a spherical catalyst particle, the Thiele modulus may be approximated as [26,27,40]:

$$\phi = R_p \sqrt{\frac{k}{D_{eff}}}$$

where R_p is particle radius, k is the first-order rate constant, and D_{eff} is the effective diffusivity. When $\phi \ll 1$, internal diffusion resistance is small and $\eta \approx 1$. When $\phi \gg 1$, diffusion limitations are significant and $\eta \ll 1$.

Heavy petroleum fractions are particularly susceptible to diffusion limitations because large sulfur-containing molecules diffuse slowly through catalyst pores. This is one reason why severe hydrotreating or hydrocracking conditions are required for heavy feeds.

4.3 Damköhler number and limiting regimes

The Damköhler number compares the characteristic rate of reaction with the characteristic rate of transport. For a first-order liquid-phase process influenced by external mass transfer, a practical form is:

$$Da = \frac{k_{app}}{k_L a}$$

where k_{app} is an apparent first-order reaction constant and $k_L a$ is the volumetric mass-transfer coefficient. In this definition [26,27]:

- $Da \ll 1$: reaction is slower than mass transfer; the system is mainly reaction-controlled;
- $Da \approx 1$: reaction and mass transfer are comparable; the system is in a mixed regime;
- $Da \gg 1$: reaction is faster than mass transfer; the system is mainly mass-transfer-limited.

This regime interpretation is important for process intensification. If a system is reaction-controlled, improving catalyst activity or temperature may be effective. If it is mass-transfer-limited, increasing intrinsic rate may provide little benefit unless interfacial transport is improved. If internal diffusion is limiting, smaller catalyst particles, hierarchical pores, mesoporous supports, or lower-viscosity operation may be required.

4.4 Observed versus intrinsic kinetics

A central problem in desulfurization research is that measured apparent rate constants are often treated as intrinsic constants even when experiments are influenced by mixing, phase transfer, adsorption, diffusion, or catalyst deactivation. A robust kinetic study should therefore include [26,27]:

- Variation of stirring speed or flow velocity to test external mass-transfer effects;
- Particle-size variation to test internal diffusion effects;
- Independent measurement or estimation of $k_L a$;
- Catalyst-free and oxidant-free controls;
- Non-cavitating controls when cavitation is used;
- Sulfur speciation before and after reaction;
- Product separation and mass balance;
- Repeated catalyst or adsorbent regeneration cycles.

Without these checks, fitted rate constants should be described as apparent rather than intrinsic.

5. Proposed Kinetic–Process Framework

5.1 Conceptual structure

The proposed framework treats overall desulfurization performance as the result of four interacting layers:

1. Intrinsic chemical kinetics;
2. Catalytic, adsorptive, and interfacial phenomena;
3. Mass transfer, diffusion, and hydrodynamics;
4. Process intensification.

The proposed framework can be represented as a diagnostic sequence that begins with feed sulfur speciation and the required treatment target, then evaluates the dominant kinetic, surface, transport, intensification, and separation layers that control overall performance. This structure is intended to prevent overinterpretation of apparent rate constants and to guide the selection of reactor configuration, operating window, validation strategy, energy-efficiency metric, and scale-up pathway. The framework is not a universal predictive model; rather, it is a regime-classification tool for identifying whether a given desulfurization system is mainly reaction-controlled, mass-transfer-limited, diffusion-limited, separation-limited, or governed by mixed resistances.

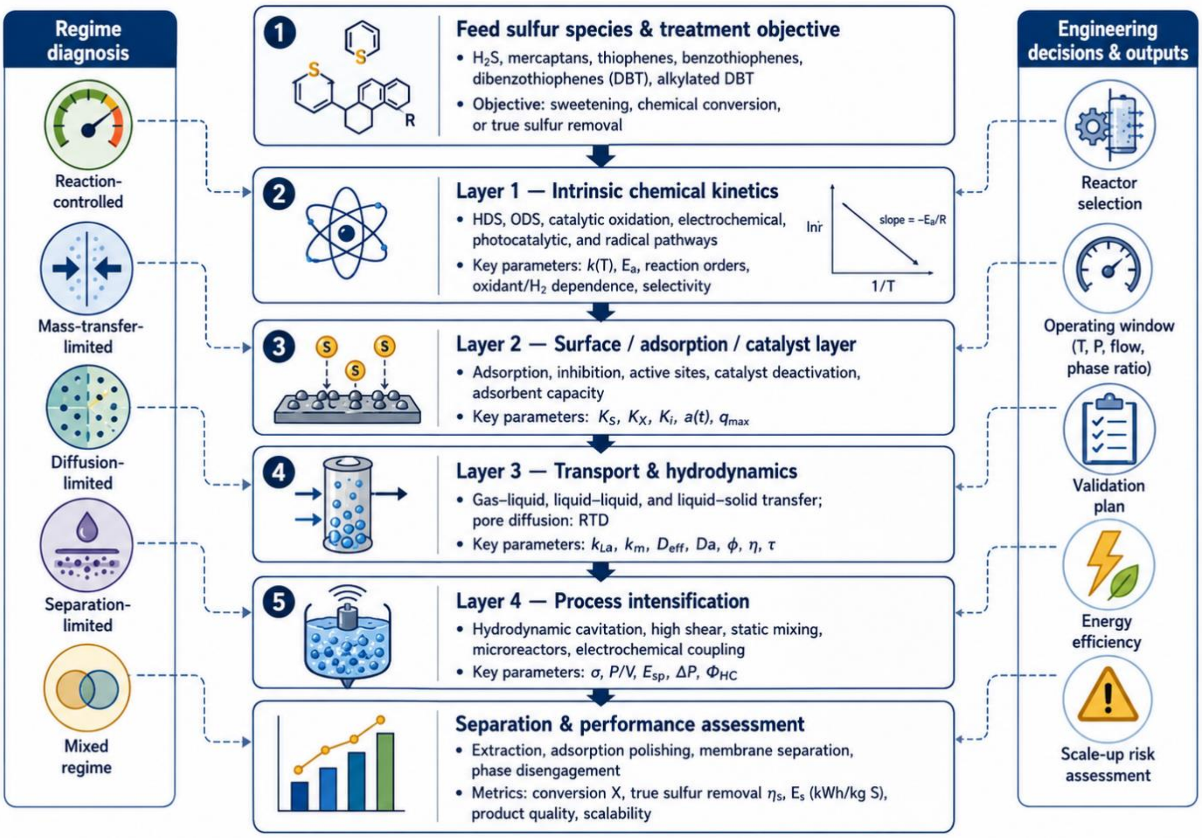


Figure 1. Conceptual diagnostic workflow for intensified desulfurization.

As shown in Figure 1, the same apparent sulfur-removal performance may arise from different controlling regimes. For example, a low observed rate may reflect slow intrinsic reaction kinetics, poor catalyst accessibility, external mass-transfer resistance, internal diffusion limitations, inefficient phase separation, or excessive energy input. Therefore, apparent kinetic constants should be interpreted together with sulfur speciation, $k_L a$, effectiveness factor, adsorption capacity, Damköhler number, residence time, separation efficiency, and energy-normalized sulfur removal. This regime-based interpretation is especially important for intensified systems such as hydrodynamic cavitation, where physical mass-transfer enhancement and chemical oxidant activation may occur simultaneously [26-28].

