

Kinetic Models of Deep Hydrotreating Reactions to Produce Ultralow Sulfur Diesel

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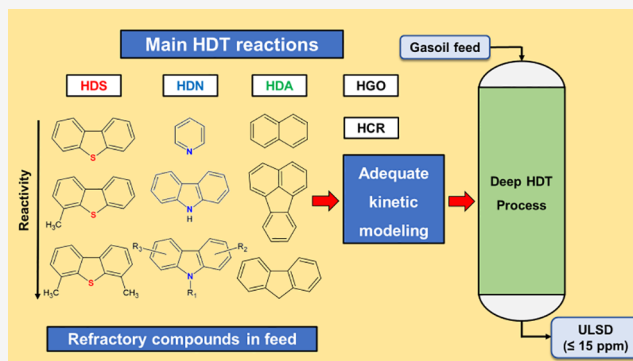
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ABSTRACT: Due to the current worldwide environmental problems caused by high emissions of polluting gases such as CO, NO_x, and SO_x resulting from the combustion of fossil fuels, many organizations and governments have established standards aimed at producing cleaner and more environmentally friendly fuels. These standards focus on eliminating hazardous substances, particularly the sulfur compounds in diesel, as they are among the most harmful organic compounds to both human health and the environment. Hydrotreating is the main refinery process used to produce ultralow sulfur diesel. For proper modeling and simulation of this process, it is mandatory to develop adequate kinetic models that include all the reactions taking place during the hydrotreating of gas oil, as well as the removal of the most refractory compounds present in the chemical composition of diesel, such as 4-MDBT and 4,6-DMDBT. This work reports an exhaustive discussion of the kinetic models of hydrotreating reactions for the production of ultralow sulfur diesel reported so far in the literature. The main topics include the reaction systems, type of catalysts, and operating conditions. A comparison of the reported kinetic parameters was also carried out. Finally, a set of kinetic models to be considered for the simulation of the hydrotreating process to produce ultralow sulfur diesel is proposed.



1. INTRODUCTION

The development of appropriate kinetic models to adequately predict the production of ultralow sulfur diesel (ULSD) is a relevant task that has continuously increased in importance worldwide in recent years. Diesel is a liquid fuel extensively used in highway vehicles (e.g., cars, trucks, and buses) and non-highway vehicles (e.g., marine vessels, locomotives, agricultural equipment, and aircraft). At the production end of the petroleum value chain, it has been estimated that around 60% of the total crude oil produced is upgraded into transportation fuels by refineries.^{1,2} Regarding energy consumption, in accordance with the Energy Information Administration, in 2020, approximately 95% of the whole transportation energy consumed was acquired from liquid and gas petroleum-derived fuels, and diesel represented 37.4% of the total. This percentage is forecasted to start to decline in the upcoming decades due to renewable energy alternatives; however, diesel fuels share is estimated to be nearly 30% in 2050.^{3,4} Diesel engines are 25–40% more efficient than gasoline engines, but diesel combustion can emit particulate matter, CO, NO_x, and SO_x gases, which are harmful to human health and the environment. As a result, increasingly stringent regulations in many countries require the sulfur content of diesel fuel to be in the range of 10 to 15 ppm or less to reduce harmful emissions from diesel engines and improve air quality.

Catalytic hydrotreating (HDT) is the most important and widely used process to produce ULSD in the petroleum refining industry due to its technical, economic, and environmental advantages. This process has been used for more than 60 years to produce fuels with improved quality and low content of polluting species (sulfur, nitrogen, aromatics). It typically consists of feeding a mixture of middle distillates and hydrogen gas at high pressures and temperatures into a trickle-bed reactor (TBR) to react in the presence of one or more heterogeneous catalysts. A general view of the TBR used in an HDT unit is shown in Figure 1. Various studies have focused on the modeling of the TBR for HDT.^{5–10} Such models consider the three main reactions that take place during hydrotreating: hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodearomatization (HDA). Other relevant reactions are the hydrogenation of olefins (HGO) and hydrocracking (HCR). HDS is the primary studied reaction

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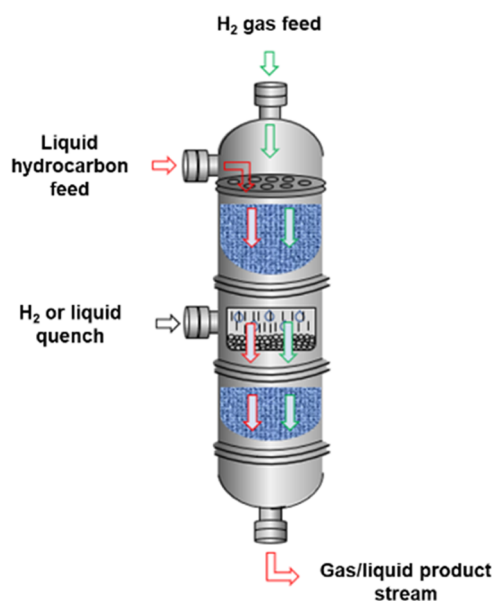


Figure 1. General schematic diagram of deep hydrotreating of the gas oil process.

because the removal of sulfur compounds is the most important task in the production of ULSD.^{10–13} However, for the design, simulation, and optimization of HDT reactors, all reactions must be considered for proper representation of the reaction kinetics. Therefore, the development of suitable kinetic models that accurately predict the production of ULSD is mandatory.^{7,9,11,12}

To produce ULSD, more than 99.9% of the sulfur compounds present in the feedstock must be removed. The main problems with ultradeep HDS are the presence of sterically hindered alkyl-substituted dibenzothiophene (DBT)

species and the inhibitory effects of various poisons such as H_2S , nitrogen compounds, and aromatic compounds.⁴ From the alkyl-substituted DBT family of compounds, the 4,6-dimethyldibenzothiophene (4,6-DMDBT) molecule is normally used as the model compound for HDS kinetic studies because of its significant abundance in petroleum and higher steric effect—due to both methyl substituents placed in the nearest available C atoms next to the S atom—making it the most refractory sulfur compound for conventional CoMo- and NiMo-supported HDS catalysts. As reported elsewhere,^{14–16} the HDS of 4,6-DMDBT occurs via two parallel routes. The first route is the direct desulfurization (DDS), leading to the formation of 3,3-dimethylbiphenyl (3,3-DMBPH), and the second route involves hydrogenation (HYD) of one of the benzene rings of the DBT to form 4,6-dimethylhexahydrodibenzothiophene (4,6-DMHHDBT) in the first step, which is further desulfurized to 1-methyl-3-(3-methylcyclohexyl)-benzene, (1-M-3-(3-MCH)B). Additionally, an isomerization step could move one or both methyl substituents further from the S atom, and a disproportionation reaction between two 4,6-DMDBT molecules could yield a monosubstituted- and a trisubstituted-DBT species, thus, diminishing the substituent's steric effect and increasing its reactivity toward HDS. The HDS of 4,6-DMDBT through isomerization or disproportionation reactions is not considered in this work because these reactions are only relevant for acid-containing HDT catalysts, and ultimately, the elimination of the S atom must go through one of both main HDS routes yielding H_2S and the respective hydrocarbon compounds; as shown—for an isomerization step of 4,6-DMDBT—in Figure 2.^{17,18}

Some authors have previously reported the development and use of kinetic models that predict only HDS,^{10,12,13} but not deep HDS for ULSD production. For example, the commonly used Langmuir–Hinshelwood (L–H) kinetic model considers only the inhibitory effect of H_2S

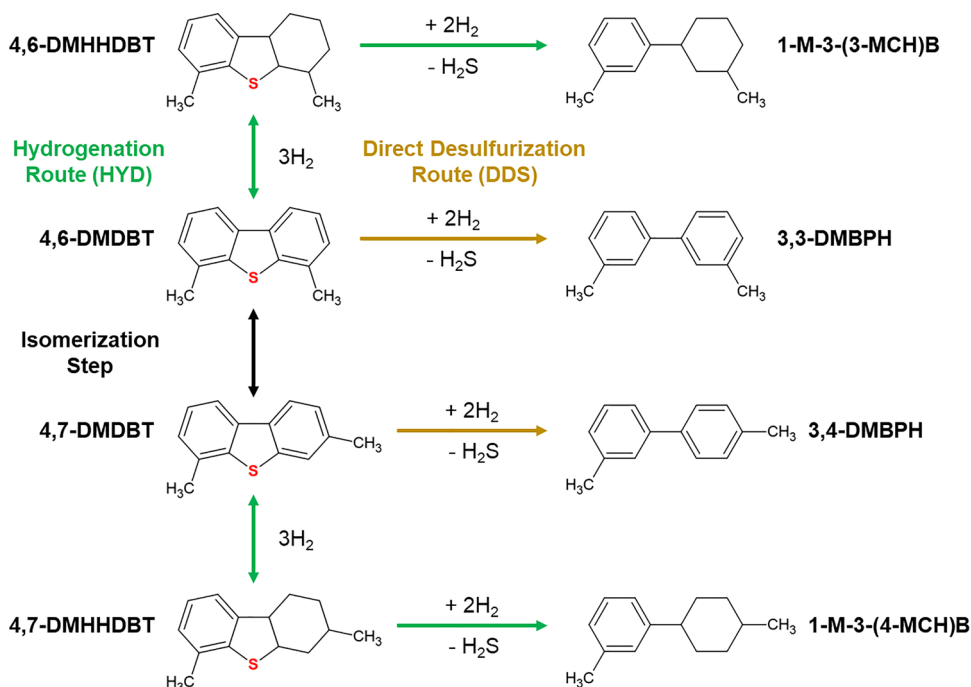


Figure 2. Simplified HYD (green) and DDS (yellow) reaction routes for HDS of 4,6-DMDBT and the isomerization step for acid HDS catalysts (black).^{16,56}

$$r_{\text{HDS}}^{\text{L}} = \frac{k'_{\text{in,HDS}} (C_{\text{SLS}}^{\text{S}})^{m_1} (C_{\text{SLH}_2}^{\text{S}})^{m_2}}{(1 + K_{\text{H}_2\text{S}} C_{\text{SLH}_2}^{\text{S}})^2} \quad (1)$$

where $k'_{\text{in,HDS}}$ is the intrinsic reaction rate coefficient for HDS, $K_{\text{H}_2\text{S}}$ is the adsorption-equilibrium constant of H_2S on active sites of the catalyst, $C_{\text{SLS}}^{\text{S}}$ is the molar concentration of the sulfur species at the surface of the solid covered by the liquid phase, $C_{\text{SLH}_2}^{\text{S}}$ is the molar concentration of hydrogen at the surface of solid covered by the liquid phase, $C_{\text{SLH}_2\text{S}}^{\text{S}}$ is the molar concentration of hydrogen sulfide at the surface of the solid covered by the liquid phase, and m_1 and m_2 are the reaction orders of sulfur species and hydrogen, respectively.

The main issue with such a kinetic model is that it only considers total sulfur, and many sulfur compounds with different HDS reactivities that should be considered are neglected, such as benzothiophene (BT), DBT, and 4,6-DMDBT; high, intermediate, and low HDS reactivity, respectively. This highlights the need for more detailed kinetic models that incorporate all of the features required to adequately predict ULSD production, e.g., Langmuir–Hinshelwood–Hougen–Watson (LHHW) models, lumped models, and detailed kinetic models.^{19–22}

However, it is important to note that there are significant differences between simple power-law kinetic models and Langmuir–Hinshelwood models because both are different approaches used to study chemical reactions. Power-law models describe the rate of a chemical reaction as a function of the concentration of reactants raised to a power and do not consider inhibition effects. On the other hand, L–H type models are used to describe heterogeneous catalytic reactions where a solid catalyst phase is present. These models are based on the idea that the reactants adsorb on the catalyst surface and then react with each other. L–H models consider the adsorption of the reactants, their interaction on the catalyst surface, and the desorption of the products. In general, this latter approach is useful for studying reactions in which the catalyst surface plays an important role in the overall kinetics and where the inhibition effect of compounds is included, which is the case for appropriate modeling of HDT reactions for ultralow sulfur diesel production.^{12,15}

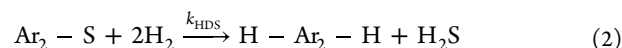
The aim of this work is to perform an exhaustive and critical analysis of kinetic models reported in the literature for deep-HDT reactions focused on the production of ULSD. Different from previous reports that focused only on the HDS of model compounds and not on ULSD, the present work discusses from the simplest kinetic models (single-lumped power-law models) to the most complete ones (LHHW). Particular emphasis is put on those models that include the removal of the most refractory sulfur compounds and all of the hydrotreating reactions carried out in the deep hydrotreating process. The work aims at discussing in detail all of the current literature reported on kinetic models to produce ULSD and serves as a reference for subsequent works focused on HDT kinetic and reactor modeling.

2. HYDRODESULFURIZATION REACTIONS

HDS kinetic models are grouped based on similarities between them, considering the type of model (power-law and LHHW) and the degree of speciation of the sulfur-containing compounds. First, kinetic models considering the total sulfur of real feedstocks are described. Then, kinetic models based on

experimental data obtained from pure model compounds, such as DBT and 4,6-DMDBT, among others, are commented. Finally, kinetic models containing sulfur compounds in real feedstocks lumped into separate groups according to reactivity, chemical structure, or physicochemical properties are described.

2.1. Kinetic Models Based on Total Sulfur Concentration. To model HDS reactions, the following general stoichiometric chemical equation for DBT and its derivatives has been proposed



where Ar_2-S is the sulfur-containing compound, $\text{H}-\text{Ar}_2-\text{H}$ is the aromatic compound free of sulfur, H_2 is hydrogen, H_2S is hydrogen sulfide, and k_{HDS} is the reaction rate coefficient of HDS.

For instance, Bhaskar et al.²³ suggested a kinetic model based on total sulfur as represented by eq 1. The second order exponent in the denominator represents the number of active sites involved in the adsorption of hydrogen sulfide, whose equilibrium constant $K_{\text{H}_2\text{S}}$ is a function of temperature using the Van't Hoff equation (eq 3), and the effect of temperature on reaction rate coefficients was modeled by the Arrhenius equation (eq 4). In the latter, k_0 is the pre-exponential or frequency factor, E_{a} is the activation energy of reaction i , T is the absolute temperature (K or °R), and R is the ideal gas constant.

$$K_{\text{H}_2\text{S}} = K_{0,\text{H}_2\text{S}} \exp \frac{\Delta H_{\text{ads,H}_2\text{S}}}{RT_{\text{S}}^{\text{S}}} \quad (3)$$

$$k_i = k_0 \exp \left(-\frac{E_{\text{a}_i}}{RT} \right) \quad (4)$$

This kinetic model for the HDS reaction was part of an attempt to simulate the main reaction occurring during HDT within a TBR reactor. The reactor simulation was based on the two-film theory on the heterogeneous catalyst surface at a steady state and formulated all the reactions considering differential mass balances across the gas–liquid and liquid–solid interfaces. The reactions considered for a conventional feedstock, such as straight-run gas oil (SRGO), were HDS, HDN, HGO, and HDA, while HCR was neglected.

The experimental tests were conducted in a continuous trickle-flow reactor unit of 80 cm in length and 2.54 cm in diameter with a catalyst bed of 45 cm using 200 mL of catalyst to process a blend of SRGO from crude distillation units at reaction conditions of 320 to 360 °C, 4.0 MPa, H_2 /oil ratio of 200 L/L, and an LHSV of 2.0 h^{−1}. A boundary value problem (BVP) was set to calculate the parameters, as the concentrations of various components at the reactor inlet and outlet are known. For this problem, the shooting method was used to solve the BVP to determine the kinetic parameters. The fourth-order Runge–Kutta method was used to solve the system of differential equations along the length of the catalyst bed, and the Newton–Raphson method to solve the nonlinear algebraic equations concerning the surface concentrations of several components. However, the reported model only considers some aspects of this reaction and lacks accuracy when it comes to adequately predicting the deep HDS of diesel.

Mederos et al.¹⁴ used a similar LHHW kinetic model to represent the HDS reaction (eq 1) in a broader dynamic heterogeneous one-dimensional model of a TBR for catalytic HDT. This TBR model considers the same main HDT reactions as the previous one and includes the HCR reaction because the continuous trend of using heavier crude oil as refining feedstock increases the importance of this reaction during HDT. Many following TBR simulation studies have been based on this HDS kinetic model for crude oil HDT²⁴ and ULSD production from non-conventional feedstocks like vacuum gas oil (VGO)^{25,26} and high-temperature coal tar (HTCT).²⁷

To estimate the model parameters, Levenberg–Marquardt algorithm based on the nonlinear least-squares method was used with the sum of squared errors (SSE) as the objective function

$$\text{SSE} = \sum_{j=1}^m (C_{i,j}^{\text{cal}} - C_{i,j}^{\text{exp}})^2 \quad (5)$$

This type of model also attempts to predict the ultradeep HDS but lacks accuracy when applying it in the hydrodesulfurization for ULSD production because the model omits several inhibiting effects caused by some species and the different reactivity of sulfur refractory compounds. Nevertheless, valuable information can be extracted from this work for a better understanding of the hydrotreating reactions to produce ULSD.

The experimental data were obtained in a reaction system with a bench-scale TBR operating in downflow and isothermal mode. The feed was SRGO obtained from the distillation of heavy crude oil and passed over an alumina-supported cobalt molybdenum catalyst. The experiments were carried out at a pressure of 5.3 MPa, reaction temperatures in the range of 340–380 °C, and liquid hourly space velocities (LHSV) from 1 to 3 h^{−1}, a diameter of 2.54 cm and a length of 25.2 cm for the reactor. In a later work from the same research group, the authors employed this kinetic model for the HDS reaction to simulate a slurry-phase reactor for HDT of heavy crude oil with promising results.²⁸

Fan et al.²⁷ also established a kinetic model where the main objective was to calculate kinetic parameters and simulate a TBR for deep HDS. The experimental tests were conducted in a continuous isothermal TBR of 4.5 cm of outer diameter and 2.9 cm of inner diameter where the temperature of the reactor was varied between 375 and 405 °C, the pressure from 12 to 16 MPa, the LHSV from 0.25 to 0.35 h^{−1}, and a H₂/oil ratio kept constant at 2000 L/L. The feedstock used was HTCT distillates, a non-conventional feedstock for producing ultralow S transportation fuels, such as ULSD. Samples were collected from a coking plant in Shanxi and had a high content of resin and asphaltene with a low H/C atom ratio. The catalyst used was a commercial sample of NiMo/Al₂O₃-SiO₂ with the following composition: 21.76 wt % MoO₃, 6.38 wt % NiO, and 2.58 wt % P₂O₅.