The conceptual relationship can be written as:

$$r_{overall} = f(r_{intrinsic}, r_{surface}, r_{transport}, r_{intensification})$$

where $r_{overall}$ is the observed sulfur-removal rate (mol L^{-1} s^{-1} or mol kg_cat^{-1} s^{-1}). This expression is not intended as a directly fitted equation; it defines the structure of the problem. A more practical generalized rate expression is:

$$r_{overall} = \eta\, k(T) C_S^n C_X^m \Phi_{MT} \Phi_{PI}$$

where:

- η is the dimensionless effectiveness factor for porous catalyst/adsorbent;
- $k(T)$ is the temperature-dependent kinetic constant (depends on reaction order);
- C_S is the concentration of the target sulfur compound (mol L^{-1});

- C_X is the concentration of the relevant co-reactant, such as hydrogen, oxygen, peroxide, ozone, or electro-generated oxidant (mol L^{-1});
- n and m are dimensionless apparent reaction orders;
- Φ_{MT} is a dimensionless correction factor for mass transfer;
- Φ_{PI} is a dimensionless process-intensification factor.

For hydrodynamic cavitation, Φ_{PI} may be replaced by Φ_{HC}, discussed in Section 6.

This expression is a diagnostic engineering form, not a universal mechanistic rate law. It should not be fitted with all correction factors simultaneously unless each factor is independently measured or constrained; otherwise, the model becomes non-identifiable. For example, if Φ_{MT} and Φ_{PI} are both adjusted freely using the same conversion data, the fitted parameters may compensate for each other and lose physical meaning. The units of $k(T)$ depend on the reaction orders $n$and m. If the rate is expressed as mol L^{-1} s^{-1} and concentrations are in mol L^{-1}, then $k(T)$ must have units that make the equation dimensionally consistent [26-28].

5.2 Intrinsic kinetic layer

The intrinsic kinetic layer describes chemical transformation in the absence of transport limitations. For HDS, it includes hydrogenolysis and hydrogenation. For ODS, it includes oxygen transfer to sulfur. For radical systems, it includes radical generation and radical reaction with sulfur species [26,27]. The Arrhenius equation is used to describe temperature dependence:

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right)$$

However, the apparent activation energy can be misleading if mass transfer or diffusion is important. Intrinsic activation energy should therefore be estimated only under conditions where transport limitations are minimized or quantified.

5.3 Surface and adsorption layer

The surface layer accounts for adsorption, surface reaction, competitive inhibition, pore diffusion, and deactivation. A generalized surface expression can be written as [26,27,30,40]:

$$r_{surface} = \frac{kK_S C_S K_X C_X}{(1 + K_S C_S + K_X C_X + \sum K_i C_i)^p}$$

where K_S, K_X, and K_i are adsorption constants for sulfur species, co-reactants, and inhibitors. The exponent p depends on the mechanism. For example, reactions involving two adsorbed species may have a squared denominator, while reactions between one adsorbed species and one dissolved species may have a different form.

Catalyst or adsorbent deactivation may be included through an activity factor $a(t)$:

$$r_{surface} = a(t) r_{surface,0}$$

A simple deactivation model is:

$$\frac{da}{dt} = -k_d a^q$$

where k_d is the deactivation constant and q is the deactivation order. In desulfurization, deactivation can result from coke deposition, sulfur deposition, metal poisoning, pore blockage, oxidant attack, or adsorbent saturation.

5.4 Transport layer

The transport layer accounts for external mass transfer, interphase transfer, internal diffusion, hydrodynamic residence-time distribution, and mixing. For first-order reaction coupled with external mass transfer, an approximate correction factor may be written as [26-28]:

$$\Phi_{MT} = \frac{k_L a}{k_L a + k_{app}}$$

This expression is dimensionally valid only when both $k_L a$ and k_{app} have units of s^{-1}. Hence, the effective observed rate constant becomes:

$$k_{\mathrm{eff}} = \Phi_{MT} k_{\mathrm{app}} = \frac{k_{\mathrm{app}} k_L a}{k_{\mathrm{app}} + k_L a}$$

Then:

$$-r_S = k_{\mathrm{eff}} C_S$$

This simplified expression should be used cautiously. In real ODS systems, $k_L a$, interfacial area, oxidant partitioning, and reaction may change simultaneously. More rigorous models may require coupled differential equations for each phase:

$$\frac{dC_{S,oil}}{dt} = -r_{rxn} - k_{L,S} a (C_{S,oil} - C_{S,int})$$

$$\frac{dC_{X,polar}}{dt} = -r_{rxn} - k_{L,X} a (C_{X,polar} - C_{X,int}) - r_{decomp}$$

where r_{decomp} accounts for oxidant decomposition. Such models are more complex but may be necessary for predictive reactor design.

5.5 Process-intensification layer

The process-intensification layer includes hydrodynamic cavitation, ultrasound, high-shear mixing, static mixers, microreactors, rotating packed beds, plasma-assisted oxidation, membranes, and electrochemical enhancement. The role of this layer is not simply to increase a rate constant; it may change several physical and chemical quantities simultaneously [21-28,34,39]:

- Interfacial area;
- Mass-transfer coefficient;
- Oxidant activation rate;
- Radical generation rate;
- Catalyst surface renewal;
- Residence-time distribution;
- Emulsion stability;
- Energy consumption;
- Separation difficulty.

Therefore, intensification must be evaluated using both kinetic benefit and process cost. A useful intensification strategy should increase sulfur removal per unit energy, per unit oxidant, or per unit reactor volume without creating unacceptable separation or durability problems.

5.6 Regime diagnosis and engineering decision algorithm

The preceding sections define the kinetic, surface, transport, diffusion, intensification, and separation variables that influence observed desulfurization performance. However, these variables are useful for engineering design only when they are applied in a systematic diagnostic sequence. The purpose of the present algorithm is therefore to translate the regime-based framework into a practical decision procedure for experimental interpretation, reactor selection, and scale-up assessment. The algorithm does not assume that a single rate expression or intensification method is universally valid. Instead, it first distinguishes chemical conversion from true sulfur removal, then identifies the feed, establishes a non-intensified baseline, tests external and internal transport limitations, verifies sulfur chemistry and mass balance, classifies the controlling regime, and finally selects an appropriate reactor or hybrid process using normalized performance metrics. In this way, apparent rate improvements are interpreted in terms of their physical origin and engineering value rather than being attributed automatically to intrinsic catalytic or chemical enhancement.

Step 1 - Define the target: distinguish sweetening, chemical conversion and true sulfur removal after separation.

Step 2 - Identify the feed: report phase, sulfur speciation, total sulfur, nitrogen/aromatic inhibitors, viscosity, water content and product sulfur specification.

Step 3 - Establish a non-intensified baseline: measure apparent kinetics at fixed temperature, phase ratio, oxidant or hydrogen dose, catalyst/adsorbent loading and residence time.

Step 4 - Test external transfer: vary stirring speed, recirculation rate, gas flow rate, pressure drop, gas–liquid contact area, packing performance, or solvent circulation rate. For natural-gas absorption, estimate or measure $k_G a$, $k_L a$, H_2S partial-pressure driving force, and solvent loading. If the apparent rate changes with hydrodynamics or contactor operation, the system is transport-affected.

Step 5 - Test internal diffusion and pore accessibility: vary catalyst or adsorbent particle size and estimate the Thiele modulus and effectiveness factor when porous solids are used.

Step 6 - Close the chemistry: determine sulfur speciation before and after reaction, oxidant utilization, product distribution and sulfur balance closure.

Step 7 - Classify the regime: use Damköhler-type ratios, $k_L a$, effectiveness factors and conversion/selectivity data to assign reaction control, mass-transfer control, diffusion control, separation control or mixed behavior.

Step 8 - Select the reactor or hybrid: use cavitation or high-shear contacting only when interfacial transfer, dispersion or oxidant activation is limiting; prioritize catalyst development when intrinsic chemistry is limiting; prioritize adsorption, extraction or membranes when separation is limiting.

Step 9 - Judge scale-up by normalized metrics: sulfur removed after separation, oxidant efficiency, energy per mass of sulfur removed, catalyst/adsorbent stability, pressure drop, phase disengagement, equipment wear and safety.

6. Hydrodynamic Cavitation as an Intensification Strategy

6.1 Mechanistic basis

Hydrodynamic cavitation occurs when local pressure in a flowing-liquid drops below the vapor pressure, leading to the formation of vapor cavities that subsequently collapse when pressure recovers [21–24,38,45,46]. Cavitation may occur in Venturi tubes, orifice plates, rotor–stator devices, high-pressure nozzles, and other constricted-flow geometries [21-24,34,39].

Bubble collapse can produce localized transient hot spots, high pressure, shock waves, microjets, turbulence, and strong interfacial renewal. These effects may enhance desulfurization through several mechanisms:

1. Improved dispersion of immiscible phases;
2. Increased interfacial area and volumetric mass transfer;
3. Enhanced oxidant decomposition or activation;
4. Local generation of reactive oxygen species;
5. Surface cleaning or renewal of catalysts and adsorbents;
6. Reduction of external boundary-layer thickness.

The often-reported extreme local temperatures and pressures during cavitation should be interpreted carefully. They are localized and transient estimates associated with bubble collapse, not bulk reactor conditions. Bulk temperature, pressure, energy input, and residence time remain the relevant parameters for reactor design and safety.

6.2 Cavitation number and intensity measures

A common dimensionless descriptor is the cavitation number [21–23,28,38,45,46]:

$$\sigma = \frac{P_d - P_v}{\frac{1}{2}\rho u^2}$$

where P_d is downstream pressure, P_v is vapor pressure, ρ is liquid density, and u is characteristic velocity through the cavitating constriction. Lower cavitation number generally indicates stronger cavitation, although the relationship depends on geometry, flow regime, dissolved gas content, temperature, and pressure recovery.

Cavitation intensity may also be represented by:

$$P_V = \frac{P}{V}$$

where P_V is power density (W m^{-3}), P is hydraulic or mechanical power input and V is treated liquid volume, or by specific treatment energy (J m^{-3} or kWh m^{-3}):

$$E_{sp} = \frac{Pt}{V}$$

where t is treatment time. Different intensity definitions are useful for different purposes. Power density is relevant for instantaneous reactor operation, while specific energy input is useful for comparing batch or recirculating systems.

6.3 Hydrodynamic-cavitation enhancement factor

To incorporate cavitation into the kinetic–process framework, a dimensionless enhancement factor can be defined as:

$$\Phi_{HC} = \frac{k_{obs,HC}}{k_{obs,0}}$$

where $k_{obs,HC}$ is the apparent first-order constant under cavitating conditions and $k_{obs,0}$ is the apparent first-order constant under otherwise identical non-cavitating conditions. This definition is experimentally practical and ensures that the total apparent cavitation enhancement factor $\Phi_{HC} = 1$ when cavitation provides no enhancement.

As a first approximation, the dependence of enhancement on cavitation intensity may be written as:

$$\Phi_{HC} = 1 + \alpha \Psi_{HC}^{\beta}$$

where:

$$\Psi_{HC} = \frac{I_{HC}}{I_{ref}}$$

$$I_{ref} = \left(\frac{P}{V}\right)_{ref} \text{ or } = \left(\frac{Pt}{V}\right)_{ref}$$

Here, I_{HC} may be P_V, E_{sp}, pressure drop, or another measurable cavitation-intensity descriptor, I_{ref} is a reference cavitation intensity, α is an empirical sensitivity coefficient, and β describes nonlinearity/sensitivity exponent. This form is simple but may overpredict enhancement at high intensity because real systems often show saturation, oxidant depletion, radical scavenging, emulsion limitations, or energy inefficiency.

A more realistic saturating form is:

$$\Phi_{HC} = 1 + \frac{\Phi_{\max} \Psi_{HC}^{\beta}}{K_E^{\beta} + \Psi_{HC}^{\beta}}$$

where Φ_{max} is the maximum attainable enhancement above the non-cavitating baseline and K_E is the dimensionless half-saturation intensity parameter. This expression prevents unlimited predicted enhancement and is more consistent with physical constraints.

6.4 Avoiding double-counting of cavitation effects

Cavitation may increase both the mass-transfer coefficient and the chemical activation rate [38,45,46,49]. Therefore, care is required when using both Φ_{MT} and Φ_{HC} in the same equation. If $k_L a$ is measured under cavitating conditions and included in Φ_{MT}, then Φ_{HC} should represent only additional chemical or radical effects not already captured by $k_L a$. Alternatively, if Φ_{HC} is measured as the overall ratio $k_{obs,HC}/k_{obs,0}$, then it already includes both physical and chemical enhancement.

A practical approach is to separate cavitation effects as follows:

$$\Phi_{HC,total} = \Phi_{HC,MT}\Phi_{HC,chem}\Phi_{HC,surface}$$

where:

- $\Phi_{HC,MT}$ represents mass-transfer enhancement;
- $\Phi_{HC,chem}$ represents oxidant activation or radical generation;
- $\Phi_{HC,surface}$ represents catalyst or adsorbent surface renewal.

This decomposition is conceptually useful, although each term requires independent experimental estimation. For early-stage studies, reporting only $\Phi_{HC,total}$ is acceptable if it is clearly described as an apparent enhancement factor.

6.5 Cavitation-assisted oxidative desulfurization

In cavitation-assisted ODS, hydrodynamic cavitation may improve contact between hydrocarbon and oxidant phases and accelerate oxidation of sulfur compounds to sulfones [5,6,15,16,25,37,38]. A simplified apparent rate expression is:

$$-r_S = k_{obs,HC} C_S$$

with:

$$k_{obs,HC} = k_{obs,0}\Phi_{HC,total}$$

Potential benefits include faster conversion, reduced catalyst loading, lower temperature, improved oxidant utilization, and smaller reactor volume. However, important risks include nonselective oxidant decomposition, formation of stable emulsions, increased separation cost, erosion of reactor components, and unfavorable energy consumption [25,37,38,45,46].

Therefore, performance should not be judged only by sulfur conversion. A more complete performance index may be:

$$PI = \frac{\Delta S}{E_{input}}$$

where ΔS is sulfur removed or converted and E_{input} is energy input. More detailed indices may include oxidant consumption, solvent use, product loss, and catalyst lifetime.

Case study: oxidative desulfurization of dibenzothiophene with and without hydrodynamic cavitation

To demonstrate how hydrodynamic cavitation may shift the controlling regime in oxidative desulfurization, a simplified model case is considered for the oxidation of dibenzothiophene (DBT) in a liquid–liquid ODS system. The purpose of this case study is not to reproduce a specific experimental dataset, but to illustrate how the proposed kinetic–process framework can be used to diagnose whether the process is controlled by intrinsic oxidation kinetics, interphase mass transfer, or a mixed regime.

The simplified oxidation sequence is represented as:

$$DBT \rightarrow DBT\ sulfoxide \rightarrow DBT\ sulfone$$

Because DBT oxidation in ODS is often followed by extraction or adsorption of the more polar sulfone product, the present calculation describes **chemical conversion of DBT**, not complete sulfur removal from the fuel. True desulfurization requires a subsequent separation step and a closed sulfur balance.