The rate equation for the HDS reaction is of the L–H type, considers the inhibition effect of hydrogen sulfide on HDS, and is similar to eq 1, where the equilibrium constant follows the Van't Hoff equation (eq 3) and the reaction rate coefficient follows the Arrhenius law (eq 4). The estimation of kinetic parameters was carried out by using the well-known Levenberg–Marquardt method and the Sequential Quadratic Programming method (SQP). Based on the squared error

minimization as an objective function (eq 5), the optimal values of the parameters (frequency factor, reaction order, and activation energy) were obtained from experimental data. The model was proved to be sufficiently reliable for the production of clean fuels from non-conventional feedstocks with high heteroatom contents, like HTCT. It was found that the LHSV had the biggest effect on sulfur conversion, followed by temperature and pressure, and the obtained reaction order was higher than that for crude oil.

Yadav et al.²⁹ reported kinetic modeling and simulation for the HDS of commercial diesel in a TBR by a mixing cell network approach to simulate the multiple reactions happening in industrial settings. Regarding the reaction conditions and reactor data to carry out the simulation, the temperature was 326 °C, with a H₂ to oil ratio of 314 Nm³/m³, 350 cm of diameter, and catalyst beds of the following heights: 295, 559, and 842 cm, respectively. The reaction rate equation used to simulate the HDS reaction was an LHHW model similar to eq 1. The mixing cell network model had an acceptable agreement with the results obtained from a plug-flow reactor (PFR) for a commercial diesel HDS unit but did not take into account the HDN reaction.

Chowdhury et al.³⁰ studied the desulfurization and hydrogenation of aromatics in diesel oil using a TBR operating isothermally with a commercial NiMo/Al₂O₃ catalyst. It was found that the increase in pressure and decrease in LHSV led to deeper desulfurization and hydrogenation of aromatics. Also, a high H₂/oil ratio and low initial concentration of H₂S enhance the HDS reaction. The experimental procedure was carried out in a TBR using a catalyst of the following composition: 4 wt % of NiO, 19.5 wt % of MoO₃, 8 wt % of P₂O₅, and 68.5 wt % of Al₂O₃. The temperature was varied between 300 and 380 °C, the pressure between 2 and 8 MPa, the LHSV 1–4 h^{−1}, the gas/oil ratio of 100–500, 1.9 cm of inner diameter, and 50 cm of length regarding the reactor data. For the formulation of the mathematical model, the authors considered the following main assumptions:

- The reactor operates isothermally at steady-state and isobaric conditions.
- There was no radial profile of concentration within the reactor.
- The reactor behaves like a PFR.
- Evaporation of diesel occurs instantaneously only at the entrance of the reactor. The evaporation of the reacting components can be neglected due to their high molecular weights.
- Mass-transfer resistance lies in the G–L interface. The mass-transfer resistance at the L–S interface and the resistance to pore diffusion can be neglected.
- The gas and the liquid phases are in equilibrium at their interface.
- The HDS reaction occurs in the manner of eq 2.
- The adsorption coefficient does not depend on temperature.

The reaction rate equation for the HDS is considered to be of the LHHW type (eq 1). For the estimation of the adsorption constant, the least square method was applied using experimental data obtained by varying the initial concentration of H₂S. The reaction orders and the reaction rate coefficient were determined using experimental data by regression analysis at 320 °C, and, in the case of the reaction rate coefficient at

Table 1. Summary of Typical Properties of Feedstock Used in Hydrotreating Kinetic Studies

property	reference							
	13	10	27	30	31	11	23	22
density at 20 °C (kg/m ³)	858.8	869	1,174	865	890	858.8	857.5 ^a	-
viscosity at 20 °C (cP)	-	7.25	-	-	-	-	3.34 ^b	-
carbon content (wt %)	87.02	-	90.3	-	-	-	-	-
hydrogen content (wt %)	12.94	-	5.12	-	-	-	-	-
total aromatics content (wt %)	35.4	34.9	27.33	33.50	35.8	36	37.40	-
nitrogen content (ppm)	220	330	9,200	218	1,214	220	120	1,170
sulfur content (ppm)	12,000	21,900	6400	16,298	4,053	12,000	11,100	18,200
boiling range (ASTM-86)								
initial boiling point (IBP) (°C)	210	285	170	180	160	210	164	-
10 vol %	255	293	-	-	260	255	247	-
30 vol %	285	-	317	-	310	285	275	-
50 vol %	299	-	404	337	356	299	294	-
70 vol %	320	-	496	-	402	320	316	-
90 vol %	355	324	564	-	452	355	350	-
final boiling point (FBP)	383	329	583	434	534	383	370	-

^aAt 15 °C. ^bAt 40 °C.

Table 2. Typical Reaction System and Operating Conditions for Gas Oil Hydrotreating

ref	reaction system	reactor length (cm)	reactor diameter (cm)	T (°C)	LHSV (h ⁻¹)	P (MPa)	H ₂ /oil ratio (NPT, v/v)	catalyst
13	micropacked-bed reactor (16 TBRs)	56	0.2	300–360	0.75–12	4.4–7.4	300	NiMo/Al ₂ O ₃
14	bench-scale TBR	25.2	2.54	340–380	1–3	5.3	356	CoMo/Al ₂ O ₃
27	continuous isothermal TBR	-	2.9	374–389	0.25–0.3	12–16	2000	NiMo/Al ₂ O ₃ -SiO ₂
29	commercial TBR	-	350	326	-	-	314	NiMo/Al ₂ O ₃
30	TBR	50	1.9	300–380	1–4	2–8	100–500	NiMo/Al ₂ O ₃
31	bench-scale TBR	26.9	0.78	350–380	0.5–1.5	-	12	NiMo/γ-Al ₂ O ₃
11	high-throughput reactor system	-	-	300–360	-	4.4–7.4	300	NiMo/Al ₂ O ₃
23	continuous trickle-flow reactor unit	80	2.54	320–360	1–2.5	4	200	NiO-MoO ₃ /Al ₂ O ₃
16	perfectly mixed flow multiphase reactor	-	-	240–300	-	5–8	-	CoMo/Al ₂ O ₃
22	-	762.5	-	316.85	3.16	5	-	-
21	semi-batch mode with the continuous gas flow	-	-	270–300	-	6–8	-	monolithic CoMo
20	multiphase flow reactor	-	-	260–320	-	8	-	CoMo/Al ₂ O ₃

Table 3. Estimated Kinetic Parameters Reaction Order (*n* for S and *m* for H₂), *k*_{0,HDS} [(cm³)^{*n+m*}/(mol^{*n+m-1*}·g·s)], and *E*_{a,HDS} (kJ/mol) for Total Sulfur HDS Kinetic Models

parameter	reference					
	10	27	30	31	catalyst A	catalyst B
<i>n</i>	1.80	1.65	1.6	1.80	1.00	1.00
<i>m</i>	0.96	0.86	0.56	0.52	0.45	0.45
<i>k</i> _{0,HDS}	2.64 × 10 ¹⁷	93,958	7.55 × 10 ¹⁸	7.89 × 10 ¹²	1.07 × 10 ⁵	6.56 × 10 ⁴
<i>E</i> _{a,HDS}	150.10	26.84	19.38	116.91	57.47	54.61

different temperatures, nonlinear regression was used to determine them.

da Rocha Novaes et al.³¹ developed a phenomenological model to estimate the kinetic parameters for the HDT process using the design of experiments. All of the catalytic tests were carried out in a bench-scale unit with a feedstock of diesel with a typical commercial catalyst (NiMo/γ-Al₂O₃). The composition of the catalyst was 19 wt % of MoO₃, 5.5 wt % of NiO, and 4.1 wt % of P₂O₅. The diesel feedstock was composed of a mixture of light and heavy diesel (1:1 vol/vol). Both were obtained from atmospheric distillation. As mentioned before, the reaction system consisted of the feed section, reaction section, and product separation section. The experimental tests

were carried out in a TBR at typical HDT operating conditions, the temperature in the range of 350–380 °C, an H₂/oil ratio of 12 NL/h, LHSV between 0.50 and 1.5 h⁻¹, an inner diameter of 0.78 cm, and a length of 26.8 cm. In the mathematical model for the simulation and estimation of kinetic parameters, the authors made several assumptions in order to simplify the modeling of the HDT process, such as the PFR pattern, the absence of deactivation, resistance between the phases, and no axial dispersion; however, to ensure that the bench-scale unit operates like a TBR with the plug-flow operation, the authors established that the hydrodynamics regime must be studied. Similarly, with previous studies, the reaction rate equation for HDS follows an LHHW type model

as shown in eq 1, the adsorption constant of H_2S as in eq 3, and the reaction rate coefficient as in eq 4.

The orthogonal collocation method was applied to solve the differential-algebraic equations. Dependent variables were approximated by polynomials of degree $n + 1$. Estimation of kinetic parameters was done with the complex algorithm, which is the direct search method of the flexible polyhedrons. Some assumptions were made, such as normal distribution of errors, well-done experiment, perfect model, independent variables without error, and errors of the dependent variables are all equal and independent. The objective function (SSE) was defined according to eq 5. Table 1 shows all of the properties of the feedstocks used in the works described here; Table 2 presents reaction conditions, catalysts, and reaction systems; and Table 3 shows the estimated kinetic parameters reported for the kinetic models based on total sulfur content in real feedstocks.

From all of these reported works, it is observed that one-lump power-law kinetic models for the global HDS reaction in ULSD production have been widely used for the simulation of TBRs through multiple approaches due to their mathematical simplicity. However, because of the encapsulation of complex HDS elementary reaction networks into a few apparent kinetic parameters in this type of model, changes in operating variables—mainly feedstock nature—have an enormous impact on parameter estimations after the application of the optimization methods. Therefore, this type of kinetic model can have satisfactory accuracies in a casuistic approach but are overly sensitive to modifications of operating conditions. To broaden the reliability of the HDS kinetic models for numerous sets of operating conditions, the different reactivities of the multiple S-containing compounds present in the chemical speciation of the feedstocks for ULSD production must be considered.

2.2. Kinetic Models Based on Model Sulfur Compounds. Other strategies for modeling deep hydrodesulfurization have included the use of refractory model sulfur compounds such as DBT and 4,6-DMDBT. In addition, some reactive sulfur species, such as thiophene (TP) and BT, as well as HDS hydrocarbon products, like BPH and CHB, have been taken into consideration in LHHW kinetic models. The use of model compounds allows us to establish a detailed reaction mechanism and determine whether the reaction proceeds by DDS or HYD routes. Despite the advantage of using refractory sulfur compounds to model the HDS reaction, competition effects due to other species present in real feeds, such as nitrogen-containing compounds and aromatic hydrocarbons, are not considered.

Various authors have proposed that the hydrogenolysis and hydrogenation reaction pathways for the HDS of DBT take place on different types of active sites of the catalyst surface named σ and τ , respectively.^{19,21,32,33} Figure 3 shows the reaction network for the HDS of DBT to BPH, CHB, BCH, and H_2S through the partially hydrogenated DBT intermediates, tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT).^{1,16} Based on the σ and τ active sites approach for supported CoMo and NiMo catalysts, Vanrysselberghe and Froment¹⁶ studied the kinetics of the HDS reaction of DBT on a commercial CoMo/ Al_2O_3 catalysts in a multiphase reactor. The experimental data were acquired from a perfectly mixed flow multiphase reactor operating between 50 and 80 bar and at temperatures ranging from 240 to 300 °C (reaction conditions are shown in Table 2).

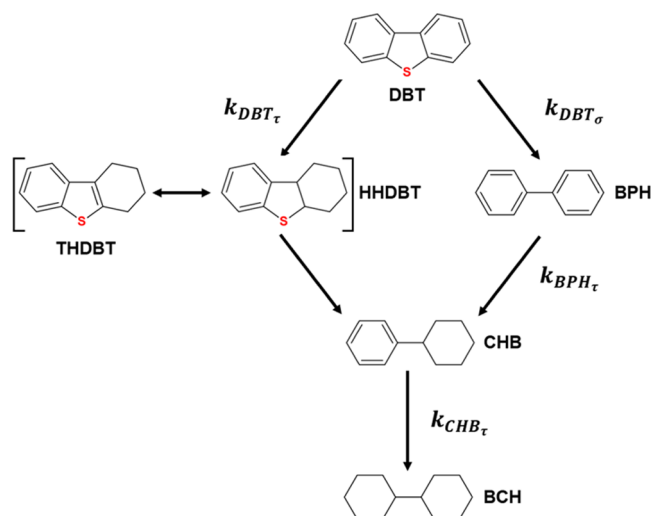


Figure 3. Reaction network for the HDS of DBT into the products BPH, CHB, BCH, and H_2S .

Parameters were estimated by a reparametrization of the rate coefficients and the adsorption-equilibrium constant, then a series of reaction mechanisms were derived as observed in eqs 6 to 9 for the following reactions: (1) hydrogenolysis of DBT to BPH and H_2S on the σ sites, (2) hydrogenation of DBT to THDBT and HHDBT on the τ sites, followed by hydrogenolysis to CHB and H_2S on the σ sites, (3) hydrogenation of BPH to CHB on the τ sites, and (4) hydrogenation of CHB to BCH on the τ sites. It is noteworthy that, by proposing an LHHW type of kinetic model and taking into account the inhibition effect on active sites, kinetic modeling is more suitable for accurately predicting deep HDS to produce ULSD.

$$r_{\text{DBT},\sigma} = \frac{k_{\text{DBT},\sigma} K_{\text{H},\sigma} K_{\text{DBT},\sigma} C_{\text{DBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\sigma} C_{\text{DBT}} + \sqrt{K_{\text{H},\sigma} C_{\text{H}_2}} + K_{\text{BPH},\sigma} C_{\text{BPH}} + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}})^3} \quad (6)$$

$$r_{\text{DBT},\tau} = \frac{k_{\text{DBT},\tau} K_{\text{H},\tau} K_{\text{DBT},\tau} C_{\text{DBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}})^3} \quad (7)$$

$$r_{\text{BPH},\tau} = \frac{k_{\text{BPH},\tau} K_{\text{H},\tau} K_{\text{BPH},\tau} C_{\text{BPH}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}})^3} \quad (8)$$

$$r_{\text{CHB},\tau} = \frac{k_{\text{CHB},\tau} K_{\text{H},\tau} K_{\text{CHB},\tau} C_{\text{CHB}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}})^3} \quad (9)$$

The differential method was used to estimate the kinetic parameters, and their respective values were obtained by minimization of the multiresponse objective function shown in eq 10 using a Marquardt routine

$$S(\theta) = \sum_{h=1}^{h=v} \sum_{k=1}^{k=v} \sigma^{hk} \sum_{i=1}^{i=n} (R_{ih} - \check{R}_{ih})(R_{ik} - \check{R}_{ik}) \xrightarrow{\theta} \min \quad (10)$$

Table 4. Estimated Kinetic Parameters $k_{0,i}$ [mol/(g·s)] and $E_{a,i}$ (kJ/mol) for the Kinetic Models of the HDS Reaction Based on Model Compounds^a

parameter	reference			
	16 ^b	21 ^b	σ	τ
$k_{0,1}$	6.79×10^6	4.81×10^{-1}	6.79×10^{6d}	7.97×10^{d1}
$k_{0,2}$	7.97×10^{12}	2.70×10^{-2}	3.65×10^7	1.18×10^{21}
$k_{0,3}$	9.48×10^{19}	1.41×10^1	1.79×10^4	1.02×10^{24}
E_{a1}	122.77	60.03	122.77	186.19
E_{a2}	186.19	56.39	133.32	269.46
E_{a3}	255.71	78.49	106.62	299.04
				2.01 $\times 10^{20}$

^aThe reaction order is 2. ^b $i = 1$ is for DBT, σ ; $i = 2$ is for DBT, τ ; and $i = 3$ is for BPH, τ . ^c $i = 1$ is for DBT; $i = 2$ is for 4-MDBT; and $i = 3$ is for 4,6-DMDBT. ^dValues taken from Vanrysselberghe and Froment.¹⁶

The number of iterations was set so that the sum of squared errors could be calculated, and the model adequacy could be tested using the F -test value.

The inhibitory effect on HDS catalytic sites by heterocyclic nitrogen compounds has also been studied by Froment et al.,²² where experiments under adiabatic conditions were performed using a mixture of BT, DBT, and 4,6-DMDBT as model sulfur compounds with quinoline as nitrogen-containing species. The properties of the feed are shown in Table 1, whereas the operating conditions are summarized in Table 2. A set of reaction rate equations has been developed to describe the HDS of BT in the liquid phase over an alumina-supported CoMo catalyst. Reactions involving desulfurization of BT to ethylbenzene (EB) by direct hydrogenolysis and hydrogenation are considered. The equations describing the above reactions are given in eqs 11 to 15

$$r_{\text{BT} \rightarrow \text{DHBT}} = k_{\text{BT},\tau} \left(\frac{C_{\text{BT}}C_{\text{H}_2} - 1 \times 10^{-3}C_{\text{DHBT}}}{K} \right) \quad (11)$$

$$r_{\text{BT} \rightarrow \text{EB}} = \frac{k_{\text{BT},\tau}C_{\text{BT}}C_{\text{H}_2}}{(1 + K_{\text{BT},\sigma}C_{\text{BT}} + K_{\text{H}_2\text{S},\sigma}C_{\text{H}_2\text{S}})} \quad (12)$$

$$r_{\text{DHBT} \rightarrow \text{EB}} = \frac{k_{\text{DHBT},\sigma}C_{\text{DHBT}}C_{\text{H}_2}}{(1 + K_{\text{BT},\sigma}C_{\text{BT}} + K_{\text{H}_2\text{S},\sigma}C_{\text{H}_2\text{S}})} \quad (13)$$

$$r_{\text{DBT} \rightarrow \text{BPH}} = \frac{k_1K_{\text{DBT},\sigma}K_{\text{H}_2,\sigma}C_{\text{DBT}}C_{\text{H}_2}}{\left(1 + K_{\text{DBT},\sigma}C_{\text{BT}} + \sqrt{K_{\text{H}_2\text{S},\sigma}C_{\text{H}_2}} + K_{\text{H}_2\text{S},\sigma}\frac{C_{\text{H}_2\text{S}}}{C_{\text{H}_2}} \right)^3} \quad (14)$$

$$r_{\text{DBT} \rightarrow \text{CHB}} = \frac{k_2K_{\text{DBT},\tau}C_{\text{DBT}}C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau}C_{\text{DBT}})^3} \quad (15)$$

The last two equations represent the HDS of DBT, where eqs 14 and 15 are the direct hydrogenolysis and the hydrogenation of DBT, respectively; such an approach has been reported elsewhere.¹⁹ To solve and simulate the proposed models, a set of Dirichlet and Neumann boundary conditions were stated. The integration in the axial direction was performed using the fourth-order Runge–Kutta method with a variable step size. The intraparticle integration was carried out with an orthogonal collocation method. For these routines, an initial guess calculated with the Newton–Raphson method was used.

Another report taking inhibition effects into account was published by Edvinsson and Irandoust,²¹ where the HDS of DBT on a commercial CoMo/Al₂O₃ catalyst was studied. The reaction rate equations followed an LHHW model, and a monolithic catalyst reactor operated in semi-batch mode with a continuous gas flow was used. The hydrogen pressure varied between 6 and 8 MPa, while the temperatures were between 270 and 300 °C (Table 2). The set of reaction rate equations is represented by eqs 16 to 21

$$r_{\text{DBT}} = r_1 + r_2 \quad (16)$$

$$r_1 = k_1\theta_{\text{DBT},\sigma}\theta_{\text{H},\sigma}^2 = \frac{k_2K_{\text{H},\sigma}K_{\text{DBT},\sigma}C_{\text{DBT}}C_{\text{H}_2}}{[1 + (K_{\text{H},\sigma}C_{\text{H}_2})^{1/2} + K_{\text{DBT},\sigma}C_{\text{DBT}}]^3} \quad (17)$$

$$r_2 = k_2\theta_{\text{DBT},\tau}\theta_{\text{H},\tau}^2 = \frac{k_2K_{\text{H},\tau}K_{\text{DBT},\tau}C_{\text{DBT}}C_{\text{H}_2}}{[1 + (K_{\text{H},\tau}C_{\text{H}_2})^{1/2} + K_{\text{DBT},\tau}C_{\text{DBT}} + K_{\text{BPH},\tau}C_{\text{BPH}}]^3} \quad (18)$$

$$r_3 = k_3\theta_{\text{BPH},\tau}\theta_{\text{H},\tau}^2 = \frac{k_3K_{\text{H},\tau}K_{\text{BPH},\tau}C_{\text{BPH}}C_{\text{H}_2}}{[1 + (K_{\text{H},\tau}C_{\text{H}_2})^{1/2} + K_{\text{DBT},\tau}C_{\text{DBT}} + K_{\text{BPH},\tau}C_{\text{BPH}}]^3} \quad (19)$$

$$r_{\text{BPH}} = r_1 - r_3 \quad (20)$$

$$r_{\text{CHB+BCH}} = r_2 + r_3 \quad (21)$$

The total rate of DBT disappearance is expressed by eq 16, where the terms r_1 and r_2 are as shown in eqs 17 and 18. The rate of BPH hydrogenation at the τ -sites is expressed by eq 19, and the net rate of BPH disappearance is given by eq 20. The reaction rate equation describing the formation of CHB and BCH can also be expressed as shown in eq 21. Kinetic parameters were estimated by multiple nonlinear regressions with concentrations as dependent variables. The estimated kinetic parameters of the works described in this section are shown in Table 4.

The inhibition and self-inhibition effects of the most refractory compounds and their respective HDS products on the HDS of DBT and the subsequent hydrogenation of the aromatic hydrocarbons produced after the S atom removal has been reported by Vanrysselberghe et al.²⁰ The HDS reaction of the most and second most refractory sulfur compounds—4,6-DMDBT and 4-MDBT—on a commercial CoMo/Al₂O₃

catalyst was studied in a multiphase flow reactor. Thus, kinetic models of the LHHW type were established to predict the reaction via hydrogenolysis and hydrogenation. The HDS of 4-MDBT was carried out at the following main conditions: temperatures between 260 and 320 °C, a total pressure of 8 MPa, and molar hydrogen-to-hydrocarbon ratios between 1.4 and 4.2. Other reaction conditions are shown in Table 2. The reaction rate equations were established based on the HDS of 4-MDBT to 3-methylbiphenyl (3-MBPH), 3-methylcyclohexylbenzene (3-MCHB), 3-cyclohexyltoluene (3-CHT), and hydrogen sulfide (H₂S). As mentioned before, the hydrogenolysis reactions and the hydrogenation reactions take place on two active sites, σ and τ , respectively. The rate expressions for the HDS of DBT and 4-MDBT are

$$r_{\text{DBT},\sigma} = \frac{k_{\text{DBT},\sigma} K_{\text{H},\sigma} K_{\text{DBT},\sigma} C_{\text{DBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\sigma} C_{\text{DBT}} + \sqrt{K_{\text{H},\sigma} C_{\text{H}_2}} + K_{\text{BPH},\sigma} C_{\text{BPH}} + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}} + K_{4\text{-MDBT},\sigma} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\sigma} C_{3\text{-MBPH}})^3} \quad (22)$$

$$r_{\text{DBT},\tau} = \frac{k_{\text{DBT},\tau} K_{\text{H},\tau} K_{\text{DBT},\tau} C_{\text{DBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}})^3} \quad (23)$$

$$r_{\text{BPH},\tau} = \frac{k_{\text{BPH},\tau} K_{\text{H},\tau} K_{\text{BPH},\tau} C_{\text{BPH}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}})^3} \quad (24)$$

$$r_{\text{CHB},\tau} = \frac{k_{\text{CHB},\tau} K_{\text{H},\tau} K_{\text{CHB},\tau} C_{\text{CHB}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}})^3} \quad (25)$$

$$r_{4\text{-MDBT},\sigma} = \frac{k_{4\text{-MDBT},\sigma} K_{\text{H},\sigma} K_{4\text{-MDBT},\sigma} C_{4\text{-MDBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\sigma} C_{\text{DBT}} + \sqrt{K_{\text{H},\sigma} C_{\text{H}_2}} + K_{\text{BPH},\sigma} C_{\text{BPH}} + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}} + K_{4\text{-MDBT},\sigma} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\sigma} C_{3\text{-MBPH}})^3} \quad (26)$$

$$r_{4\text{-MDBT},\tau}^1 = \frac{k_{4\text{-MDBT},\tau}^1 K_{\text{H},\tau} K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}})^3} \quad (27)$$

$$r_{4\text{-MDBT},\tau}^2 = \frac{k_{4\text{-MDBT},\tau}^2 K_{\text{H},\tau} K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}})^3} \quad (28)$$

$$r_{3\text{-MBPH},\tau}^1 = \frac{k_{3\text{-MBPH},\tau}^1 K_{\text{H},\tau} K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}})^3} \quad (29)$$

$$r_{3\text{-MBPH},\tau}^2 = \frac{k_{3\text{-MBPH},\tau}^2 K_{\text{H},\tau} K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4\text{-MDBT},\tau} C_{4\text{-MDBT}} + K_{3\text{-MBPH},\tau} C_{3\text{-MBPH}})^3} \quad (30)$$

According to the set of equations, the hydrogen is adsorbed competitively and dissociated on both active sites of the catalyst. The parameters were obtained by minimization of an objective function as shown in eq 31, which is the weighted least absolute error method using the Levenberg–Marquardt algorithm.

$$\text{SSE}_i = \sum_{k=1}^{15} \sum_{j=1}^4 W_i^{pj} |(C_i^{pj})_{\text{cal}} - (C_i^{pj})_{\text{exp}}| \quad (31)$$

The HDS of 4,6-DMDBT was carried out under similar operating conditions compared with the HDS of 4-MDBT. In this case, the reaction products were 3,3-DMBPH, *cis*- and *trans*-[1-M-3-(3-MCH)B], and H₂S. The reaction rate equations for HDS of 4,6-DMDBT are

$$r_{\text{DBT},\sigma} = \frac{k_{\text{DBT},\sigma} K_{\text{H},\sigma} K_{\text{DBT},\sigma} C_{\text{DBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\sigma} C_{\text{DBT}} + \sqrt{K_{\text{H},\sigma} C_{\text{H}_2}} + K_{\text{BPH},\sigma} C_{\text{BPH}} + K_{\text{H}_2\text{S},\sigma} C_{\text{H}_2\text{S}} + K_{4,6\text{-DMDBT},\sigma} C_{4,6\text{-DMDBT}} + K_{3,3\text{-DMBPH},\sigma} C_{3,3\text{-DMBPH}})^3} \quad (32)$$

$$r_{\text{DBT},\tau} = \frac{k_{\text{DBT},\tau} K_{\text{H},\tau} K_{\text{DBT},\tau} C_{\text{DBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{\text{H}_2\text{S},\tau} C_{\text{H}_2\text{S}} + K_{4,6\text{-DMDBT},\tau} C_{4,6\text{-DMDBT}} + K_{3,3\text{-DMBPH},\tau} C_{3,3\text{-DMBPH}})^3} \quad (33)$$

$$r_{\text{BPH},\tau} = \frac{k_{\text{BPH},\tau} K_{\text{H},\tau} K_{\text{BPH},\tau} C_{\text{BPH}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4,6\text{-DMDBT},\tau} C_{4,6\text{-DMDBT}} + K_{3,3\text{-DMBPH},\tau} C_{3,3\text{-DMBPH}})^3} \quad (34)$$

$$r_{\text{CHB},\tau} = \frac{k_{\text{CHB},\tau} K_{\text{H},\tau} K_{\text{CHB},\tau} C_{\text{CHB}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{4,6\text{-DMDBT},\tau} C_{4,6\text{-DMDBT}} + K_{3,3\text{-DMBPH},\tau} C_{3,3\text{-DMBPH}})^3} \quad (35)$$

$$r_{4,6\text{-DMDBT},\sigma} = \frac{k_{4,6\text{-DMDBT},\sigma} K_{\text{H},\sigma} K_{4,6\text{-DMDBT},\sigma} C_{4,6\text{-DMDBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\sigma} C_{\text{DBT}} + \sqrt{K_{\text{H},\sigma} C_{\text{H}_2}} + K_{\text{BPH},\sigma} C_{\text{BPH}} + K_{\text{H}_2\text{S},\sigma} C_{\text{H}_2\text{S}} + K_{4,6\text{-DMDBT},\sigma} C_{4,6\text{-DMDBT}} + K_{3,3\text{-DMBPH},\sigma} C_{3,3\text{-DMBPH}})^3} \quad (36)$$

$$r_{4,6\text{-DMDBT},\tau} = \frac{k_{4,6\text{-DMDBT},\tau} K_{\text{H},\tau} K_{4,6\text{-DMDBT},\tau} C_{4,6\text{-DMDBT}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{\text{H}_2\text{S},\tau} C_{\text{H}_2\text{S}} + K_{4,6\text{-DMDBT},\tau} C_{4,6\text{-DMDBT}} + K_{3,3\text{-DMBPH},\tau} C_{3,3\text{-DMBPH}})^3} \quad (37)$$

$$r_{3,3\text{-DMBPH},\tau} = \frac{k_{3,3\text{-DMBPH},\tau} K_{\text{H},\tau} K_{3,3\text{-DMBPH},\tau} C_{3,3\text{-DMBPH}} C_{\text{H}_2}}{(1 + K_{\text{DBT},\tau} C_{\text{DBT}} + \sqrt{K_{\text{H},\tau} C_{\text{H}_2}} + K_{\text{BPH},\tau} C_{\text{BPH}} + K_{\text{H}_2\text{S},\tau} C_{\text{H}_2\text{S}} + K_{4,6\text{-DMDBT},\tau} C_{4,6\text{-DMDBT}} + K_{3,3\text{-DMBPH},\tau} C_{3,3\text{-DMBPH}})^3} \quad (38)$$

As in the case of 4-MDBT, the kinetic parameters were estimated by minimization of the objective function, as shown in eq 31. The reaction rate coefficients followed the Arrhenius law (eq 4) and the Van't Hoff equation (eq 3). The values of the corresponding kinetic parameters are listed in Table 4 for the two active sites in the reaction σ and τ , respectively.

Early LHHW kinetic models based on the HDS reaction routes, considering inhibition effects, and validated through experimental catalytic evaluations of HDS with model sulfur compounds were thoroughly reviewed by Girgis and Gates¹² and will not be further discussed here. In recent years, other reports published in the literature^{34–41} also consider both HDS reaction pathways, catalyst's active sites, and inhibition effects in the LHHW kinetic models included in the TBR modeling, mostly with catalyst prototype screening purposes. Ali et al.³⁸ studied the effect of phosphorus addition on CoMo catalysts in the HDS reactions of DBT, 4-MDBT, and 4,6-DMDBT model compounds by using a series of CoMoP/Al₂O₃ catalysts prepared with different quantities of added P₂O₅ and estimated the respective kinetic parameters of the L–H proposed models. The kinetic model was validated with the experimental results obtained from catalytic evaluations of the presulfided CoMoP catalysts in a 100 mL batch reactor under a 6.2 MPa pressure of hydrogen gas at 320 °C for 16 h. Two distinct HDS tests were made with two mixtures of sulfur model compounds loaded in the autoclave reactor. The first mixture was DBT and 4-MDBT at a 0.5 g/L concentration of sulfur of each compound, and the second one was DBT and 4,6-DMDBT

at the same concentrations. Both pairs of compounds were dissolved in 50 g of decalin and introduced in the reactor along with 0.5 g of catalyst. Liquid samples were obtained at 15, 30, 45, and 60 min of reaction time. The proposed differential reaction rate equations of the L–H kinetic model for the first and second pairs of the sulfur model compounds are

$$-\frac{dC_{\text{DBT}}}{dt} = \frac{(k_{\text{DBT},\text{DDS}} + k_{\text{DBT},\text{HYD}}) K_{\text{DBT}} C_{\text{DBT}} \sqrt{K_{\text{H}_2} C_{\text{H}_2}}}{(1 + K_{\text{DBT}} C_{\text{DBT}} + K_{4\text{-MDBT}} C_{4\text{-MDBT}} + \sqrt{K_{\text{H}_2} C_{\text{H}_2}})^2} \quad (39)$$

$$-\frac{dC_{4\text{-MDBT}}}{dt} = \frac{(k_{4\text{-MDBT},\text{DDS}} + k_{4\text{-MDBT},\text{HYD}}) K_{4\text{-MDBT}} C_{4\text{-MDBT}} \sqrt{K_{\text{H}_2} C_{\text{H}_2}}}{(1 + K_{\text{DBT}} C_{\text{DBT}} + K_{4\text{-MDBT}} C_{4\text{-MDBT}} + \sqrt{K_{\text{H}_2} C_{\text{H}_2}})^2} \quad (40)$$

$$-\frac{dC_{\text{DBT}}}{dt} = \frac{(k_{\text{DBT},\text{DDS}} + k_{\text{DBT},\text{HYD}}) K_{\text{DBT}} C_{\text{DBT}} \sqrt{K_{\text{H}_2} C_{\text{H}_2}}}{(1 + K_{\text{DBT}} C_{\text{DBT}} + K_{4,6\text{-DMDBT}} C_{4,6\text{-DMDBT}} + \sqrt{K_{\text{H}_2} C_{\text{H}_2}})^2} \quad (41)$$

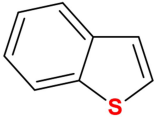
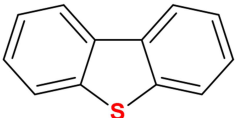
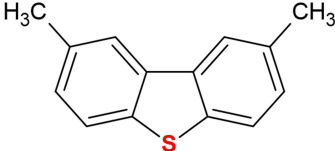
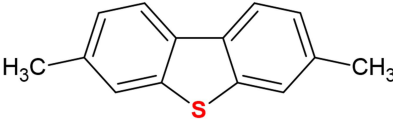
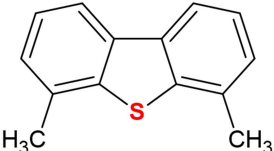
$$-\frac{dC_{4,6\text{-DMDBT}}}{dt} = \frac{(k_{4,6\text{-DMDBT},\text{DDS}} + k_{4,6\text{-DMDBT},\text{HYD}}) K_{4,6\text{-DMDBT}} C_{4,6\text{-DMDBT}} \sqrt{K_{\text{H}_2} C_{\text{H}_2}}}{(1 + K_{\text{DBT}} C_{\text{DBT}} + K_{4,6\text{-DMDBT}} C_{4,6\text{-DMDBT}} + \sqrt{K_{\text{H}_2} C_{\text{H}_2}})^2} \quad (42)$$

Some assumptions were made to simplify the kinetic model: all HDS reactions are irreversible, the thermal cracking of the model compounds is negligible, and the reaction occurs under isothermal conditions. The model was evaluated through the fitting of the least-squares of the experimental results, the kinetic parameters were determined with the Levenberg–Marquardt algorithm, and the differential equations were solved with the Runge–Kutta–Gill method by using the Mathematica software's respective tools.

The conclusions derived from this work were that the L–H kinetic models satisfactorily fitted the HDS experimental data in both cases. However, calculations of the rate constants obtained with this L–H model follow trends similar to those estimated with a pseudo-first-order power-law kinetic model by the same research group.⁴² The absolute estimated kinetic values from the L–H model are between 5 and 10% higher than the ones obtained from the power-law model; thus, the pseudo-first-order kinetic model is a reasonable approximation, even for HDS reactions of model compounds.

In summary, while these types of kinetic models offer mathematically elaborate expressions and employ a more detailed representation of the elementary chemical reactions involved in multisite HDS of refractory sulfur compounds than total sulfur power-law kinetic models, their accuracy is limited for simulating and predicting the performance of real feedstock HDT at industrial settings because of two main factors. First, many of the LHHW kinetic studies of sulfur model compounds

Table 5. Chemical Structure of Organic Sulfur-Containing Refractory Compounds in Diesel

Compound	Chemical structure
Thiophene (TP)	
Benzothiophene (BT)	
Dibenzothiophene (DBT)	
2,8-dimethyldibenzothiophene (2,8-DMDBT)	
3,7-dimethyldibenzothiophene (3,7-DMDBT)	
4-methyldibenzothiophene (4-MDBT)	
4,6-dimethyldibenzothiophene (4,6-DMDBT)	

are carried out under conditions set to eliminate external and internal mass-transfer limitations because the research aim usually focuses on the HDS reaction kinetics alone; therefore, if the incorporation of the mass-transfer factors is needed for industrial scaling-up to commercial reactors, further TBR modeling studies would be required to achieve it.⁴³ Second, the complexity of the reaction network during HDT of real feedstocks increases the determined kinetic parameters errors and the difficulty in estimating adsorption parameters for all species involved. Furthermore, when simulating a TBR, including mass and energy balances, and using LHHW kinetic models, the computational complexity augments compared with employing power-law kinetic models and might not yield significantly more accurate results.^{1,38,42} For these reasons, their usage in recent HDS kinetic modeling studies for ULSD production is scarce.