For an apparent first-order batch model, the sulfur-compound concentration is described by:

$$\frac{dC_S}{dt} = -k_{\mathrm{eff}} C_S$$

where C_S is the concentration of DBT or target sulfur species in the hydrocarbon phase, and k_{eff} is the observed effective first-order rate constant. Integration gives:

$$C_S(t) = C_{S,0} \exp\left(-k_{\mathrm{eff}} t\right)$$

and the corresponding DBT conversion is:

$$X_S(t) = 1 - \frac{C_S(t)}{C_{S,0}} = 1 - \exp\left(-k_{\mathrm{eff}} t\right)$$

To account for coupling between intrinsic oxidation and interphase transport, the effective rate constant is approximated using a two-resistance expression:

$$k_{\mathrm{eff}} = \frac{k_{\mathrm{rxn}} k_L a}{k_{\mathrm{rxn}} + k_L a}$$

This two-resistance expression is used only as a lumped diagnostic approximation for first-order apparent behavior under constant hydrodynamic and phase-contacting conditions. It assumes constant k_{rxn}, constant $k_L a$, negligible oxidant depletion, unchanged interfacial area, no catalyst deactivation, and no downstream separation limitation. Therefore, it should not be interpreted as a universal mechanistic rate law for ODS systems.

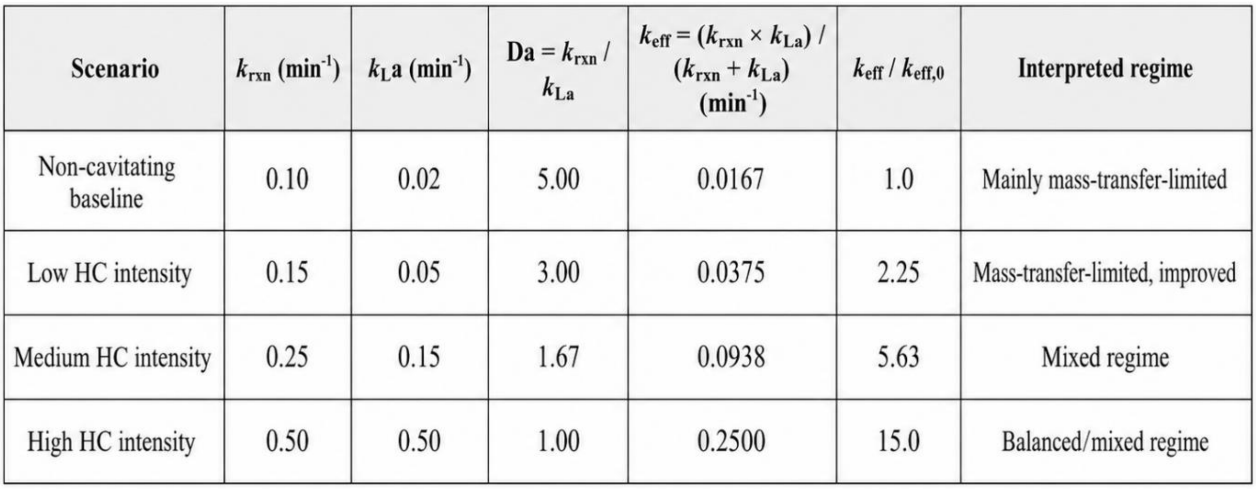
Here, k_{rxn} is the apparent chemical oxidation constant and $k_L a$ is the volumetric liquid-side mass-transfer coefficient. In the illustrative sensitivity calculation below, both parameters are expressed in min^{-1} to remain consistent with the time scale used in Table 3 and Figure 2. The corresponding Damköhler number is:

$$Da = \frac{k_{\mathrm{rxn}}}{k_L a}$$

In this definition, $Da \ll 1$indicates reaction-controlled behavior, $Da \approx 1$indicates a mixed regime, and $Da \gg 1$indicates mass-transfer-limited behavior.

For the non-cavitating baseline case, the system is assumed to have a relatively low volumetric mass-transfer coefficient because the oxidant-rich phase and hydrocarbon phase are poorly contacted. For the cavitating case, hydrodynamic cavitation is assumed to increase both interfacial renewal and apparent oxidant activation. The assumed parameters are shown in Table 2. The numerical values used in this illustrative case are intentionally hypothetical and are selected only to demonstrate possible regime transitions between mass-transfer-limited, mixed, and reaction-influenced operation. They should not be interpreted as representative industrial or laboratory ODS rate constants. The purpose of the calculation is therefore diagnostic rather than predictive: it shows how changes in apparent chemical oxidation rate and volumetric mass-transfer coefficient can alter the controlling regime. Quantitative application to a real ODS system would require experimentally measured sulfur speciation, oxidant concentration, interfacial area, $k_L a$, oxidant decomposition, phase disengagement behavior, and energy input.

Table 2. Sensitivity scenarios for the illustrative DBT–ODS model. Values are hypothetical and used only to demonstrate regime diagnosis, not to represent universal ODS kinetics.



Scenario	k_{rxn} (min^{-1})	k_{L}a (min^{-1})	Da = k_{rxn} / k_{La}	$k_{\mathrm{eff}} = (k_{\mathrm{rxn}} \times k_{\mathrm{La}}) / (k_{\mathrm{rxn}} + k_{\mathrm{La}})$ (min^{-1})	k_{eff} / $k_{\mathrm{eff,0}}$	Interpreted regime
Non-cavitating baseline	0.10	0.02	5.00	0.0167	1.0	Mainly mass-transfer-limited
Low HC intensity	0.15	0.05	3.00	0.0375	2.25	Mass-transfer-limited, improved
Medium HC intensity	0.25	0.15	1.67	0.0938	5.63	Mixed regime
High HC intensity	0.50	0.50	1.00	0.2500	15.0	Balanced/mixed regime

HC = hydrodynamic cavitation; DBT-ODS = dibenzothiophene oxidative desulfurization

The sensitivity calculation shows that hydrodynamic cavitation can produce modest, moderate, or large apparent improvements depending on how strongly it affects interphase mass transfer and apparent oxidant activation. In the baseline case, $Da = 5.0$, indicating that chemical oxidation is faster than interphase transport and that the observed process is mainly mass-transfer-limited. Under low HC intensity, both $k_{rxn}$and $k_La$increase, but the system remains primarily mass-transfer-limited. Under medium HC intensity, Daapproaches unity and the process enters a mixed regime. Under high HC intensity, $k_{rxn}$and $k_La$become comparable, and the effective rate increases substantially; however, this scenario should be interpreted as an upper illustrative case rather than a general expectation.

This result supports the central argument of the framework: the benefit of cavitation is not determined by cavitation intensity alone, but by whether the baseline process is limited by interphase transport, oxidant activation, intrinsic reaction, internal diffusion, or downstream separation. Once mass transfer is no longer the dominant resistance, further increases in cavitation intensity may produce diminishing returns unless they also improve oxidant utilization, catalyst accessibility, or separation efficiency. Therefore, apparent enhancement factors should always be reported together with $k_L a$, cavitation number, pressure drop, power density, residence time, temperature rise, sulfur speciation, and specific energy input.

The conversion values in Table 3 describe disappearance of the parent DBT compound only; they do not by themselves demonstrate fuel desulfurization unless oxidized sulfur products are subsequently removed and a closed sulfur balance confirms sulfur removal from the hydrocarbon phase.

The predicted DBT conversion as a function of time is shown in Table 3 and Figure 2.

Table 3. Predicted DBT conversion for the hypothetical sensitivity scenarios using $X_s = 1 - \exp(-k_{eff} t)$.