2.3. Lumped Sulfur Compounds Kinetic Models.

Another type of kinetic model to be discussed in the HDS reactions is those that lump the various sulfur compounds in

the feeds into two or more groups, considering the lower HDS activity of refractory sulfur compounds. The lumping criteria may be based on their HDS reactivity, chemical structure, and/or physicochemical properties. The reactivity of S-containing compounds is proportional to the steric hindrance around the S atom and inversely proportional to their boiling point and the presence of aromatic structures adjacent to the heteroatom. One or more independent rate equations for refractory compounds are such an important feature of these models because they represent the highest percentage found in the speciation of organosulfur compounds of the HDT products and must be efficiently removed to achieve ULSD standards.⁴⁴ These compounds, such as the DBT, 4-MDBT, and 4,6-DMDBT, among others, are the most refractory compounds present in the diesel chemical composition, with 4,6-DMDBT being the most refractory compound. Some chemical structures for refractory sulfur compounds are shown in Table 5.^{12,45}

As it has been pointed out previously, particularly for ULSD production, joining all of the S-containing compounds into a single lump to develop HDS kinetic models is an inadequate approach, regardless of the type of kinetic model (power-law, L–H, or LHHW). This is due to the fact that single-lump kinetic models of HDS neglect the different reactivities of sulfur compounds and are useless if the HDT feedstock composition is changed; therefore, it has been observed that this kind of model is prone to yield optimistic predictions of the S content in the hydrotreated products.^{46,47} Considering single-lump kinetic models as the simplest approach to simulate HDS reactions, detailed kinetic models would be at the opposite end of complexity. It can be thought that a detailed kinetic model would produce the best predictions of deep HDS; nevertheless, they have the disadvantage that to achieve complete kinetic modeling of all or most S-containing molecules present in petroleum derivatives, a vast number of parameters must be estimated, which also significantly increases the number of experimental test and computational capacity required. For example, Te et al.⁴⁸ calculated that a thorough Hougen–Watson type kinetic modeling of the HDS, considering the DDS and HYD pathways of DBT, 4-MDBT, 4,6-DMDBT, 1,6-dimethyldibenzothiophene, and 1,2,6-trimethyldibenzothiophene, would yield an impractical total of 1133 parameters—497 kinetic rate constants and 636 adsorption constants. To reduce the number of parameters, there are kinetic modeling approaches reported in the literature, like the structural approach, the linear-free-energy-relationship, the continuum lumping, and the classical discrete lumping. Among these four approaches, the most used one for kinetic modeling of deep HDS to produce ULSD and the most discussed in this work—because of its simplicity and good fitting of predictions with experimental data—is the discrete lumping, where the total speciation of sulfur compounds is divided into reactive and refractory lumps.^{13,46,49–52} Even though the number of parameters is dramatically reduced in a two-lump HDS kinetic model, the development and validation of any lumped kinetic model for real feedstocks must include sulfur speciation analysis.⁴⁹ The sulfur speciation techniques employ a separation technique, commonly gas chromatography (GC), with a high-resolution capillary column and a sulfur-selective detector, like a sulfur chemiluminescence detector, a pulsed flame photometric detector, and an atomic emission detector, among others.⁴⁸ However, when realizing extended exploratory studies, these detailed analyses are usually avoided due to unavailability or economic concerns.

To prove that the lumped HDS kinetic models are able to minimize the difference between experimental results and predictions, Rodriguez et al.⁴⁹ made a thorough comparison of 5 distinct reactor and kinetic models of a trickle-bed bench-scale reactor for HDS of VGO. The first approach to reactor modeling was performed by employing a simple pseudo-homogenous one-dimensional model, along with a single-lump *n*th-order power-law kinetic model for the HDS reaction. The second approach was different from the first because it considered a packed-bed reactor instead of an unpacked reactor; this modification affects the liquid linear velocity and the estimations of the kinetic parameters. The third approach used the same reactor model as the second one; however, it included a two-lump first-order power-law HDS kinetic model based on the assumption that reactive and refractory (DBT and alkyl-substituted DBT derivatives) sulfur compounds HDS are two parallel reactions. The fourth approach was a

heterogeneous one-dimensional reactor model, and the kinetic model was the same as the first approach (single-lump *n*th-order power-law kinetics). Finally, the fifth approach was a heterogeneous reactor model reported before by Mederos⁵³ and used a single-lump L–H kinetic model, including the inhibition effect of H₂S. All predictions and parameter estimations were performed by minimization of an SSE objective function (eq 5) by testing distinct reaction orders and used as initial values in a nonlinear regression equation for each approach.

After comparing the results of each approach, it was observed that even though the third approach had a simpler reactor model compared with the fourth and fifth approaches, the lumping of the S species into reactive and refractory compounds was a better approach than the single-lump kinetic approach (power-law and L–H types) of the HDS reaction because it provided the minimal differences between the experimental and calculated data.

The lumping criteria for S-containing compounds into reactive (or high reactivity) and refractory (or low reactivity) compounds has not been homogeneous in the literature. For example, De la Paz-Zavala et al.⁵⁰ proposed a lumped HDS kinetic model for the production of ULSD from multiple feedstocks (SRGO, light cycle oil (LCO), light cracked gas oil (LCGO), and their mixtures) hydrotreated with 3 different commercial catalysts. The proposed kinetic model represented reactive sulfur compounds as mercaptans, sulfides, disulfides, thiophenes, BT, and DBT with the DBT molecule and refractory sulfur compounds as 4-MDBT, 4,6-diethyldibenzothiophene, and 4,6-DMDBT with the 4,6-DMDBT compound. DDS and HYD pathways were considered to occur in the σ and τ active sites, respectively. The rate equations were of the LHHW type, considering the inhibition effects of the aromatic and hydrogen sulfide compounds, and were similar to the LHHW kinetic models for the respective model compounds described in the previous section. The authors concluded that although the kinetic model gave a good representation of the HDS reaction in a pilot plant TBR, there is room for improvement of the kinetics by accounting for the inhibition effects of the organonitrogen species present in the feeds. Another example of a different two-lump HDS kinetic model was published by Ramírez-Castelán et al.;⁵² BT was selected as the representative compound of the reactive sulfur species (mercaptans, thiols, BT, etc.) and DBT as the representative of the refractory sulfur species (DBT and alkyl-substituted DBTs). BT and DBT kinetics were taken from the work by Chowdhury et al.,³⁰ who proposed an L–H kinetic model with a reaction order of 1.6 for both sulfur compounds and 0.56 for H₂ and only considered the H₂S inhibition effect on each reaction. The authors observed that such an HDS kinetic model led to slightly high predictions of sulfur content in the end products under the applied operating conditions and settings. The limited accuracy of these types of models is probably due to the significantly different reactivities present among the refractory sulfur compounds (DBT, 4-MDBT, and 4,6-DMDBT). Hence, further separations of refractory sulfur compound lump into two or more lumps have yielded better predictions than two-lump kinetic models.

Tang et al.⁵⁴ proposed and compared three different HDS and HDN lumped kinetic models for the hydrotreating of middle distillates from shale oils (MDSO). The used power-law reaction rate equations were of the first-order for S_i concentration of each lump (*n_i* = 1) and of the *m*th-order for

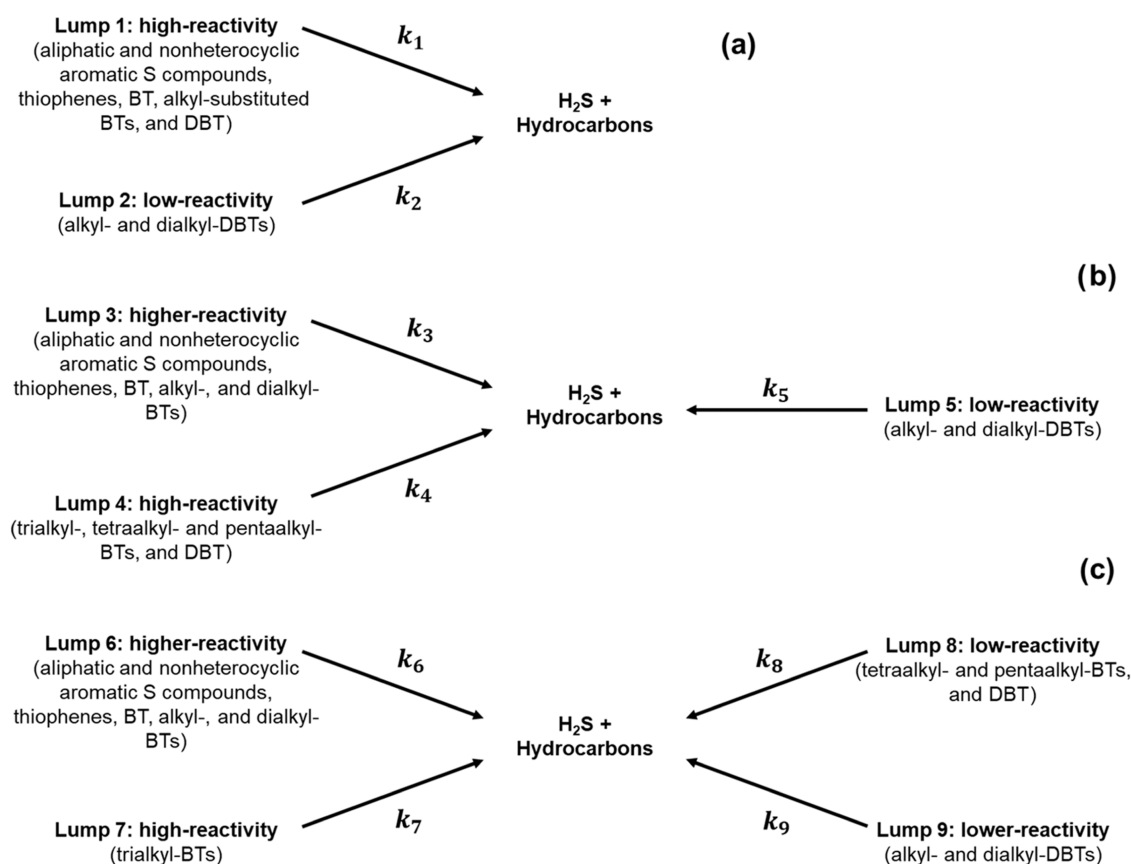


Figure 4. Reaction networks of the 3 different HDS lumping kinetic models proposed and compared by Tang et al.⁵⁴

Table 6. Estimated Kinetic Parameters Reaction Order (n_i for S and m_i for H_2), $k_{0,i}$, and $E_{a,i}$ (kJ/mol) for Lumped HDS Kinetic Models for ULSD Production

parameter	reference					
			11 ^c		44 ^d	
	54 ^a	13 ^b	DDS	HYD	model 3	model 4
n_1	1	2		1	1	1
n_2	1	1.5		1	1.19	-
n_3	1	-	1	1	-	-
n_4	-	-	-	-	-	-
m_1	0.42	0		1	1	1
m_2	1.06	0.5		1	1	1
m_3	1.18	-	0.5	0.5	-	1
m_4	-	-	-	-	-	1
$k_{0,1}$	8.31×10^3	4.47×10^{18}		1.95×10^{13}	292	307
$k_{0,2}$	8.31×10^4	1.93×10^{17}		2.38×10^{12}	2.47×10^3	1.10×10^3
$k_{0,3}$	1.13×10^6	-	6.73×10^{39}	1.34×10^7	-	2.30×10^3
$k_{0,4}$	-	-	-	-	-	2.00×10^3
$E_{a,1}$	60.00	153.63		106.20	115.4	115.1
$E_{a,2}$	132.00	161.9		106.90	130.1	122.8
$E_{a,3}$	170.83	-	407.50	10.30	-	-
$E_{a,4}$	-	-	-	-	-	-

^a $k_{0,i}$ units are [Pa/h]. ^b $k_{0,i}$ units are [(cm³)²/(mol·g·s)]. ^c $k_{0,i}$ units are [cm³/(mol·MPa^m)]. ^d $k_{0,i}$ units are [s⁻¹].

the hydrogen pressure (m_i). For the HDS reaction, they divided the sulfur-containing compounds present in the feedstock into 2, 3, and 4 lumps and assumed that the reaction rate equations for each lump were of the pseudo-first-order power-law type and the total sulfur concentration was determined as the sum of the concentrations of all of the lumps. The hydrotreated feedstock was the middle fraction of

Chinese Huadian shale oil (180–360 °C) and was processed in a bench-scale TBR loaded with a commercial NiMoW/Al₂O₃. The H₂/oil ratio was set as 600 L/L, and the other operating conditions were varied in the following ranges: temperatures between 280 and 380 °C, LHSV of 0.5–2.5 h⁻¹, and pressure from 4 to 7 MPa. The organosulfur compounds present in the feedstock were speciated by GC and divided

into eight families according to their chemical structure. The families of sulfur compounds were aliphatic and non-heterocyclic aromatic sulfur compounds, thiophenes, BT, alkyl-substituted BT derivatives, DBT, alkyl-DBTs, and dialkyl-DBTs. The first kinetic model consisted of 2 lumps (Figure 4a), lump 1 considered the high-reactivity compounds (all sulfur compounds except alkyl- and dialkyl-DBTs), and lump 2 the low-reactivity compounds (alkyl- and dialkyl-DBTs). The second kinetic model of three lumps (Figure 4b) separated the sulfur-containing compounds in lump 3 (higher reactivity), lump 4 (high reactivity), and lump 5 (low reactivity); lump 5 was the same as lump 2, and the compounds in lump 1 were distributed in lumps 3 and 4, where lump 3 included aliphatic and aromatic nonheterocyclic sulfur compounds, BT, alkyl-BTs, and dialkyl-BTs, and lump 4 contained the trialkyl-, tetraalkyl-, and pentaalkyl-BTs, along with DBT. The four-lump kinetic model (Figure 4c) comprised lump 6 (higher reactivity), lump 7 (high reactivity), lump 8 (low reactivity), and lump 9 (lower reactivity). In this case, lump 6 was equal to lump 3, and lump 9 to lumps 2 and 5; while lump 4 was divided into lumps 7 and 8 (Figure 4c).

They compared the results obtained from the three different lumped kinetic models to define the best number of lumps for the HDS reaction. The comparison was made according to two parameters, the r^2 value of the parity plot (experimental values vs estimated values) and the root mean square error (RSME). The higher r^2 values were obtained with the three and four lumps models, and both exceeded 0.99; however, the lowest RMSE value was obtained with the 3-lump model. The estimated parameters of the 3-lump model are presented in Table 6. This work is an example of a significant improvement from the 2-lump kinetic model to the 3- and 4-lump kinetic models; however, not always a larger number of lumps is going to yield the best fit for the kinetic model in every case.

More recent lumping kinetic studies of the HDS reaction for ULSD production under industrial operating conditions and representative settings are available in the literature. Yang et al.⁵⁵ proposed two 3-lump kinetic models for the HDS and HDN reactions during the HDT of coker gas oil (CGO). For the HDS reaction kinetics, the S compounds of the feedstock were divided into three lumps; the first one accounted for BT and its derivatives, the second one considered DBT and its derivatives, and the third included benzonaphthothiophene and its derivatives. Even though the last type of compound is not present in significant quantities in conventional ULSD feedstocks and its relative reactivity toward HDS is known to be higher compared with alkyl-substituted DBTs, this lumping kinetic model highlights the flexibility of this kind of model because depending on the feedstock that will be hydrotreated, the number and nature of the lumps can be modified to achieve reliable predictions of the S content in the products.

Wu et al.¹³ reported a set of kinetic models based on lumps of sulfur compounds to predict HDS reactions. The model considers splitting the sulfur content into two different reaction pathways, DDS and HYD, for the two lumps. Also, the model takes into account the inhibiting effect of H_2S (which is produced by the reaction between sulfur and H_2), nitrogen and aromatic compounds (because both HDN and HDA reactions compete for the active sites of the catalyst), and the refractory compounds, which is crucial for developing kinetic models for ULSD production. The rate law equations of this reaction are represented by

$$r_{S,1} = \frac{k_1 C_S^{n_1} C_{H_2}^{m_1}}{1 + K_{H_2S} C_{H_2S} + K_N C_N K_A C_A} \quad (43)$$

$$r_{S,2} = \frac{k_2 C_S^{n_2} C_{H_2}^{m_2}}{1 + K_N C_N + K_A C_A + K_{S,r/S} \frac{C_{S,r}}{C_S}} \quad (44)$$

In eq 44, $K_{S,r/S}$ represents the ratio of the adsorption-equilibrium constants of refractory sulfur compounds to total sulfur. Due to the unchanged behavior during the process of this concentration, the equation can be arranged as follows

$$r_{S,2} = \frac{k_2 C_S^{n_2} C_{H_2}^{m_2}}{1 + K_N C_N + K_A C_A + \frac{\gamma_{S,r}}{C_S}} \quad (45)$$

The authors used a NiMo/Al₂O₃ catalyst with a specific surface area of 177 m²/g and an average pore volume of 0.343 mL/g. The feedstock is a blend of SRGO and catalytically cracked gas oil in a ratio of 4:1 (w/w). All of the properties of the feed and product are shown in Table 1. The operating conditions and reaction system used were temperatures from 300 to 360 °C, 4.4 to 7.4 MPa of pressure, H₂/oil ratio of 300–800 m³/m³, LHSV from 0.18 to 1.33 h^{−1}, and a micropacked-bed reactor consisting of sixteen identical TBRs in parallel of 0.2 cm in diameter and 56 cm in length. The reaction conditions and reactor data are presented in Table 2.