Time (min)	Baseline (%)	Low HC (%)	Medium HC (%)	High HC (%)
5	8.0	17.1	37.4	71.3
15	22.1	43.0	75.5	97.6
30	39.4	67.5	94.0	99.9
60	63.2	89.5	99.6	>99.9

These scenarios illustrate how different levels of hydrodynamic-cavitation-assisted transport and apparent oxidant activation can shift the system from a mass-transfer-limited regime toward a mixed reaction–transport regime.

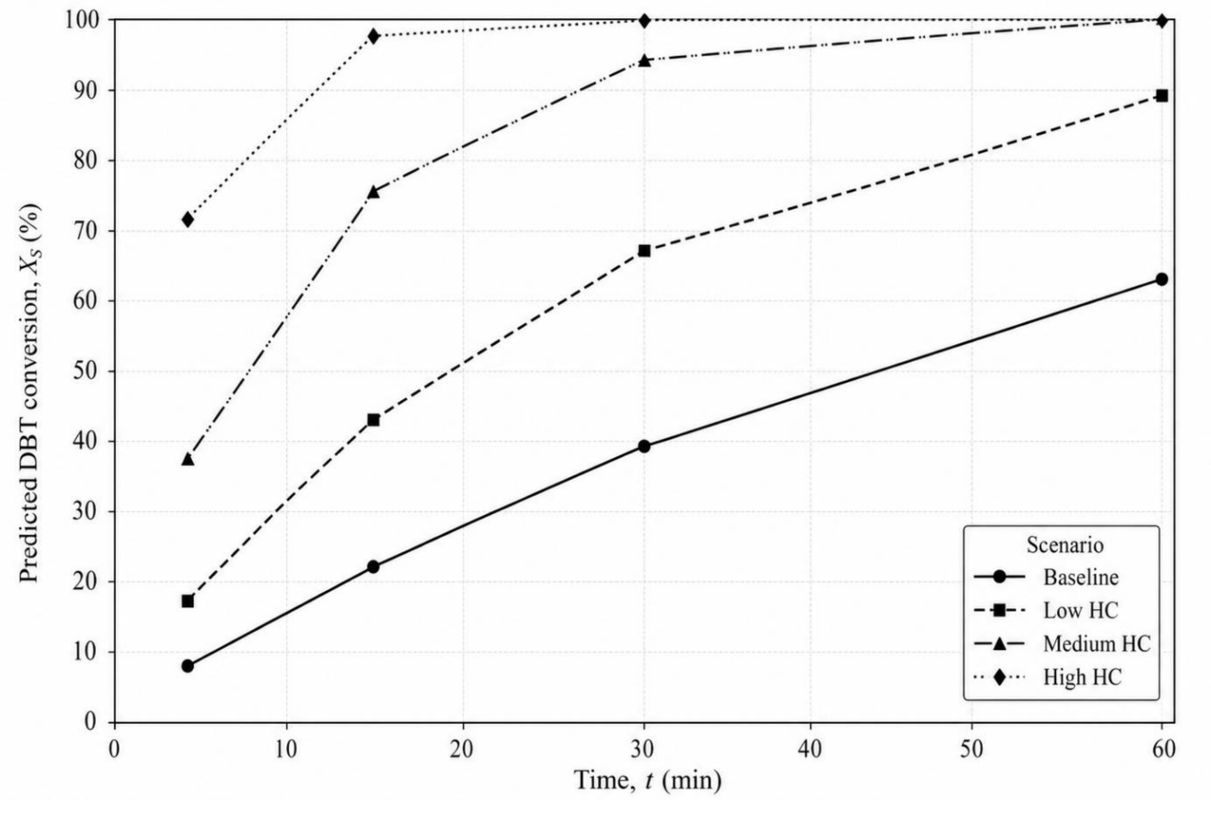


Figure 2. Sensitivity of predicted DBT conversion to hypothetical HC-assisted changes in k_{rxn} and $k_L a$. The curves are illustrative and intended for regime diagnosis rather than prediction of a specific ODS reactor.

This illustrative sensitivity calculation demonstrates three important points. First, hydrodynamic cavitation may increase the observed ODS rate not only by increasing apparent chemical activation, but also by improving interphase transport through enhanced dispersion, interfacial renewal, and volumetric mass transfer. Second, the magnitude of improvement depends strongly on the initial controlling regime. When the non-cavitating baseline is mainly mass-transfer-limited, increasing $k_L a$ can produce a substantial increase in the effective observed rate constant. However, once the system approaches a mixed reaction–transport regime, further increases in cavitation intensity may provide diminishing returns unless they also improve oxidant utilization, catalyst accessibility, or downstream separation. Third, the apparent enhancement factor should not be interpreted as a purely intrinsic kinetic effect unless $k_L a$, oxidant decomposition, interfacial area, mixing intensity, and temperature rise have been independently evaluated.

The case study also shows why the Damköhler number is useful for process diagnosis. In the non-cavitating baseline scenario, $Da = 5.0$, indicating that the apparent chemical oxidation step is faster than interphase transport and that the observed process is mainly mass-transfer-limited. As the assumed HC intensity increases, both k_{rxn} and $k_L a$ increase, while Da decreases from 5.0 toward values closer to unity. This indicates a transition from a mass-transfer-limited regime toward a mixed reaction–transport regime. Therefore, the role of HC is not simply to increase a single rate constant, but to alter the relative importance of chemical and transport resistances.

However, the calculated conversion refers only to disappearance of the parent DBT compound, not complete sulfur removal from the fuel. Complete desulfurization requires that DBT sulfoxide and DBT sulfone be removed from the hydrocarbon phase by extraction, adsorption, crystallization, membrane separation, or another downstream separation method. Therefore, a practical HC-assisted ODS process should be evaluated using sulfur removal after separation, oxidant utilization, energy input per mass of sulfur removed, product loss, phase disengagement behavior, and equipment durability. This prevents overestimating the industrial value of cavitation based only on rapid chemical conversion.

6.6 Cavitation-assisted catalytic oxidation and adsorption

In catalytic oxidation, cavitation can enhance oxygen or oxidant transfer to the catalyst surface and reduce liquid-film resistance. In reactive adsorption, cavitation may promote local oxidation of adsorbed sulfur species and partially regenerate active sites. However, cavitation may also damage fragile catalysts, cause attrition, detach active phases from supports, or increase fines formation [21-25,33,34].

For porous catalysts, the observed rate under cavitation may be written as:

$$r_{overall,HC} = \eta_{HC} a_{HC}(t) k(T) C_S^n C_X^m \Phi_{MT,HC}$$

where η_{HC} is the effectiveness factor under cavitating conditions and $a_{HC}(t)$ is time-dependent catalyst activity. Cavitation may increase external transfer but may not eliminate internal diffusion limitations inside micropores. Therefore, catalyst design should include mesoporosity, mechanical stability, and resistance to oxidative degradation.

7. Reactor Selection Based on the Assigned Controlling Regime

The proposed framework supports rational selection of reactor configurations based on the dominant limitation. If the system is reaction-controlled, improved catalyst or higher temperature may be effective. If the system is mass-transfer-limited, hydrodynamic intensification, static mixing, cavitation, micro-reaction, or high-interfacial-area contactors may be useful. If the system is diffusion-limited, catalyst-pore design and particle size become critical. If separation is limiting, extraction, adsorption, membranes, or phase-management strategies may dominate process design [21-28].