Yin et al.¹¹ consider a set of reaction rate equations for the HDS of gas oil. A three-lump kinetic model was developed to simulate the kinetics of HDS, where the organosulfur compounds in the diesel feed were classified into three lumps, namely, S₁, S₂, and S₃, respectively. Lump S₁ consists of thiophene, BT, and its alkyl derivatives. Lump S₂ consists of DBT and other DBTs (C₁–C₂) with two alkyl substituents at neither 4- nor 6-position, and lump S₃ consists of the most refractory compounds like 4- or/and 6-substituted DBTs and heavily substituted C₃-DBTs. Both eqs 46 and 47 follow the first-order reaction rate equation. According to the authors, under the conditions where HDS is typically carried out, the concentrations of lumps S₁ and S₂ are reduced to low values, which increases the relative errors between simulations and sulfur characterization results. Therefore, the experimental data for the concentrations of S₁ and S₂ were summed up to produce new data and regressed them using eq 48. Then, eq 49 shows the model for lump S₃, which includes the inhibitory effects of N, confirming that the hydrodenitrogenation of gas oil is a reaction that competes for the active sites during HDS.

$$r_{S_1} = k_{f,S_1} C_{S_1} P_{H_2} \quad (46)$$

$$r_{S_2} = k_{f,S_2} C_{S_2} P_{H_2} \quad (47)$$

$$r_{S_1} + r_{S_2} = k_{f,S_1} C_{S_1} P_{H_2} + k_{f,S_2} C_{S_2} P_{H_2} \quad (48)$$

$$r_{S_3} = k_{f,S_3} (C_{S_3} - C_{S_e}) P_{H_2}^{n_4} + \frac{k'_{f,S_3} (C_{S_3} - C_{S_e})}{(1 + K_{N_1} C_{N_1} + K_{N_2} C_{N_2})} P_{H_2}^{n_5} \quad (49)$$

The experimental conditions are listed in Table 2. The catalyst used by the authors is a NiMo/Al₂O₃ with a specific surface area of 177 m²/g, an average pore volume of 0.343 cm³/g, and an average pore diameter of 7.74 nm. The weighted least absolute error method (eq 31) is used to estimate the kinetic parameters for three reactions (HDS, HDN, and

HDA). The interior point method was chosen as the optimization method, which was carried out in MATLAB software. The kinetic parameters obtained by this method are reported in Table 6.

This type of model differs from a power-law kinetic model because it includes the inhibition effects of compounds that are present in the feedstock (mainly N-containing compounds and aromatics). Therefore, the LHHW models reported by Yin et al.¹¹ are very promising because they provide useful information for the production of ULSD and take into account the different reactivities between the various S-containing chemical species present in the feed.

Aleksandrov et al.⁴⁴ studied the catalytic HDS reaction of five different feedstocks in a bench-scale TBR with a CoMo/Al₂O₃ catalyst under reaction conditions ranges of 335–365 °C, 0.8–2.5 h⁻¹, and 3.5–5.1 MPa, with a constant H₂/hydrocarbon ratio of 300 Nm³/m³. The hydrotreated feeds were SRGO with high sulfur content (2.062 wt % S), CGO, SRGO (1.045 wt % S), and two blends of CGO at 15 and 30% with the SRGO with high S content each. The authors proposed and compared four different kinetic models to simulate the HDS reaction within the TBR.

Model 1: a simple *n*th-order power-law kinetic model for the S conversion.

$$r_s = -k_s C_s^n \quad (50)$$

Model 2: a single-lump LHHW type of model considering the inhibition effects of H₂S and NH₃ gases and the competitive adsorption of the H₂ reactant over the catalyst surface. The reaction order was of the *n*th order for the S concentration and of the first order with respect to hydrogen pressure.

$$r_s = \frac{k_s C_s^n P_{H_2}}{(1 + K_{H_2S} C_{H_2S} + K_{NH_3} C_{NH_3})(1 + K_H P_{H_2})} \quad (51)$$

Model 3: a two-lump HDS kinetic model, where all of the S species were divided into an easy-to-convert sulfur compound lump (*S_e*) comprised of mercaptans, TP, and any other reactive S compound; and a refractory sulfur compound lump (*S_r*), including DBT and its alkyl-substituted derivatives. The rate reaction equations were of first-order power-law kinetics for *S_e*, and for *S_r*, it was similar to the LHHW type equation of model 2 (eq 51).

$$r_{S_e} = -k_{S_e} C_{S_e} \quad (52)$$

$$r_{S_r} = \frac{-k_{S_r} C_{S_r}^n P_{H_2}}{(1 + K_{H_2S} C_{H_2S} + K_{NH_3} C_{NH_3})(1 + K_H P_{H_2})} \quad (53)$$

$$C_S = C_{S_e} + C_{S_r} \quad (54)$$

Model 4: in this model, the authors further divided the refractory sulfur compound lump into three lumps: DBT without any alkyl-substituent on 4 or 6 carbon atoms (*S₂*), 4-MDBT and its derivatives (*S₃*), and 4,6-DMDBT and its derivatives (*S₄*); in accordance with their differences in relative reaction rates (Figure 5). For the first lump of reactive sulfur compounds (*S₁*) the HDS rate equation was equal to eq 52, and for lumps 2 and 3, the rate equations were similar to the LHHW type rate equation for the *S_r* lump of the third model (eq 53). However, for the HDS kinetic modeling of the most refractory sulfur compounds (*S₄*), the rate equation also

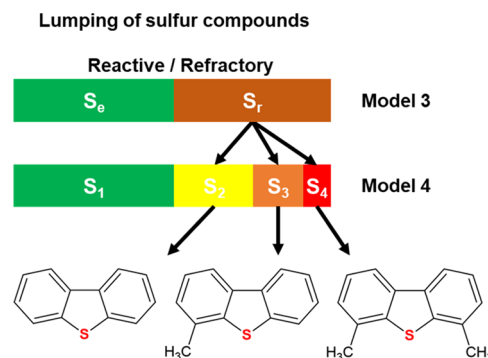


Figure 5. Scheme of the S-containing compound lumping for HDS kinetic models 3 and 4 reported by Aleksandrov et al.⁴⁴ *S₁* (also referred to as *S_e*): all sulfur compounds more reactive than DBT, *S₂*: DBT and its derivatives without alkyl substituents in the 4 or 6 positions, *S₃*: 4-MDBT and its derivatives, *S₄*: 4,6-DMDBT and its derivatives, and *S_r*: all of the refractory sulfur compounds in lumps *S₂*, *S₃*, and *S₄*.

included the N compound inhibition effect in the denominator.

$$r_{S_1} = -k_{S_1} C_{S_1} \quad (55)$$

$$r_{S_2} = \frac{-k_{S_2} C_{S_2}^n P_{H_2}}{(1 + K_{H_2S} C_{H_2S} + K_{NH_3} C_{NH_3})(1 + K_H P_{H_2})} \quad (56)$$

$$r_{S_3} = \frac{-k_{S_3} C_{S_3}^n P_{H_2}}{(1 + K_{H_2S} C_{H_2S} + K_{NH_3} C_{NH_3})(1 + K_H P_{H_2})} \quad (57)$$

$$r_{S_4} = \frac{-k_{S_4} C_{S_4}^n P_{H_2}}{(1 + K_{H_2S} C_{H_2S} + K_{NH_3} C_{NH_3})(1 + K_H P_{H_2})(1 + K_N C_N)} \quad (58)$$

$$C_S = C_{S_1} + C_{S_2} + C_{S_3} + C_{S_4} \quad (59)$$

All kinetic parameters were estimated by fitting the model calculations to the experimental results through the minimization of a relative SSE objective function (eq 60) and employing a linear least-squares method with a 95% confidence limit for the four kinetic models. Fifty-three catalytic evaluations of the high S content SRGO and its blends with CGO were done, and the reliability of the models was compared with the result of the average relative deviation of their predictions. The results of the average relative deviation were 11.04, 5.07, 5.06, and 4.62 ppm, respectively.

$$OF = \sum_{i=1}^N \frac{(C_i^{\text{exp}} - C_i^{\text{cal}})^2}{C_i^{\text{exp}}} \quad (60)$$

They concluded that more accurate predictions of the S content of the products were obtained using models 3 and 4. Therefore, for kinetic modeling of the ultradeep HDS reaction with feedstocks of diverse nature, the models should consider the different reactivities of refractory sulfur compounds and the inhibition effects of N-containing compounds in the feed and also of the gases produced during the HDS and HDN reactions.

As it has been discussed, lumped kinetic models of HDS of S-containing compounds present in real feedstocks have

Table 7. Families of Organonitrogen Compounds Present in Petroleum Middle Distillates and Diesel Precursor Streams.^{54,56,58}

Organonitrogen compounds family	Chemical structure	Acidity type	Structure type	HDN reactivity
Aliphatic amines (ALA)		Basic	Non-heterocyclic	Highest
Nitriles (NTL)		Basic	Non-heterocyclic	Higher
Anilines (ANL)		Basic	Non-heterocyclic	High
Pyridines (PDN)		Basic	Pyridinic species	Fair
Pyrroles (PYR)		Non-basic	Pyrrole species	Moderate
Quinolines (QNL)		Basic	Pyridinic species	Medium
Acridines (ACD)		Basic	Pyridinic species	Subpar
Indoles (IND)		Non-basic	Pyrrole species	Low
Carbazole (CAR)		Non-basic	Pyrrole species	Lower
Alkyl-substituted carbazoles (ASCAR)		Non-basic	Pyrrole species	Lowest

several advantages over kinetic models of total sulfur, model sulfur compounds (i.e., DBT, 4-MDBT, and 4,6-DMDBT), and detailed kinetic models. In summary, the advantages of using lumped HDS kinetic models over kinetic models of total sulfur or sulfur model compounds include improved accuracy, better representation of real feedstocks, increased flexibility, and reduced computational complexity. These advantages make lumping HDS kinetic models an attractive choice for representing the reaction occurring during ULSD production and other applications where sulfur removal is critical.

The relevant kinetic parameters reported from the studies discussed in this section are summarized in Table 6. The recently published papers confirm that lump kinetic modeling of the HDS reaction of real feedstocks is an emerging problem that needs to be solved. In addition to HDS kinetic modeling for ULSD production, other reactions such as the HDN, HDA, HGO, and HCR must be taken into consideration to have better approaches to real behavior in kinetics and reactor design, simulation, and operation.

3. HYDRODENITROGENATION REACTIONS

Hydrodenitrogenation (HDN) is the second most important reaction occurring in the hydrotreating process because nitrogen is also an abundant heteroatom present in petroleum.

The heterocyclic organonitrogen compounds present in hydrocarbon feeds have the highest inhibition effect for the HDS and HDA reactions as well as a strong HDN self-inhibition among all hydrotreating inhibitors, such as polyaromatics, O-containing compounds, H₂S, and monoaromatics; which can lead to poisoning effect, especially for acid catalysts used in subsequent refining steps.^{56,57} In addition, N-containing compounds present in fossil fuels can lead to the production of harmful and polluting gases such as nitrogen oxides (NO_x) upon combustion. Organonitrogen compounds in diesel fuel also reduce stability and can cause unwanted color, odor, and gumming.^{58,59}

The concentration of nitrogen-based compounds depends on the source of the feedstock and increases with the boiling temperature of the fraction. However, there is an increasing need to refine alternative feedstocks to produce diesel fuel in addition to conventional crude oil distillates. Some examples of the alternative sources of diesel fuel precursor streams are MDSO, middle-low temperature coal tars (MLCT), heavy gas oils from oil sands bitumen (HGOSB), VGO, LCO, and CGO. It has been observed that these types of feedstocks tend to have a higher content of heterocyclic N-containing compounds, aromatics, and asphaltenes compared with conventional middle distillates such as SRGO, resulting in the need

for more severe operating conditions, more HDN active catalyst, and better kinetic models.^{60–62} For these reasons, the kinetics of ultradeep HDT reactions of heterocyclic N-containing compounds has attracted greater interest in several research groups in recent years, leading to the development of better and more detailed kinetic models for HDN, HDA, HDO, etc.

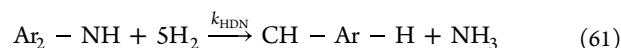
The HDN kinetic models were grouped similarly to the HDS kinetic models, based on the similarities between them, considering the type of model (power-law models and LHHW) and the nature of the hydrotreated feed used to determine the kinetic parameters of the models. Thus, kinetic models considering total nitrogen are described first, followed by the kinetics for model N-containing compounds, and finally, the kinetic models considering two or more lumps, depending on the reactivity of nitrogen compounds in real feedstocks, are discussed.

3.1. Kinetic Models Based on Total Nitrogen Concentration.

N-containing compounds in diesel precursors are mainly heterocyclic aromatic species; nonheterocyclic N compounds such as aliphatic amines and nitriles are also found, but the elimination of the N atom from these functional groups occurs faster under common HDT operating conditions, and their inhibition strength is considerably lower than that of heterocyclic nitrogen species. These compounds can be divided into two groups based on the ability of the N atom to donate its lone pair of electrons: basic and neutral (also known as nonbasic). In the case of basic nitrogen compounds, such as quinoline (QNL) and acridine (ACD) derivatives (pyridinic heterocycles), the electrons remain on the N atom and are available for donation to Lewis acids, and in the other case, the electrons are delocalized in the aromatic moiety of the molecule, making them less available to be donated, such as indole (IND) and carbazole (CAR) derivatives (pyrrole heterocycles).¹² Both groups poison the active sites of the HDS catalyst, the basic N species mostly blocking the acidic sites and the neutral nitrogen species predominantly affecting the sulfided active phase. Furthermore, N-containing compounds cause competitive inhibition of hydrogenation reactions (such as HDA and HDS of refractory sulfur compounds) related to the loss of available hydrogen atoms at the catalyst surface due to their higher proton affinity.⁶³ The chemical structures, classifications, and relative HDN reactivity of the most representative families of organonitrogen molecules found in petroleum products are shown in Table 7.

Despite the significant differences in HDN activity and inhibition effect of HDS and HDA reactions among the different nitrogen species mentioned above, these kinetic models of total N content have been shown to be sufficiently accurate for the following reasons: (1) N content in the vast majority of feedstocks is about 2 orders of magnitude lower than their respective S content; (2) most of the N-containing compounds present in diesel feedstocks are similar, the heterocyclic nitrogen compounds can account for up to 97% of all of the N species, and (3) HDN reaction mechanism of basic and neutral species goes through the same steps, where the hydrogenation of the aromatic ring in the neutral N-containing compounds forms basic intermediates.⁶⁴ Moreover, carbazole and indole derivatives represent two-thirds of the total N content in many crude oils, and nitrogen compound speciation of middle distillates after deep HDS has shown that almost all unreacted organonitrogen compounds are carbazoles and carbazole alkyl derivatives.^{10,65–67} Consequently, most of

the HDN kinetic models found in the literature group all of the N-containing species of the feedstock into one lump^{14,23,28,31,52,67–69} and represent the HDN reaction of CAR and its derivatives with a generalized stoichiometric equation as follows



where Ar_2-NH is the organic nitrogen compound, $\text{CH}-\text{Ar}-\text{H}$ is the N-free hydrocarbon compound with a cyclohexane ring (CH) bonded to an aromatic ring (Ar-H), H_2 is hydrogen, NH_3 is ammonia, and k_{HDN} is the reaction rate coefficient of HDN.

Bhaskar et al.²³ proposed a kinetic model to simulate the main hydrotreating reactions of the gas oil fraction, such as HDS, HDN, HDA, HGO, and HCR. HDS was represented by an LHHW-based model, while all N-containing compounds were considered as a single lump, and the following pseudo-first-order reaction rate equation was assumed

$$r_{\text{N}} = k_{\text{app,N}} C_{\text{N}}^{\text{S}} \quad (62)$$

where $k_{\text{app,N}}$ is the apparent rate constant for the HDN reaction, and C_{N}^{S} is the concentration of N species on the catalyst surface. The parameter estimation procedure described above also applies to the estimation of HDN kinetic parameters. The authors concluded that the simulated results were in good agreement with the experimental data. Nevertheless, as shown in Table 1, the N content of the diesel feedstock is significantly lower than the S content, which reduces the magnitude of errors in the HDN simulations. The proposed kinetic models neglect the inhibition of the HDS reaction by competitive adsorption of N compounds, the HDN self-inhibition effect (especially by carbazole species), and the HDN reaction mechanism of heterocyclic nitrogen compounds.

Another example of a single-lump power-law kinetic model for HDN was reported by Mederos et al.¹⁰ They justify the use of this type of model due to the significantly lower content of nitrogen species in the feedstock compared with sulfur and aromatic compounds (as shown in Table 1), the CoMo catalyst employed in this work is more selective for sulfur removal via the DDS pathway, and the fact that the inhibitory effects of nitrogen compounds on the HDS reactions are relevant when producing ULSD, which is not the case of said work.

Another single-lumped power-law model for the HDN reaction, as observed in eq 63, has been reported elsewhere.²⁷ The reaction rate is expressed in terms of N and H_2 concentrations, and the superscripts m_{HDN} and n_{HDN} correspond to the reaction order for nitrogen and hydrogen, respectively. The model prediction improved but was still not sufficient to be considered for ULSD production.

$$r_{\text{HDN}} = k_{\text{HDN}} C_{\text{N}}^{m_{\text{HDN}}} C_{\text{H}_2}^{n_{\text{HDN}}} \quad (63)$$

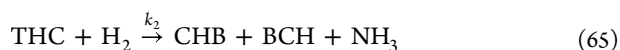
As the most relevant N-containing species in diesel feedstocks are CAR and ASCAR, the HDN reaction mechanism of CAR proposed elsewhere has been used in modeling.⁶⁴ Wu et al.¹³ grouped the nitrogen compounds in one lump, considering the self-inhibition by N compounds involved in two steps of the HDN reaction mechanism of CAR. The first step occurs when carbazole molecules occupy the active sites to undergo partial hydrogenation and produce tetrahydrocarbazole (THC), as represented in eq 64. The

Table 8. Estimated Kinetic Parameters Reaction Order (n for N and m for H_2), $k_{0,i}$ [s^{-1}], and $E_{a,i}$ (kJ/mol) for the HDN Reaction

parameter	reference				
	10	13 ^a	27 ^b	23 ^c	
n	1	1	1.11	1	1
m	-	1	0.17	-	-
$k_{0,1}$	5.59×10^{15}	1.00×10^{11}	1.43×10^{12}	17.67	33.4
$k_{0,2}$	-	1.00×10^{11}	-	-	-
$E_{a,1}$	172.28	120.55	156.61	46.76	49.42
$E_{a,2}$	-	98.45	-	-	-

^a $k_{0,i}$ units are [$(\text{cm}^3)^2/(\text{mol} \cdot \text{g} \cdot \text{s})$]. ^b $k_{0,i}$ units are [$\text{cm}^3/(\text{g} \cdot \text{s} (\text{mol} \cdot \text{cm}^3)^{(1-n)})$]. ^c $k_{0,i}$ units are [$\text{cm}^3/(\text{g} \cdot \text{s})$].

second step is the cleavage of the nitrogen atom from the THC molecule to give ammonia and the corresponding N-free hydrocarbons such as CHB and BCH (eq 65). The presence of these N-containing molecules on the catalyst surface hinders hydrogen adsorption and slows the completion of the HDN reaction. The decrease in LHSV increases the conversion of the CAR and desorption of hydrocarbons from the active sites. The strong adsorption of these N compounds on the active sites causes a self-inhibition effect of the HDN reaction; furthermore, the inhibition effect of S compounds and aromatics can be neglected as a consequence of their smaller adsorption constants compared with N compounds. Consequently, a pseudo-first-order reaction rate equation, including a power-law component for the partial hydrogenation of CAR to THC and a Langmuir–Hinshelwood model for the second step of the HDN reaction (eq 66), are considered.



$$r_{\text{HDN}} = k_1 C_N C_{\text{H}_2} + \frac{k_2 C_N C_{\text{H}_2}}{1 + K_N C_N} \quad (66)$$

Due to the inhibitory effect of nitrogen species on the HDS reaction, particularly for ultradeep HDS reactions, the S content of the hydrotreated products can be expressed as a function of the N content. Ho⁶⁷ proposed a simplified mathematical model to simulate trickle-bed reactors loaded with two different catalysts in stacked-bed and mixed-bed configurations. The mathematical model took into account the influence of the concentration and type of organonitrogen compounds in ultradeep HDS processes; since catalyst inhibition is particularly important for the hydrogenation reaction path, H_2S and polyaromatic species were neglected. Thus, a mathematical expression was obtained to predict the optimum stacked-bed scheme for ULSD production with two different HDS catalysts, while HDS and HDN reactions are assumed to occur in steady-state isothermal in a pseudo-homogeneous plug-flow reactor with the following mass balance equations

$$v \frac{dS}{dz} = \frac{(1 - \varepsilon) \rho_p k_s q_m}{(1 + K_N C_N / k_{\text{HDN}})} \times C_S \quad (67)$$

$$v \frac{dN}{dz} = \frac{(1 - \varepsilon) \rho_p k_n q_m}{(1 + K_N C_N / k_{\text{HDN}})} \times C_N \quad (68)$$

where v is the superficial fluid velocity, ε is the bed void fraction, ρ_p is the catalyst particle density, and q_m is the active site density. The boundary values are $z = 0$, $C_S = C_{S0}$, and $C_N = C_{N0}$ at the reactor inlet and $z = L$, $C_S = C_{SL}$, and $C_{NL} = C_N$ at the reactor outlet. Due to the convenience of using dimensionless variables, the following terms have been used: $s = C_S / C_{S0}$, $n = C_N / C_{N0}$, $\eta \equiv k_s q_m \tau$, $\mu \equiv k_n q_m \tau$, $g \equiv k_n C_{N0} / k_{\text{HDN}}$, and $\xi \equiv z / L$, where $\tau \equiv (1 - \varepsilon) \rho_p L / v$ is the residence time, L is the length of the reactor, η is the catalytic activity of HDS, μ is the activity of HDN, and g is the inhibition number, a measure of the intensity of inhibition by N compounds. The dimensionless mass balance equations are as follows

$$\frac{ds}{d\xi} = \frac{\eta s}{(1 + gn)} \quad (69)$$

$$\frac{dn}{d\xi} = \frac{\mu n}{(1 + gn)} \quad (70)$$

where the dimensionless boundary conditions at the reactor inlet are $\xi = 0$ and $s = n = 1$.

Since HDS is determined by the inhibition of nitrogen species, the total S content can be expressed in terms of the N content. After dividing eqs 69 and 70, the resulting equation is $s = c_1 n^p$, where c_1 is an integration constant. Integration of this equation gives the sulfur and nitrogen contents, respectively

$$s(\xi) = s_f [n(\xi) / n_f]^p \quad (71)$$

$$n(\xi) e^{g n(\xi)} = n_f e^{g n_f} e^{-\mu \xi} \quad (72)$$

Solving eqs 69 to 72 gives the profiles for S and N contents, taking into account the parameters for supported and bulk catalysts.

To summarize the kinetic models discussed in this section, single-lumped power-law rate equations can only provide accurate predictions when the N content of the feed is at least 2 orders of magnitude lower than the S content, which is typically the case for middle distillates such as SRGO, and ULSD production is not the main objective of the HDS process. For HDS processes aimed at producing diesel with an S content less than 15 ppm from conventional diesel feedstocks, L–H models taking into account the self-inhibition of N-containing compounds can improve the accuracy of HDN kinetic model predictions. However, especially for alternative diesel feedstocks where the N content is significantly higher and CAR species are not the main N compounds, the use of more complex kinetic models is strongly recommended. Table 8 shows the estimated kinetic parameters for HDN models based on the total nitrogen content in real feedstocks.

3.2. Kinetic Models Based on Model Nitrogen Compounds. Nitrogen compounds found in diesel feedstocks are shown in Table 7. It is worth noting that for heavy and extra-heavy crude oils and unconventional feedstocks such as coal-derived crudes, tar sands, and shale oils, porphyrin and its derivatives are other important nitrogen-containing compounds, but such compounds are not significantly present in diesel feedstocks and are not considered in this work. Due to the wide variety of N compounds present in the feedstocks for ULSD production, the reaction mechanism and kinetics of each of them were initially studied separately by HDN testing of model nitrogen compounds. Although these studies were important in elucidating the reaction mechanism of each family of organonitrogen molecules on the surface of heterogeneous hydrotreating catalysts, the kinetic parameters obtained from them proved to be inadequate for hydrotreating real feedstocks. One of the most common deviations observed between kinetic parameters calculated from model compounds or mixtures of model compounds and evaluations of real feedstocks is the higher reaction orders for real feedstocks due to the limited consideration of interactions, mainly the inhibition of hydrotreating reactions by competitive adsorption on the catalyst's active sites caused by the multiple chemical species present. In addition, model compound tests have usually been carried out in laboratory-scale experimental settings such as batch reactors and continuous gas-phase microreactors, resulting in parameters that are not suitable for industrial-scale ultra-deep HDT of real feedstocks. For these reasons, recent kinetic studies have tended to calculate parameters from industrially relevant scale catalytic evaluations, such as pilot and semi-industrial plants, to develop more accurate and useful models for ULSD production in refineries.

ANL, QNL, IND, and CAR and their derivatives are typically the most abundant organonitrogen compounds in feedstocks for diesel.⁵⁹ However, CAR and ASCAR are the most important nitrogen refractory compounds in ULSD production due to their lower HDN reactivities, which are highly concentrated in hydrotreated products.^{67,70–73} Literature dealing with HDN of model compounds and describing in detail the kinetics of PDN, QNL, ACR, PYR, IND, and ANL species is reviewed elsewhere.^{12,64–66} However, a discussion of the kinetics of CAR and ASCAR is lacking, and the scope of this section will include this topic.

Most of the kinetic models proposed in the literature for CAR and ASCAR species are pseudo-first-order equations and of the L–H type, similar to the HDS reaction kinetics of DBT and its derivatives. Nevertheless, the removal of the N atom from these compounds by HDN is much more difficult to achieve than the removal of the S atom from thiophene by HDS due to the higher bond strength of the C=N bond, 615 kJ/mol, compared with the C=S bond, 477–536 kJ/mol, and the smaller atomic radius of nitrogen (0.075 nm for N versus 0.109 nm for S).⁵⁷

The most commonly referenced carbazole HDN reaction network in kinetic modeling studies of the HDN reaction was proposed by Nagai^{74–76} and Szymańska⁶⁴ (Figure 6). Although the studies are based on the HDN of CAR on molybdenum sulfides, nitrides, and carbides, the reaction path has shown to be adequate for kinetic modeling using a NiMo sulfide catalyst as well. Figure 6 shows two reaction pathways: (1) the carbazole HDN reaction scheme with more intermediates (black arrows) and (2) a simplified version^{77,78} (blue arrows) over NiMo/Al₂O₃-SiO₂(x) catalysts. The first

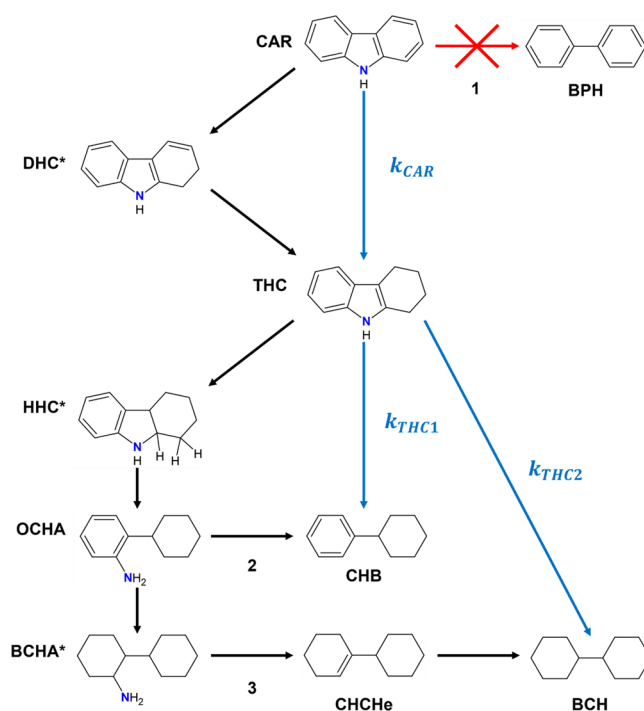


Figure 6. Detailed (black arrows)⁶⁴ and simplified (blue arrows)⁷⁸ HDN reaction network of carbazole conversion.

reaction route includes three very reactive partially hydrogenated intermediates, i.e., dihydrocarbazole (DHC), hexahydrocarbazole (HHC), and bicyclohexylamine (BCHA), which were not detected in hydrotreating products, but it was proposed that their formation during the reaction is due to the favored cleavage of the C(sp³)-N bond over the C(sp²)-N bond. According to the literature, the hydrogenolysis pathway of carbazole shown in pathway 1 in Figure 6 is the least likely thermodynamic route under hydrogen pressure for the majority of hydrotreating catalysts⁷⁹ and is generally neglected. CAR is hydrogenated to DHC and then to THC, which presumably undergoes further hydrogenation to form HHC before the C–N bond is cleaved to give the barely detectable orthocyclohexylaniline (OCHA) intermediate molecule. Subsequent N removal from OCHA can occur via denitrogenation (route 2) and hydrogenation pathways (route 3). Pathway 2 produces CHB and ammonia, whereas pathway 3 produces the cyclohexyl-cyclohexene (CHCHe) and ammonia molecules, followed by an HGO reaction of CHCHe that eventually forms BCH. It was also observed that the final HGO of CHCHe to BCH is strongly inhibited by S- and N-containing heterocyclic compounds due to the weaker adsorption of naphthenes on the catalyst surface.

The HDN kinetic model of carbazole on NiMo/Al₂O₃-SiO₂(x), where x represents 0 or 10 wt % of SiO₂ in the support (blue arrows in Figure 6), considers the following assumptions: (1) the reaction rate is of the first order; (2) the H₂ concentration remains constant during the reaction; (3) the apparent adsorption constants of H₂S and NH₃ were included; (4) the disappearance rate of CAR and appearance rate of BCH were not inhibited by naphthalene; and (5) the formation rates of THC and CHB were not affected by the presence of 4,6-DMDBT and naphthalene presence in the feedstock. The kinetic model of HDN of CAR is presented in the following equations.

$$-r_{\text{CAR}} = \frac{k_{\text{CAR}} C_{\text{CAR}}}{(1 + K_{4,6\text{-DMDBT}} C_{4,6\text{-DMDBT}} + K_{\text{CAR}} C_{\text{CAR}} + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}} + K_{\text{NH}_3} C_{\text{NH}_3})^2} \quad (73)$$

$$-r_{\text{THC}} = \frac{k_{\text{CAR}} C_{\text{CAR}} - (k_{\text{THC1}} + k_{\text{THC2}}) C_{\text{THC}}}{1 + K_{\text{CAR}} C_{\text{CAR}} + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}} + K_{\text{NH}_3} C_{\text{NH}_3}} \quad (74)$$

$$-r_{\text{CHB}} = \frac{k_{\text{THC1}} C_{\text{THC}}}{1 + K_{\text{CAR}} C_{\text{CAR}} + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}} + K_{\text{NH}_3} C_{\text{NH}_3}} \quad (75)$$

$$-r_{\text{BCH}} = \frac{k_{\text{THC2}} C_{\text{THC}}}{1 + K_{4,6\text{-DMDBT}} C_{4,6\text{-DMDBT}} + K_{\text{CAR}} C_{\text{CAR}} + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}} + K_{\text{NH}_3} C_{\text{NH}_3}} \quad (76)$$

The reactions were carried out in a batch reactor loaded with 200 mg of catalyst to process 40 mL of a 70/30 wt % mixture of decane/*m*-xylene and reactants (1000 ppm of S as 4,6-DMDBT, 5 wt % of naphthalene, and/or 100 ppm of N as CAR). The reaction conditions for the catalytic evaluations were a temperature of 325 °C, a pressure of 4 MPa, and a stirring speed of 1000 rpm during reaction times ranging between 0 and 3 h at 0.5 h intervals. The Powell's minimization method contained in MicroMath was used to estimate the kinetic parameters fed with experimental data and the rate equations, and the objective function was R^2 . CAR showed a higher reactivity than 4,6-DMDBT due to its higher adsorption strength on the catalyst surface, which also explains its strong inhibitory effect on the HDS of 4,6-DMDBT. However, the apparent adsorption constant of CAR takes into account the adsorption constants of the partially hydrogenated products, which were observed to be higher than the CAR adsorption constant due to the higher basic character of these molecules.⁸⁰ Finally, the adsorption of CAR on the catalyst surface was not observed to be altered by the presence of hydrogen sulfide and ammonia.

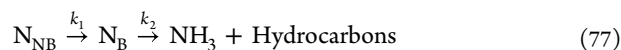
Updated studies of HDN of organonitrogen model compounds, such as QNL, ACR, and IND, to determine the effect of the support acidity on the adsorption and HDN reactivity of such N-containing compounds have been reported with promising results.^{55,56,58}

3.3. Lumped Nitrogen Compounds Kinetic Models. In recent years, many works on the development of new HDN kinetic models have classified organonitrogen compounds into two or more lumps based on their HDN reactivity, chemical structure, and/or physical and chemical properties. Similar to S-containing molecules, the reactivity of N-containing compounds is inversely proportional to their boiling point and the presence of aromatic structures adjacent to the heteroatom. Nevertheless, according to Liu et al.,⁸⁰ by using a combination of density functional theory (DFT) calculations and dispersion correction, N-containing heterocyclic compounds and their hydrogenated derivatives have greater adsorption strengths on the active sites of the HDS catalysts (multisite NiMoS nanoclusters) in the following order: corner $\approx$ Mo-edge > S-edge, than BT, DBT, and their derivatives. This phenomenon causes the strong inhibition of the DDS pathway of HDS where the corner and Mo-edge active sites are commonly associated with the DDS pathway, over the HYD pathway with the S-edge active sites by the competitive

adsorption of the heterocyclic N compounds. Furthermore, the authors concluded that the stronger inhibitors are not the N compounds themselves but their respective partially or fully saturated intermediates and the HDN by-product (ammonia). These findings, together with the previously mentioned differences between the types of N-containing compounds present in conventional and alternative petroleum products, highlight the importance of classifying the N compounds into distinct lumps.

For the HDT of conventional crude oil fractions, the development of lumped kinetic models for the reaction of N compound removal was considered unnecessary due to the low N content in the feedstocks such as SRGO. However, the increasingly stringent environmental requirements for transport fuels and the use of unconventional gas oil sources have shown that taking into account the differences between N-containing compounds and lumping N species with analogous structure and reactivity leads to more accurate predictions of the final N content in the ultradeep hydrotreating products compared with single kinetic models (regardless of whether they are of the power-law or LHHW kinetic model type). Table 9 shows examples of lumped N compounds kinetic models found in the literature, their respective lumping criteria, the number of lumps, and the N species considered in each lump.

The first proposed lumped HDN reaction kinetic models separated all organonitrogen compounds into lumps accordingly to their acidity. One lump was constituted by ALA, NTL, ANL, PRD, QNL, and ACD, while another lump was formed by PYR, IND, CAR, and ASCAR. A study of the HDN reaction of an HGOSB over a commercial NiMo/Al₂O₃ catalyst was carried out to determine the influence of operating conditions on the reaction rates of total, basic, and nonbasic N-containing compounds.⁵² The kinetic model considers the following reaction scheme



where the governing assumption is that the hydrogenation (k_1) of a nonbasic N compound (N_{NB}) yields an intermediate basic N compound (N_{B}) prior to the removal of the N atom and the formation of ammonia and hydrocarbons (k_2). Another kinetic model considers the elimination of nitrogen from all N-containing compounds in a one-step concerted reaction, and its apparent reaction rate constant is represented by k_3 . The reaction of nonbasic (k_1) and total (k_3) N compounds was described by a power-law model, and the apparent kinetic constants were calculated by using eq 78 for reaction orders $n > 1$ and by eq 79 for $n = 1$. After testing different reaction orders, the best fit was obtained with $n = 1.5$.

$$k = \frac{1}{n-1} \left[\frac{1}{\text{N}_{\text{p}}^{n-1}} - \frac{1}{\text{N}_{\text{f}}^{n-1}} \right] \text{LHSV} \quad (78)$$

$$\ln \left(\frac{\text{N}_{\text{f}}}{\text{N}_{\text{p}}} \right) = \frac{k}{\text{LHSV}} \quad (79)$$

To estimate the apparent reaction rate constants, k_1 and k_2 , the following equation was used

$$-\frac{\text{dN}_{\text{B}}}{\text{dt}} = k_1 \text{N}_{\text{NB}}^{1.5} - k_2 \text{N}_{\text{B}}^{1.5} \quad (80)$$

Table 9. Examples of Lumped N Compounds Kinetic Models Found in the Literature, Their Lumping Criteria, Number of Lumps, and N Species Considered in Each Lump

ref	type of feedstock	lumping criteria	no. of lumps	lump 1 name and N species	lump 2 name and N species	lump 3 name and N species	lump 4 name and N species
62	HGOSB	acidity	2	nonbasic (PYR, IND, CAR, ASCAR)	basic (ALA, NTL, ANL, PDN, QNL, ACD)	-	-
92	CGO		2				
25	VGO		2				
54	MDSO (180–360 °C)	HDN reactivity	2	high reactivity (NTL)	low reactivity (ANL, PDN, QNL, ACD, IND, CAR, ASCAR)	-	-
			3	higher reactivity (NTL)	high reactivity (ANL, PDN, QNL, ACD)	low reactivity (IND, CAR, ASCAR)	-
			4	higher reactivity (NTL)	high reactivity (ANL)	low reactivity (PDN, QNL, ACD)	low reactivity (IND, CAR, ASCAR)
51	MDSO (<360 °C)	HDN reactivity	2	high reactivity (ALA, NTL, ANL)	low reactivity (PRD, QNL, ACD, IND, CAR, ASCAR)	-	-
61	SRGO, LCO, CGO, and mixtures	chemical structure	3	directly converted at the reactor inlet (PYR, IND)	basic pseudo-compounds (ANL, PRD, QNL, ACD)	carbazoles and derivatives (CAR, ASCAR)	-
55	CGO	HDN reactivity	3	PRD, ACD, QNL, and derivatives	CAR and derivatives (ASCAR)	other N compounds (ALA, NTL, ANL, PYR, IND)	-
58	two diesel oils	chemical structure and HDN activity	2	ASCAR	other N compounds (ALA, NTL, ANL, PRD, PYR, QNL, ACD, IND, CAR)	-	-
60	MLCT	HDN reactivity	3	high reactivity (ALA, NTL, ANL, PRD, PYR, QNL)	middle reactivity (IND)	low reactivity (ACD, CAR, ASCAR)	-