Selection of an intensified or hybrid reactor should be based on the dominant rate-limiting step rather than on the intensification method alone. Hydrodynamic cavitation, static mixing, slurry contacting, membrane coupling, and electrochemical enhancement can provide benefits only when their effects are matched to the controlling limitation, such as interphase mass transfer, oxidant activation, catalyst wetting, feed dispersion, electrode mass transfer, or downstream separation. Table 4 summarizes representative hybrid reactor concepts, their most suitable applications, principal design variables, expected benefits, and applied concerns. The table is intended as a reactor-screening guide rather than a universal ranking, because the best configuration depends on feed composition, sulfur speciation, phase behavior, catalyst or adsorbent stability, energy input, separation requirements, and scale-up constraints. Therefore, intensified reactors should be evaluated using both reaction performance and engineering penalties such as pressure drop, energy input, erosion, catalyst attrition, emulsion stability, and downstream separation efficiency [42,48,49].

Table 4. Representative hybrid reactor concepts for intensified desulfurization, including suitable applications, design variables, potential benefits, and applied concerns.

Reactor concept	Suitable application	Main design variables	Potential benefits	Main applied concerns
Venturi-loop cavitation reactor	HC-assisted ODS and oxidant activation	pressure drop, cavitation number, recirculation ratio, residence time, phase ratio	improved mixing, higher interfacial renewal, possible rate enhancement	energy cost, erosion, emulsion formation, scale-up of pressure recovery
Orifice-plate cavitation reactor	continuous oxidation or pretreatment	orifice diameter, number of holes, inlet pressure, downstream pressure	simple geometry, strong cavitation zones	clogging, erosion, limited control of residence-time distribution
Rotor–stator cavitation reactor	high-viscosity feeds or slurry systems	rotor speed, gap size, power density, catalyst loading	strong mixing, controllable shear	mechanical complexity, heat generation, catalyst attrition
Packed-bed reactor with HC pretreatment	catalytic oxidation, adsorption polishing	pretreatment severity, bed particle size, flow distribution	improved feed dispersion before catalyst bed	pressure drop, catalyst fouling, mismatch between pretreatment and bed residence time
Slurry HC reactor	catalyst-assisted ODS	catalyst concentration, particle size, mixing intensity, separation method	good contact among catalyst, oxidant, and oil	catalyst recovery, attrition, filtration cost
Membrane–cavitation hybrid	oxidation followed by selective separation	membrane material, solvent compatibility, fouling resistance, pressure	integrated reaction and separation	membrane fouling, solvent swelling, emulsion control

The reactor concepts summarized in Table 4 should be evaluated using multiple performance metrics rather than sulfur conversion alone. Important criteria include sulfur removal after separation, selectivity toward desired sulfur products, oxidant utilization efficiency, energy consumption, catalyst or adsorbent stability, product quality, separation efficiency, scalability, safety, corrosion behavior, and economic feasibility. A key distinction is between conversion and removal. Oxidizing DBT to DBT sulfone represents chemical transformation but not complete desulfurization unless the sulfone is separated from the fuel. Similarly, oxidizing mercaptans to disulfides is sweetening rather than true sulfur removal unless the disulfides are extracted, adsorbed, or otherwise removed. Therefore, hybrid reactor design should be assessed using complete sulfur balance, energy-normalized sulfur removal, and downstream separation performance.

Case study: hydrodesulfurization with and without hydrodynamic cavitation-assisted contacting

Hydrodesulfurization is fundamentally a catalytic hydrogenolysis and hydrogenation process that requires hydrogen availability, active sulfided catalyst sites, sufficient temperature, and appropriate reactor residence time. Therefore, hydrodynamic cavitation should not be interpreted as directly replacing the intrinsic catalytic function of HDS catalysts. Instead, its possible role in HDS-related systems is more realistically associated with improving feed dispersion, hydrogen–liquid contacting, external mass transfer, pretreatment of difficult feeds, or slurry-phase contacting where compatible reactor designs are used.

To illustrate this distinction, a simplified plug-flow model is considered for sulfur conversion in an HDS reactor. The purpose of this case study is not to reproduce a specific refinery dataset, but to demonstrate how the kinetic–process framework can be used to evaluate whether hydrodynamic cavitation could provide benefit when the observed HDS rate is partly limited by hydrogen contacting or external mass transfer.

For a pseudo-first-order plug-flow reactor, sulfur conversion may be written as:

$$X_S = 1 - \exp\left(-k_{\mathrm{eff}}\tau\right)$$

where X_S is sulfur conversion, k_{eff} is the observed effective first-order HDS rate constant, and τ is the reactor residence time.

The effective rate constant is approximated using a two-resistance expression:

$$k_{\mathrm{eff}} = \frac{k_{\mathrm{cat}} k_{La,H_2}}{k_{\mathrm{cat}} + k_{La,H_2}}$$

This expression is a simplified diagnostic approximation used to separate catalytic limitation from hydrogen-transfer or contacting limitation. It assumes pseudo-first-order HDS behavior, constant hydrogen availability, constant catalyst activity, negligible intraparticle diffusion limitation, and unchanged reactor hydrodynamics. It should not be interpreted as a universal HDS kinetic model.

where k_{cat} is the catalyst-controlled pseudo-first-order HDS constant and k_{La,H_2} is an apparent hydrogen contacting or hydrogen-transfer coefficient. Both parameters have units of min^{-1}. This expression is not a universal HDS rate law; it is a simplified diagnostic model that separates catalytic limitation from hydrogen-transfer/contacting limitation.

The corresponding Damköhler-type ratio may be written as:

$$Da_{HDS} = \frac{k_{\text{cat}}}{k_{La,H_2}}$$

In this definition, $Da_{HDS} \ll 1$ indicates that the catalytic step is slower than hydrogen transfer, while $Da_{HDS} \gg 1$ indicates that hydrogen transfer or external contacting is limiting. Values near unity indicate a mixed regime.

For the conventional HDS case, the system is assumed to be partly limited by hydrogen contacting. For the HC-assisted case, hydrodynamic cavitation is assumed to improve contacting before or within a compatible intensified contacting zone, while the intrinsic catalyst-controlled rate constant remains unchanged. The assumed parameters are summarized in Table 5.

Table 5. Assumed parameters for the illustrative HDS case study**.**

Parameter	Symbol	Conventional HDS	HC-assisted contacting	Unit
Catalyst-controlled HDS constant	k_{cat}	0.025	0.025	min^{-1}
Hydrogen contacting coefficient	k_{La,H_2}	0.020	0.100	min^{-1}
Damköhler-type ratio	$k_{\text{cat}}/k_{La,H_2}$	1.25	0.25	-
Effective observed rate constant	k_{eff}	0.0111	0.0200	min^{-1}
Residence time	τ	60	60	min
Predicted sulfur conversion	X_S	48.7	69.9	%

Using the assumed parameters, the conventional case gives:

$$k_{\text{eff,0}} = \frac{(0.025)(0.020)}{0.025 + 0.020} = 0.0111 \text{ min}^{-1}$$

and therefore:

$$X_{S,0} = 1 - \exp\left[-(0.0111)(60)\right] = 0.487$$

or approximately 48.7% sulfur conversion.

For the HC-assisted contacting case:

$$k_{\text{eff,HC}} = \frac{(0.025)(0.100)}{0.025 + 0.100} = 0.0200 \text{ min}^{-1}$$

and therefore:

$$X_{S,HC} = 1 - \exp\left[-(0.0200)(60)\right] = 0.699$$

or approximately 69.9% sulfur conversion.

The apparent process enhancement is therefore:

$$\frac{k_{\mathrm{eff,HC}}}{k_{\mathrm{eff,0}}} = \frac{0.0200}{0.0111} \approx 1.8$$

This simplified calculation shows that hydrodynamic cavitation-assisted contacting could improve observed HDS performance when the baseline process is partly limited by hydrogen transfer, feed dispersion, or external contacting. In the example, increasing k_{La,H_2} from 0.020 to 0.100 min^{-1} increases the predicted sulfur conversion from 48.7% to 69.9% at the same residence time. However, the enhancement is moderate compared with the ODS case because the catalytic constant k_{cat} is unchanged. Once hydrogen contacting becomes sufficiently fast, further increases in k_{La,H_2} provide diminishing returns unless the catalyst activity, temperature, hydrogen pressure, pore accessibility, or inhibition behavior is also improved.

This case study highlights an important engineering distinction. In ODS, hydrodynamic cavitation can potentially enhance both interphase oxidant transfer and oxidant activation. In HDS, by contrast, the primary chemistry remains governed by the catalyst, hydrogen pressure, sulfur-compound structure, temperature, and pore diffusion. Therefore, hydrodynamic cavitation should be considered only as an auxiliary intensification layer for contacting or pretreatment, not as a direct substitute for catalytic HDS.

The model also shows how regime analysis can prevent overinterpretation of apparent improvements. In the conventional case, $Da_{HDS} = 1.25$, indicating a mixed regime with appreciable hydrogen-contacting resistance. In the HC-assisted case, $Da_{HDS} = 0.25$, indicating that hydrogen contacting is improved and the process moves closer to catalyst-controlled behavior. Under these conditions, additional cavitation intensity would have limited value unless it also improves catalyst accessibility, reduces fouling, lowers viscosity, or enhances feed distribution without causing erosion, catalyst attrition, excessive pressure drop, or safety concerns.

For industrial implementation, this type of HC-assisted HDS configuration would be most plausible as a pretreatment or contacting-enhancement step upstream of a catalyst bed, or in slurry/reactive-contacting systems where cavitation can be applied without damaging fixed-bed catalyst structures. It is less suitable for direct application inside conventional high-pressure fixed-bed HDS reactors unless reactor materials, catalyst mechanical stability, hydrogen safety, pressure control, and erosion risks are carefully addressed.

Therefore, hydrodynamic cavitation is most likely to be beneficial when the baseline process is limited by interphase transport, poor dispersion, slow oxidant activation, external film resistance, or catalyst surface fouling. It is less likely to provide major benefit when the dominant limitation is intrinsic catalytic chemistry, internal pore diffusion, equilibrium adsorption capacity, downstream sulfone separation, oxidant cost, catalyst deactivation, or excessive energy consumption. Therefore, HC should be selected only after identifying the controlling regime using Da, k_La, apparent activation energy, particle-size tests, sulfur mass balance, and energy-normalized sulfur removal.

8. Validation Strategy for the Proposed Framework

The proposed framework requires quantitative validation before it can be used predictively. A recommended validation strategy includes the following steps [26-28]:

Table 6. Minimum evidence required for assigning controlling regimes and selecting corrective engineering actions.

Assigned regime	Minimum evidence required	Typical corrective design action
Reaction-controlled	Apparent rate is insensitive to stirring, flow rate and particle size; activation energy is physically plausible; sulfur speciation confirms the intended reaction pathway.	Improve catalyst, temperature, active sites, oxidant activation or hydrogen availability.
External-mass-transfer-limited	Apparent rate increases with stirring, recirculation, gas flow, interfacial area or pressure drop; Da is greater than unity when $k_{\mathrm{rxn}}/k_L a$ is used.	Increase $k_L a$ using better dispersion, static mixing, cavitation, smaller bubbles/droplets or improved contactor design.
Internal-diffusion-limited	Smaller catalyst/adsorbent particles or larger pores increase rate/capacity; Thiele modulus is high and effectiveness factor is below unity.	Use smaller particles, hierarchical/mesoporous supports, improved pore architecture or lower-viscosity operation.
Adsorption/separation-limited	Sulfur is converted but remains in the hydrocarbon phase; extraction, adsorption or membrane step controls final sulfur level.	Improve solvent/adsorbent/membrane selectivity, phase disengagement, regeneration and product recovery.
Energy/intensification-limited	Rate improves under cavitation or high shear, but energy per mass sulfur removed, erosion, heat generation or emulsion formation becomes unfavorable.	Optimize pressure drop, residence time and geometry; compare against non-intensified baseline and alternative contactors.

8.1 Baseline kinetic experiments

Experiments should first be conducted without cavitation or other intensification to estimate baseline apparent kinetics. For ODS, model compounds such as thiophene, benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene can be used before moving to real fuels. The experiments should vary sulfur concentration, oxidant concentration, catalyst loading, temperature, and phase ratio.

The rate law can be fitted using:

$$-r_S = kC_S^n C_X^m$$

or pseudo-first-order form when appropriate:

$$\ln\left(\frac{C_S}{C_{S,0}}\right) = -k_{obs}t$$

The fit should be supported by sulfur speciation, not only total sulfur measurement, because conversion of one sulfur compound into another may be misinterpreted.

8.2 Mass-transfer assessment

Mass-transfer limitations should be evaluated by varying stirring speed, flow velocity, gas flow rate, or recirculation rate. If the apparent rate changes significantly with mixing intensity, the system is not purely reaction-controlled. Independent measurement of $k_L a$ is recommended when possible.

The regime can be classified using **Damköhler number**:

$$Da = \frac{k_{app}}{k_L a}$$

The following number interpretation is correct **only when both k_{app} and $k_L a$ have units of $\mathbf{s^{-1}}$**:

- $Da \ll 1$: reaction-controlled;
- $Da \approx 1$: mixed regime;
- $Da \gg 1$: mass-transfer-limited.

8.3 Diffusion assessment

For catalysts or adsorbents, particle-size variation can reveal internal diffusion limitations. If smaller particles produce higher apparent rates or capacities at the same chemistry, internal diffusion is likely important. The Thiele modulus and effectiveness factor should be estimated when possible:

$$\phi = R_p\sqrt{\frac{k}{D_{eff}}}$$

$$\eta = \frac{\text{observed rate}}{\text{intrinsic rate without diffusion limitation}}$$

8.4 Cavitation validation

For hydrodynamic cavitation, experiments should compare cavitating and non-cavitating conditions at otherwise identical temperature, residence time, oxidant dose, catalyst loading, and phase ratio. The apparent enhancement can then be calculated as:

$$\Phi_{HC} = \frac{k_{obs,HC}}{k_{obs,0}}$$

Cavitation intensity should be reported using at least one measurable parameter such as cavitation number, pressure drop, power density, or specific energy input. Ideally, more than one descriptor should be reported to improve comparability across reactor geometries.

8.5 Product analysis and sulfur balance

A strong validation study should include a sulfur mass balance:

$$S_{feed} = S_{product} + S_{extract} + S_{adsorbent} + S_{gas} + S_{loss}$$

where $S_{product}$ is residual sulfur in treated fuel or gas, $S_{extract}$ is sulfur in the extraction phase, $S_{adsorbent}$ is sulfur captured by adsorbent, S_{gas} is sulfur in gaseous products, and S_{loss} represents unaccounted sulfur. This is essential because apparent sulfur disappearance may result from phase transfer, adsorption, volatilization, or analytical error rather than chemical destruction.

8.6 Energy and economic indicators

For industrial relevance, the process should be evaluated using energy-normalized and reagent-normalized metrics, such as:

$$E_S = \frac{E_{input}}{m_{S,removed}}$$

where E_S is energy consumed per mass of sulfur removed. Oxidant efficiency may be expressed as:

$$\eta_{ox} = \frac{\text{moles of sulfur oxidized}}{\text{moles of oxidant consumed}/\nu}$$

where ν is the stoichiometric oxidant requirement per mole of sulfur. These metrics help determine whether apparent kinetic improvement is practically meaningful.