The values of the calculated kinetic parameters are given in Table 10. The apparent kinetic constants were calculated at different temperatures ranging from 365 to 415 °C. The limiting step in the HDN reaction is the hydrogenation of the nonbasic N compounds, which are also the main type of organonitrogen compounds. In addition, higher pressures, H₂-to-oil ratios, and catalysts with higher hydrogenation activity can improve the total nitrogen conversion in HDN processes. Other authors also lumped the N compounds as basic⁷⁴ and neutral²⁸ (nonbasic). The kinetic model proposed by Wei et al.⁹² is shown in eq 81, where the term TN is total nitrogen, BN is basic nitrogen, and NBN is nonbasic nitrogen. Patil et al.²⁵ considered a reaction order of 1.5 for neutral nitrogen compounds and used the LHHW model as observed in eqs 82 and 83, taking into account the inhibitory effect of H₂S.

$$r_{\text{HDN}} = k_{\text{TN}} C_{\text{TN}} C_{\text{BN}} C_{\text{NBN}} \quad (81)$$

$$r_{\text{HDN}_{\text{NB}}} = \frac{k_{\text{NB}} C_{\text{NB}}^{1.5} C_{\text{H}_2}}{(1 + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}})^2} \quad (82)$$

$$r_{\text{HDN}_{\text{b}}} = \frac{k_{\text{NB}} C_{\text{NB}}^{1.5} C_{\text{H}_2} - k_{\text{BN}} C_{\text{BN}}^{1.5} C_{\text{H}_2}}{(1 + K_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}})^2} \quad (83)$$

Yin et al.¹¹ studied the HDN reaction according to the pathways shown in Figure 7, and the kinetics was modeled by the LHHW model (eq 84) considering two lumps. The first lump includes the CAR and ASCAR compounds (N₁), whereas the second one groups the partially hydrogenated CAR molecules (N₂). Authors considered a first pathway following a direct denitrogenation step (eq 85), and the second stage assumes that the adsorption strength of the N₂ compounds is significantly lower than the N₁ compounds; thus, the inhibition factor in *r*₂ and *r*₃ equations (eqs 86 and 87, respectively) only depends on the concentration of the N₁ lump. Their assumptions disagree with the findings of Szymańska et al.⁶⁴ using a bulk molybdenum carbide catalyst to process a synthetic feed made of carbazole as the N-containing model compound.

$$r_{\text{HDN}} = k_{\text{N}_1} C_{\text{N}_1} P_{\text{H}_2}^{n_1} + \frac{k_{\text{N}_2} C_{\text{N}_2} P_{\text{H}_2}^{n_2}}{(1 + K_{\text{N}_2} C_{\text{N}_1})^2} \quad (84)$$

$$r_1 = k_{\text{N}_1} C_{\text{N}_1} P_{\text{H}_2}^{n_1} \quad (85)$$

$$r_2 = \frac{k_{\text{N}_2} C_{\text{N}_1} P_{\text{H}_2}^{n_2}}{(1 + K_{\text{N}_1} C_{\text{N}_1})^2} \quad (86)$$

$$r_3 = \frac{k_{\text{N}_3} C_{\text{N}_2} P_{\text{H}_2}^{n_3}}{(1 + K_{\text{N}_2} C_{\text{N}_1})^2} \quad (87)$$

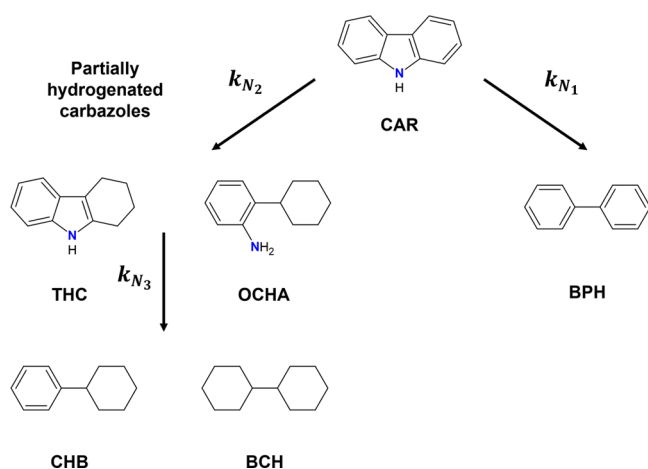
The squared denominator terms in eqs 86 and 87 were derived from initial experiments because the concentration profiles of the two N lumps did not depict the inhibition effect when using order 1. Another assumption was that the adsorption-equilibrium constant of the CAR species (N₁) in the direct denitrogenation pathway (eq 86) should be 0.

Avraam et al.⁸¹ proposed eq 88 to describe the kinetics of the HDN reaction where the term β₁ is the fraction of reactive nitrogen compounds. Thus, the term 1-β₁ should be the fraction of refractory N compounds, but β₁ was 1 or close to 1. It is also assumed that the HDN reaction of reactive and

Table 10. Estimated Parameters Reaction Order (n_i), $k_{0,i}$, and $E_{a,i}$ (kJ/mol) of Lumped HDN Kinetic Models Found in the Literature

parameter	reference					
	54 ^a	55 ^b	CoMo	NiMo	NiMoW	60 ^d
n_1	1	1.69	0.71	0.62	0.65	
n_2	1	1.54	1.89	1.32	1.78	
n_3	1	1.16	-	-	-	
n_4	1	-	-	-	-	
$k_{0,1}$	3.02×10^3	2.40×10^7	1.14×10^8	6.90×10^8	5.82×10^8	45.83
$k_{0,2}$	1.00×10^4	3.67×10^6	7.87×10^7	2.07×10^7	3.52×10^7	3.03×10^2
$k_{0,3}$	3.17×10^4	3.22×10^7	-	-	-	5.64×10^4
$k_{0,4}$	2.23×10^5	-	-	-	-	-
$E_{a,1}$	81.99	133	120	125	126	35.45
$E_{a,2}$	123.00	135	129	117	127	60.18
$E_{a,3}$	149.86	152	-	-	-	90.01
$E_{a,4}$	239.62	-	-	-	-	-

^a $k_{0,i}$ units are [Pa/h]. ^b $k_{0,i}$ units are [(cm³)⁽ⁿ⁻¹⁾·mol⁽¹⁻ⁿ⁾/s]. ^c $k_{0,i}$ units are [ppm⁻ⁿ/s]. ^d $k_{0,i}$ units are [s⁻¹].

Figure 7. Two-lump of the carbazole HDN reaction.¹¹

refractory N compounds occurs at different active sites, and the inhibitory effects of the H₂S and the presence of aromatic molecules were taken into account, while the self-inhibition effect was ignored. This HDN model was further used as a part of the modeling of an industrial reactor for the hydrotreating of VGOs, including the HDS, HDN, and HDA reactions.^{40,41}

$$r_{\text{HDN}} = \frac{\beta_1 k_1 C_{\text{H}_2}^S C_{\text{N}}^S}{(1 + K_{1,\text{H}_2\text{S}} C_{\text{H}_2\text{S}}^S + K_{1,\text{A}} C_{\text{A}}^S)^2} + \frac{(1 - \beta_1) k_2 C_{\text{H}_2}^S C_{\text{N}}^S}{(1 + K_{2,\text{H}_2\text{S}} C_{\text{H}_2\text{S}}^S + K_{2,\text{A}} C_{\text{A}}^S)^2} \quad (88)$$

Three different types of lump kinetic models for HDN of the middle distillate from a Chinese shale oil hydrotreated in a TBR with a commercial NiMoW/Al₂O₃ catalyst were compared by Tang et al.⁵⁴ The best fit for the HDN reaction was found with the four-lump model, with errors between experimental and calculated data of less than 5%. The proposed reaction rate equations were of the pseudo-first-order power-law type, and the total nitrogen concentration was determined as the sum of all of the lump concentrations.

A study of the HDN carried out in an isothermal high-throughput reactor loaded with three different catalysts for the

production of ULSD has been reported.⁵⁸ The respective influence of each operating condition was studied, as well as the self-inhibition of N compounds in the proposed kinetic models. One model is based on a single lump where all of the N-containing compounds are considered, while the second model takes into account two lumps formed by alkyl-substituted carbazole molecules and by bare carbazole and other N compounds. Catalysts such as CoMo, NiMo, and NiMoW were tested, and the two-lump kinetic model was used to simulate different catalyst stacking schemes in the same catalyst proportion. The authors found agreement between the predicted and experimental nitrogen content in the products. The proposed two-lump kinetic model was based on experimental results showing that the reaction profiles of carbazoles with alkyl chains are very similar, whereas carbazole and the rest of the N-containing compounds are more reactive than substituted carbazole molecules. In this way, ASCAR compounds were lumped together, while CAR and other organonitrogen compounds were also lumped, and the self-inhibition for organonitrogen heterocycles was taken into account. The proposed kinetics are as follows

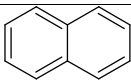
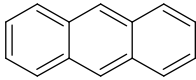
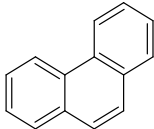
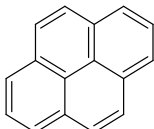
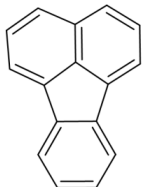
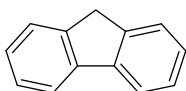
$$\frac{dC_{\text{N1}}}{d\tau} = \frac{-k_{\text{N1}} C_{\text{N1},0}^{\alpha_{\text{N1}}} P_{\text{H}_2}^{\alpha_{\text{N1}}} \left(\frac{H_2}{\text{oil}}\right)^{\beta_{\text{N}}} \eta_{\text{N}}^{\text{ed}}}{1 + f_{\text{N1}} C_{\text{N1}} + f_{\text{N1}} C_{\text{N2}}} \quad (89)$$

$$\frac{dC_{\text{N2}}}{d\tau} = \frac{-k_{\text{N2}} C_{\text{N2},0}^{\alpha_{\text{N2}}} P_{\text{H}_2}^{\alpha_{\text{N2}}} \left(\frac{H_2}{\text{oil}}\right)^{\beta_{\text{N}}} \eta_{\text{N}}^{\text{ed}}}{1 + f_{\text{N2}} C_{\text{N1}} + f_{\text{N2}} C_{\text{N2}}} \quad (90)$$

$$\eta_{\text{N}}^{\text{ed}} = \tanh(\text{parp}_{\text{N}} \times \nu) \quad (91)$$

The authors used a Levenberg–Marquardt multivariate function to optimize the model parameters where the objective function was the sum of the relative deviation of the calculated and the experimental mass percentage values. In the case of the two-lump kinetic model, the experimental results were the total nitrogen content, and the calculated results were the sum of the two lumps. The effects of the reaction temperature on the reaction rate and the adsorption-equilibrium constants followed the Arrhenius and the Van't Hoff equations, respectively.

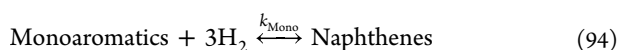
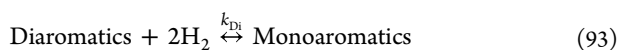
Table 11. Chemical Structure of Aromatic Hydrocarbon Compounds in Gas Oil

Compounds	Chemical structure
Naphthalene	
Anthracene	
Phenanthrene	
Pyrene	
Fluoranthene	
Fluorene	

The comparison of the estimated HDN kinetic parameters of the works discussed in this section is shown in Table 10. Other examples of these types of kinetic models can be found in the literature.^{45–47,51} The recent publications involve lump kinetic models of the HDN reaction using non-conventional feedstocks, and they are a current approach to the HDT simulation of TBR.

4. HYDRODEAROMATIZATION REACTIONS

It is well-known that aromatic compounds are present in the distillation fractions of crude oil and are therefore highly present in diesel fuel as part of its chemical composition. The removal of these components is therefore as important as the removal of sulfur and nitrogen. It has been reported that HDA undergoes the following reactions¹⁰



In most cases, aromatic compounds are referred to as polyaromatics (more than two aromatic rings), diaromatics (two aromatic rings), and monoaromatics (one aromatic ring). The main aromatic species involved in the HDA reactions are naphthalene, anthracene, phenanthrene, and others. The chemical structure of these compounds is shown in Table 11. In general, the HDA reaction follows a pseudo-first-order when hydrogen is in excess, while the dehydrogenation fits to first-order kinetics.³⁰ It has previously been shown that poly-

and diaromatics inhibit the hydrogenation of monoaromatics, but mono- and diaromatics have no effect on the hydrogenation of polyaromatics.⁸²

The reaction rate equations predicting the HDA of aromatics in gas oil are usually represented by power-law models that take into account the three main groups of aromatic compounds, as reported by Mederos et al.⁷

$$r_{\text{HDA}_{\text{Poly}}}^{\text{L}} = k'_{\text{in,HDA}_{\text{Poly}}} (C_{\text{SLPoly}}^{\text{S}}) - k'_{\text{in,HDA}_{\text{Poly}}} (C_{\text{SLDi}}^{\text{S}}) \quad (95)$$

$$r_{\text{HDA}_{\text{Di}}}^{\text{L}} = k'_{\text{in,HDA}_{\text{Di}}} (C_{\text{SLDi}}^{\text{S}}) - k'_{\text{in,HDA}_{\text{Di}}} (C_{\text{SLMono}}^{\text{S}}) \quad (96)$$

$$r_{\text{HDA}_{\text{Mono}}}^{\text{L}} = k'_{\text{in,HDA}_{\text{Mono}}} (C_{\text{SLMono}}^{\text{S}}) - k'_{\text{in,HDA}_{\text{Mono}}} (C_{\text{SLNaph}}^{\text{S}}) \quad (97)$$

$$r_{\text{HDA}_{\text{Naph}}}^{\text{L}} = -k'_{\text{in,HDA}_{\text{Mono}}} (C_{\text{SLMono}}^{\text{S}}) + k'_{\text{in,HDA}_{\text{Mono}}} (C_{\text{SLNaph}}^{\text{S}}) \quad (98)$$

where r_j^{L} corresponds to the rate of reaction j per unit of catalyst mass in the liquid phase $\left(\frac{\text{mol}_i}{\text{g}_s \text{S}}\right)$, $k'_{\text{in},j}$ is the intrinsic reaction rate coefficient for heterogeneous reaction $j \left(\frac{\text{cm}_i^3}{\text{mol}_i \text{g}_s \text{S}}\right)$, and $C_{\text{SLi}}^{\text{S}}$ is the molar concentration of compound i at the surface of solid covered by the liquid phase $\left(\frac{\text{mol}_i}{\text{cm}_i^3}\right)$. In addition, the following kinetic equations can be obtained

$$k'_{\text{in,HDA}_{\text{Poly}}} = k_{\text{in,HDA}_{\text{Poly}}}^* (p_{\text{H}_2}^{\text{G}})^{n_1} \quad (99)$$

Table 12. Estimated Kinetic Parameters k [(m³)²/(mol·kg·h)] and E_a (kJ/mol) for the HDA Reaction

parameter	reference				
	10	13	11	23	
				catalyst A	catalyst B
k_1	11.14	1.51		7.17×10^{-3}	7.89×10^{-3}
k_2	2.85×10^8	9.43		3.1×10^{-3}	3.45×10^{-3}
k_3 (m ³)(MPa·kg·h) ⁻¹	2.41×10^{10}	4.94×10^2		1.45×10^{-3}	1.6×10^{-3}
k_4 (m ³)(kg·h) ⁻¹	-	1.41×10^4		-	-
k_5	-	2.52×10^5		-	-
k_6	-	9.81×10^6		-	-
E_{a1}	54.31	42.42	52.4	-	-
E_{a2}	131.91	47.86	90	-	-
E_{a3}	156.09	73.85	82.8	-	-
E_{a4}	-	84.04	95.6	-	-
E_{a5}	-	102.28	-	-	-
E_{a6}	-	115.75	-	-	-

$$k'_{\text{in,HDA}_{\text{Di}}} = k_{\text{in,HDA}_{\text{Di}}}^* (p_{\text{H}_2}^G)^{n_2} \quad (100)$$

$$k'_{\text{in,HDA}_{\text{Mono}}} = k_{\text{in,HDA}_{\text{Mono}}}^* (p_{\text{H}_2}^G)^{n_3} \quad (101)$$

Where p_i^G is the partial pressure of component H_2 in the bulk gas phase (MPa), and n is the reaction order.

The experimental setup includes the use of excess hydrogen to avoid limitations on the concentration of dissolved hydrogen in the liquid phase due to hydrogen solubility, which keeps the hydrogen partial pressure constant.

The kinetic parameters for the HDA equations were estimated by optimization using the Levenberg–Marquardt nonlinear regression algorithm. The values of these parameters are shown in Table 12 using the following nomenclature: $k_{\text{HDA}_{\text{Mono}}} = k_1$; $k_{\text{HDA}_{\text{Di}}} = k_2$; and $k_{\text{HDA}_{\text{Poly}}} = k_3$.

Wu et al.¹³ also reported a set of reaction rate equations to predict the HDA reaction using a similar reaction pathway as previously reported³ where polyaromatics form diaromatics and then monoaromatics to give naphthenes and paraffins. The proposed set of kinetic equations is as follows

$$r_{\text{PA}} = k_1 C_{\text{H}_2}^m C_{\text{PA}} - k_2 C_{\text{DA}} \quad (102)$$

$$r_{\text{DA}} = (k_3 C_{\text{H}_2}^m C_{\text{DA}} - k_4 C_{\text{MA}}) - (k_1 C_{\text{H}_2}^m C_{\text{PA}} - k_2 C_{\text{DA}}) \quad (103)$$

$$r_{\text{MA}} = \frac{(k_5 C_{\text{H}_2}^m C_{\text{MA}} - k_6 C_{\text{NA}})}{1 + K_A C_{\text{DA}}} - (k_3 C_{\text{H}_2}^m C_{\text{DA}} - k_4 C_{\text{MA}}) \quad (104)$$

$$r_{\text{NA}} = -\frac{(k_5 C_{\text{H}_2}^m C_{\text{MA}} - k_6 C_{\text{NA}})}{1 + K_A C_{\text{DA}}} \quad (105)$$

The reaction rate coefficients and the adsorption–equilibrium constants were calculated using the Arrhenius and Van't Hoff equations, respectively. The objective function is a weighted least absolute error equation (eq 31) and was used together with the Levenberg–Marquardt algorithm. The values obtained from this procedure are presented in Table 12. These equations consider the concentration of H_2 as it is consumed, which means that its concentration is not constant throughout the reaction.