9. Industrial Translation and Scale-Up Considerations

Industrial desulfurization technologies must satisfy performance, reliability, safety, and economic requirements. A process that performs well with model fuel in batch laboratory experiments may not be suitable for refinery or gas-processing operation [1-4,10-12,28]. Key scale-up issues include the following.

9.1 Feed complexity

Real fuels contain many competing compounds, including aromatics, olefins, nitrogen compounds, oxygenates, metals, asphaltenes, and water. These components can compete for catalyst or adsorbent sites, scavenge radicals, consume oxidant, stabilize emulsions, or deactivate catalysts. Therefore, experiments with model compounds should be followed by tests using real feedstocks [1-4,10-12,29].

9.2 Downstream separation

ODS and radical oxidation usually convert sulfur compounds into more polar products rather than directly removing sulfur. Extraction, adsorption, membrane separation, or filtration is then required. The separation step can dominate process cost and product yield. Solvent recovery, product loss, extractant stability, and wastewater generation must be considered [5,6,15,16,25].

9.3 Energy efficiency

Hydrodynamic cavitation, high-shear mixing, ultrasound, plasma, and electrochemical methods all require energy input. Their value depends on whether they reduce total cost or improve product quality enough to justify energy consumption. Energy-normalized sulfur removal is therefore a critical metric [21-25,28,34].

9.4 Materials durability

Cavitation can cause erosion of metal surfaces and damage to catalysts or adsorbents. Oxidants can corrode equipment or degrade supports. Sulfur deposition can plug reactors or foul electrodes. These effects must be evaluated under realistic operating times, not only short laboratory tests [21-25,28].

9.5 Safety

Desulfurization systems may involve hydrogen, hydrogen sulfide, oxygen, ozone, peroxides, high pressure, high temperature, or flammable hydrocarbons. Hybrid processes must be designed to avoid unsafe combinations, uncontrolled oxidant decomposition, overpressure, and ignition hazards.

9.6 Integration with existing infrastructure

New processes are more likely to be adopted if they can operate as polishing units, pretreatment steps, or revamp options for existing units. For example, ODS or adsorptive polishing may be more practical downstream of conventional HDS than as a complete replacement. Cavitation-assisted oxidation may be useful as a compact pretreatment or intensification step if energy and separation costs are favorable.

10. Conclusions

This paper developed a kinetic–process framework for advanced desulfurization of natural gas and petroleum fractions. The central argument is that sulfur removal is governed not only by intrinsic chemical reaction rates but also by catalytic surface behavior, adsorption, interphase mass transfer, internal diffusion, hydrodynamics, oxidant utilization, and downstream separation [1-28]. Conventional and emerging desulfurization routes were reviewed and compared, including hydrodesulfurization, oxidative desulfurization, catalytic oxidation, adsorptive desulfurization, electrochemical and photocatalytic processes, and radical-assisted oxidation.

The framework organizes desulfurization into four coupled layers: intrinsic kinetics, surface and interfacial phenomena, transport and hydrodynamics, and process intensification. This structure allows reaction-controlled, mass-transfer-limited, diffusion-limited, and mixed regimes to be identified using dimensionless tools such as the Damköhler number, Thiele modulus, effectiveness factor, and mass-transfer correction factors.

Hydrodynamic cavitation was examined as a promising but not universally beneficial intensification strategy. It may enhance mixing, interfacial renewal, oxidant activation, radical formation, and apparent reaction rates. A dimensionless cavitation enhancement factor was proposed to connect observed kinetic improvement with measurable cavitation intensity. However, the model must be applied carefully to avoid double-counting mass-transfer and chemical effects.

Saturating enhancement expressions are more realistic than unlimited power-law forms at high cavitation intensity.

From an applied perspective, hybrid systems such as cavitation-assisted oxidative desulfurization, cavitation-assisted catalytic oxidation, reactive adsorption, and membrane–cavitation processes may offer useful advantages under selected conditions. Nevertheless, their industrial relevance depends on sulfur removal after separation, energy efficiency, oxidant utilization, catalyst stability, materials durability, safety, and compatibility with existing infrastructure.

In gas-treatment systems, quantitative evaluation should include gas–liquid absorption driving force, solvent loading, mass-transfer coefficients, reaction enhancement, regeneration energy, and sulfur recovery, because these variables often determine performance more directly than intrinsic reaction chemistry alone.

The proposed framework should therefore be viewed as a structured basis for experimental design and process modeling rather than as a fully validated predictive model. Future research should focus on controlled kinetic studies, sulfur mass balances, real-feed testing, independent mass-transfer measurements, cavitation-energy and -efficiency characterization, catalyst durability, and pilot-scale validation. With such validation, the framework could support the rational development of efficient, selective, and scalable desulfurization technologies.

Nomenclature

Symbol	Definition
A	pre-exponential factor
$a(t)$	time-dependent catalyst or adsorbent activity
a_e	electrode area per reactor volume
C	bulk concentration
C^*	equilibrium concentration at interface
C_i	concentration of inhibitor or competing species
C_R	radical concentration
C_S	concentration of sulfur-containing compound
C_X	concentration of co-reactant or oxidant
D_{eff}	effective diffusivity
Da	Damköhler number
E_a	apparent activation energy

E_{cav}	cavitation intensity parameter
E_{input}	energy input
E_{ref}	reference cavitation intensity
E_S	energy consumed per mass of sulfur removed
F	Faraday constant
i	current density
K_E	cavitation intensity at half-maximum enhancement
K_i	adsorption or inhibition constant for species i
K_L	Langmuir adsorption constant
K_S	adsorption constant for sulfur species
k	kinetic rate constant
k_{app}	fitted apparent kinetic constant under specified experimental conditions
k_d	deactivation constant
$k_L a$	volumetric mass-transfer coefficient
k_m	electrode mass-transfer coefficient
k_{obs}	experimentally observed pseudo-first-order constant
$k_{obs,0}$	apparent rate constant without cavitation
k_{eff}	effective rate constant after combining reaction and transport resistances.
k_{rxn}	apparent chemical oxidation constant used in the illustrative ODS model
k_{cat}	catalyst-controlled HDS constant in the illustrative HDS model.
m	apparent reaction order with respect to co-reactant or oxidant
n	apparent reaction order with respect to sulfur compound
n_e	number of electrons transferred
P	hydraulic or mechanical power input
P_d	downstream pressure

P_v	vapor pressure
q_e	equilibrium adsorption capacity
q_t	adsorption capacity at time t
q_{max}	maximum adsorption capacity
R	universal gas constant or particle-radius context where specified
R_p	catalyst or adsorbent particle radius
r	reaction rate
$r_{overall}$	overall sulfur-removal rate
T	absolute temperature
t	time
u	characteristic flow velocity
V	treated volume or reactor volume
α	empirical cavitation sensitivity coefficient
β	empirical cavitation response exponent
η	catalyst effectiveness factor
η_{ox}	oxidant utilization efficiency
ρ	liquid density
σ	cavitation number
ϕ	Thiele modulus
Φ_{HC}	hydrodynamic-cavitation enhancement factor
$\Phi_{HC,total}$	total apparent cavitation enhancement factor
Φ_{MT}	mass-transfer correction factor
Φ_{PI}	process-intensification factor
Φ_{max}	maximum cavitation enhancement above baseline
Ψ_{HC}	dimensionless cavitation intensity

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