Yin et al.¹¹ also studied the production of ULSD by considering HDS, HDN, and HDA reactions. The properties of the feed are shown in Table 1, and it was processed into a

high-throughput reactor system with a NiMo/ Al_2O_3 catalyst under the operating conditions shown in Table 2. The authors classified the aromatic compounds into four lumps, i.e., A1 as monoaromatics, A2 as diaromatics, A3 as polyaromatics, and A4 as non-aromatic compounds. The reaction rate equations are

$$r_{\text{A3}} = k_{\text{A3}} C_{\text{A3}} P_{\text{H}_2}^n - k'_{\text{A3}} C_{\text{A2}} \quad (106)$$

$$r_{\text{A2}} = k_{\text{A2}} C_{\text{A2}} P_{\text{H}_2}^n + k'_{\text{A3}} C_{\text{A2}} - k'_{\text{A2}} C_{\text{A1}} - k_{\text{A3}} C_{\text{A3}} P_{\text{H}_2}^n \quad (107)$$

$$r_{\text{A1}} = k_{\text{A1}} C_{\text{A1}} P_{\text{H}_2}^n + k'_{\text{A2}} C_{\text{A1}} - k'_{\text{A1}} C_{\text{A4}} - k_{\text{A2}} C_{\text{A2}} P_{\text{H}_2}^n \quad (108)$$

$$r_{\text{A4}} = k'_{\text{A1}} C_{\text{A4}} - k_{\text{A1}} C_{\text{A1}} P_{\text{H}_2}^n \quad (109)$$

where n is the reaction order, C_i is the concentration of the lump, k_i is the reaction rate coefficient, and k'_i is the reaction rate coefficient for the reverse reaction. The objective function is eq 31. The interior point method was chosen as an optimization technique. Also, from the equations proposed in the previous work, the authors took into account the variations in the partial pressure of hydrogen, which tends to change as hydrogenation reactions take place after being consumed by the organic compounds.

Bhaskar et al.²³ proposed a three-phase reactor model to simulate the performance of a pilot plant with applications for hydrotreating reactions. A kinetic model for the HDA reactions was set up in which four lumps were modeled as mono-, di-, poly-, and non-aromatics. The resulting reaction rate equations are

$$r_{\text{poly}} = k_{\text{Poly}} C_{\text{Poly}}^s - k_{\text{Poly-Di}} C_{\text{Di}}^s \quad (110)$$

$$r_{\text{Di}} = k_{\text{Di}} C_{\text{Di}}^s - k_{\text{Di-Mono}} C_{\text{Mono}}^s \quad (111)$$

$$r_{\text{Mono}} = k_{\text{Mono}} C_{\text{Mono}}^s - k_{\text{Mono-Naph}} C_{\text{Naph}}^s \quad (112)$$

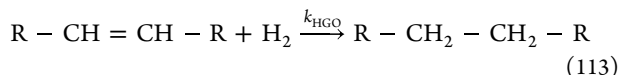
The model becomes a boundary value problem because the concentration of the different components is known, and the shooting method was used to determine the kinetic parameters, followed by the fourth-order Runge–Kutta method to integrate the differential equations. The values of the reaction rate coefficients for both catalysts used in the work are given in Table 12. Additional research dealing with the HDA reaction to process gas oil is reported elsewhere.^{22,26,28,42}

The HDA reaction becomes an important aspect during the HDT of gas oil due to the need to remove aromatic

compounds from diesel fuel and to meet the specifications for the synthesis of ULSD. Therefore, the kinetic models presented in this section must be considered for the appropriate kinetic modeling of ULSD production.

5. HYDROGENATION OF OLEFINS

During the deep catalytic hydrotreating process of gas oil, secondary reactions take place; one of these is the hydrogenation of olefins. Olefins are present in feedstocks to the HDT process due to some cracked streams.²⁵ They react rapidly with hydrogen to form saturated compounds. The following stoichiometric equation is used to represent olefin hydrogenation



Since the olefin saturation reactions are the fastest and the initial H_2S concentration is lower, the inhibition effects on this reaction are neglected. However, due to the presence of these compounds during the deep hydrotreating process and the corresponding reaction, it is important to analyze the kinetic models predicting these reactions in order to implement them in a generalized set of models of ULSD production.⁸³

A reaction rate equation of the power-law type has been reported as follows³

$$r'_{HGO} = k'_{in,HGO} C_{SLO}^s \quad (114)$$

The hydrogenation of olefins was assumed to be of pseudo-first-order with respect to the total concentration of olefins. The intrinsic reaction rate coefficient is $k'_{in,HGO}$, and C_{SLO} is the molar concentration of olefins at the solid surface covered by the liquid phase. This assumption was also reported elsewhere.²⁸

Patil et al.²⁵ also reported a kinetic model for this reaction as follows

$$r_{HGO} = k_{HGO} C_O C_{H_2} \quad (115)$$

In this case, the reaction rate of the hydrogenation of olefins depends not only on the total concentration of olefins but also on the concentration of H_2 , by which this reaction consumes hydrogen.

Avraam and Vasalos⁸¹ reported the following reaction rate equation for HGO, leaving it expressed by the Arrhenius equation (eq 4) form

$$r_{HGO} = k_{HGO} e^{-E/RT} C_{L,O} \quad (116)$$

Bhaskar et al.²³ considered the pseudo-first-order reaction in terms of olefin concentration as follows

$$r_O = k_{app,O} C_O^s \quad (117)$$

where $k_{app,O}$ is the apparent rate constant for olefin saturation reaction and C_O^s is the concentration of olefins on the catalyst surface. The values of kinetic parameters for the HGO reaction are presented in Table 13.

6. HYDROCRACKING REACTIONS

Hydrocracking reactions occur as secondary reactions during the deep catalytic HDT process. This is because, during the process, light components such as gases (C_1-C_4) and naphtha are produced due to the high temperatures and pressures at which the system operates. In addition, acidic sites on the

Table 13. Estimated Kinetic Parameters for the HGO Reaction, k [$cm^3/(g \cdot s)$] and E_a [kJ/mol]

parameter	reference		
	10	25	81
k	9.46×10^8	-	187.50
E_a	138.15	28.71	39.96

Al_2O_3 support promote mild hydrocracking reactions and produce lighter hydrocarbons in gaseous and liquid products. The products of cracking reactions are lumped as gas oil, naphtha, and light gases, as depicted in Figure 8.

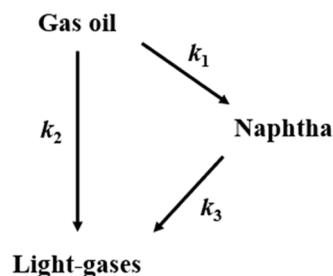


Figure 8. Pathways of HCR reactions of gas oil.^{10,23,93}

Based on the three-lump reaction observed in Figure 8, some authors have reported a set of reaction rate equations for the HCR assuming a pseudo-first-order as follows^{3,22}

$$r_{GO} = k_1 C_{SLGO}^s + k_2 C_{SLGO}^s \quad (118)$$

$$r_{Naphtha} = -k_1 C_{SLGO}^s + k_3 C_{SLNaphtha}^s \quad (119)$$

$$r_{LG} = -k_2 C_{SLGO}^s - k_3 C_{SLNaphtha}^s \quad (120)$$

where k_i is the reaction rate coefficient of i and C_{SLi}^s is the concentration of component i .

Bhaskar et al.²³ also proposed a set of three kinetic reactions considering a three-lump model consisting of gas oil, naphtha, and light gases. The reactions were also assumed to follow a pseudo-first-order.

$$r_{GO} = (k_1 + k_2) C_{GO}^s \quad (121)$$

$$r_{Naph} = -k_2 C_{GO}^s + k_3 C_{Naph}^s \quad (122)$$

$$r_{LG} = -k_1 C_{GO}^s - k_3 C_{Naph}^s \quad (123)$$

The kinetic parameters were estimated using the Levenberg–Marquardt nonlinear regression algorithm. Since the resulting problem is an initial value problem (IVP), where the initial conditions are known, i.e., the initial concentrations, then the numerical methods used to solve this problem are based on single or multistep procedures. Thus, the authors used a numerical method as the fourth-order Runge–Kutta. The values obtained for the reaction rate coefficients and activation energies are shown in Table 14.

7. DETAILED KINETIC MODELS OF ULSD PRODUCTION

Crude oil and its products are complex chemical mixtures made up of thousands of different molecules. New analytical developments make it possible to identify and quantify many molecules with different chemical compositions, but much work remains to be done to identify all of the isomers that

Table 14. Estimated Kinetic Parameters of HCR Reactions, k_i [1/s] and E_a [kJ/mol]

parameter	reference		
	10	23	
		catalyst A	catalyst B
k_1	1.38×10^{-1}	1.87×10^{-5}	2.08×10^{-5}
k_2	2.39×10^6	9.88×10^{-9}	1.11×10^{-8}
k_3	2.21×10^{16}	4.28×10^{-4}	4.82×10^{-4}
E_{a1}	56.41	4943.2	4409.5
E_{a2}	139.46	4157.2	4162.3
E_{a3}	273.78	9832.6	9535.8

in hydrocarbon mixtures. The in-depth characterization of petroleum and its products at the molecular level in order to correlate and ultimately predict their properties and behavior has been termed “petroleomics.”^{84,85}

New analytical techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) can resolve and identify each of the thousands of elemental compositions of petroleum and its derivatives. More than 60,000 different elemental monoisotopic compositions have been identified from many crude oil samples of different natures and origins by using FT-ICR MS.⁸⁴ However, since the early application of MS to the characterization of the petroleum components, ionization sources, and chromatographic techniques have had many limitations, particularly for detailed kinetic modeling of the multiple chemical processes that petroleum products undergo during refining due to the formation and disappearance of many reactive intermediates during such processes. Recent advances in ionization sources and studies using complementary information from two or more ionization sources have led to a more comprehensive characterization of the chemical composition of crude oil. The most commonly used ionization sources for FT-ICR MS of crude oils are electrospray ionization (ESI), field desorption/ionization (FD), and atmospheric pressure photoionization (APPI). The ESI technology is known to be more efficient in polar molecules to produce positive ions by the protonation of uncharged basic molecules and negative ions via the deprotonation of uncharged acidic molecules. However, it has been observed that petroleum samples typically contain 90% nonpolar hydrocarbons that can be properly detected by ESI; although the heteroatomic polar molecules are the main target for removal from the feedstocks, the nonpolar component must be known to develop detailed kinetic modeling of such processes. Continuous-flow FD FT-ICR MS can generate ions from several molecules that are not affected by ESI, such as BT, DBT, furans, PAHs, and cycloalkanes; however, the technique requires long experimental times to volatilize and ionize the chemical species in the sample, which is a problem. Finally, APPI FT-ICR MS can provide a mass spectral data set in a few seconds, and it can average hundreds of scans for increased dynamic range. Nevertheless, APPI of crude oil and its products requires ultrahigh resolution FT-ICR MS due to the greater ionization range of compound types (approximately 5 times the number of peaks in an APPI mass spectrum) compared with an ESI mass spectrum of the same petroleum sample and the formation of different ions from the same parent molecule (i.e., $M^{+\bullet}$ and $(M + H)^+$), which increases the need for higher mass resolution and accuracy in the spectrum.^{86,87}

In addition to the analytical tools to identify and measure the concentration of reactants, intermediates, and desired and undesired products at the inlet and outlet of the hydrotreating reactor, the computational capacity required to process the data set of said compounds and all of their possible reaction networks and interactions between them has been a major limitation of the detailed kinetic modeling approach to hydrotreating.⁸⁸ Recent improvements in processing capacity and the use of automated network generation algorithms to estimate kinetic parameters have begun to overcome these limitations, but research is still needed in this area to obtain reliable kinetic models that could accurately predict the properties and yield of the final product from different feedstocks and catalysts evaluated in laboratory-scale experiments, which is the ultimate goal of detailed kinetic modeling. Nowadays, to obtain reliable predictions for a specific process in an industrial deep HDS plant, pilot plant, or semi-industrial testing of a specific feedstock and catalyst over a narrow range of operating conditions is required, which is costly and time-consuming. Power-law, L–H, and even lumping kinetic models are still unable to achieve this goal because each of the calculated kinetic parameters includes many indistinguishable molecules with different reactivities and vapor–liquid equilibria, which undergo multiple elementary reactions on different adsorption configurations on the catalyst surface, forming commonly neglected reaction intermediates.^{89,90}

The detailed kinetic models proposed so far for ULSD production can be divided into two approaches: a mechanistic and a molecular approach. The mechanistic approach is considered to be more fundamental, while mechanistic models are based on a thoroughly detailed description of the reaction pathways, taking into account the reactants, the elementary steps (from homolytic bond cleavage to isomerization), and the reaction intermediates, such as ions and free radicals. These models require some a priori assumptions, and the kinetic parameters are of a more fundamental nature. The molecular approach can be described as an intermediate between the mechanistic and lumping approaches. These models simulate the chemical reaction systems neglecting the reaction intermediates; thus, the reactions are considered as molecule-to-molecule transformations, and each reaction is characterized by an overall rate constant. However, the effects of reaction intermediates in the overall chemical reaction are included in the rate equations by making assumptions when they are derived.⁹¹ Both detailed kinetic approaches can overcome most of the previously mentioned drawbacks of the more conventional kinetic models for complex mixtures because they consider a molecular description of the reaction networks throughout the reactor simulation, which allows the formulation of feedstock-independent models. Nevertheless, the molecular description of the complex reaction systems in petroleum refining processes by the aforementioned techniques may be insufficient, very costly, or both.

Molecular reconstruction modeling of the feedstock and products along the reactor length is therefore a promising cost-effective alternative to detailed analytical characterization. Molecular reconstruction approaches generally consist of two steps: the first step is the molecular reconstruction of the feedstock by transforming available analytical information and properties, such as density, viscosity, elemental analysis, SARA, NMR, molecular weight, etc., into a molecular representation of the feedstock; and the second step is a reaction modeling procedure that simulates the effect of the reaction of the set of

molecules via the kinetic Monte Carlo method. The advantages of molecular reconstruction modeling are that the reactions of each molecule can be followed step by step throughout the reactor simulation, the number of reactions of interest can be limited, and the yield and properties of the final product can be predicted. However, it is difficult to directly estimate the kinetic parameters for HDS, HDN, HDA, and other reactions of the representative molecules in the feed during hydrotreating.⁸⁸

For example, López-García et al.⁶¹ developed a feedstock molecular reconstruction method called “statistical reconstruction” to characterize the gas oil composition in the form of molar matrices of pseudo-compounds. A pseudo-compound is the most representative compound from a group of similar individual molecules present in the gas oil that influence the properties and HDT reactivities of the feedstock. The pseudo-compounds were defined by a chemical family (saturates, monoaromatics, diaromatics, triaromatics, reactive sulfur compounds, DBTs, 4-alkyl-DBTs, 4,6-dialkyl-DBTs, reactive nitrogen compounds, basic nitrogen compounds, and carbazoles, among others) and a number of carbon atoms (C_1 – C_{30})—related to the pseudo-compound’s boiling point. The analytical data necessary for the statistical reconstruction model were S and N speciation, density, simulated distillation, and MS. The method developed was applied to characterize three different gas oil streams: SRGO, LCO, and CGO.

Once the feedstock’s compositions were determined, the authors developed a first-order L–H kinetic model comprising the HDS, HDN, and HDA reactions for the respective pseudo-compounds to consider the competitive adsorption of the chemical species on the catalyst-active sites. For the HDS reactions, the authors were particularly concerned with ULSD production, and because the obtained compositions of the hydrotreated products showed that the least refractory sulfur compound present was DBT, they decided to assume that all of the sulfur compounds that are more reactive than DBT were converted into H_2S and corresponding hydrocarbons at the reactor inlet (i.e., mercaptans, thiols, BT, etc.). The modeling of the HDS kinetics included the σ and τ active sites of the catalyst for the hydrogenolysis and hydrogenation reactions of three sulfur pseudo-compounds, DBT, 4-MDBT, and 4,6-DMDBT. The HDS reaction of the DBT pseudo-compound was assumed to only occur through the DDS route, 4-MDBT HDS reaction could happen through any of the two pathways, and for 4,6-DMDBT, only the HYD route was considered. The inhibition effects were also included and were different for each active site.

The model parameter calculations were performed by a Levenberg–Marquardt algorithm to minimize an objective function of least-squares comparing the experimental and calculated contents. This was achieved by integrating a group of 597 differential equations—one for each pseudo-compound—and performing 92 HDT evaluations in a pilot plant TBR loaded with a conventional $NiMo/Al_2O_3$ catalyst under industrial operating conditions of 24 different feedstocks made of SRGO, LCO, CGO, and multiple mixtures of these streams. They concluded that the statistical reconstruction method yielded detailed information about the gas oils feeds and that it is a promising tool for developing accurate kinetic models for a wide range of feedstocks and operating conditions. However, the authors recognize that the HDS kinetic model could be upgraded and suggested that including the inhibiting effects of

the different nitrogen species, rather than total nitrogen, could improve the estimations.

In summary, the development of new analytical techniques has allowed for a more comprehensive characterization of crude oil and its products at the molecular level. The use of FT-ICR MS has enabled the identification and quantification of thousands of different molecules in hydrocarbon mixtures, giving rise to the field of “petroleomics”. However, much remains to be done to fully understand the molecular composition and behavior of petroleum products. Detailed kinetic modeling is an important tool for predicting product properties and behavior from different feedstocks, catalyst operating conditions, and experimental settings. Despite its current limitations, recent advances in computing power and automated mesh generation algorithms show promise in overcoming the limitations of this approach. The mechanistic and molecular approaches to detailed kinetic modeling can provide a more fundamental understanding of the complex reaction systems involved in petroleum refining processes. Despite the challenges, ongoing research and development in these areas continue to push the boundaries of our understanding of crude oil and its derivatives.

8. PERSPECTIVES IN KINETIC MODELING FOR ULSD PRODUCTION

When developing kinetic models for the hydrotreating process to produce ULSD, it is essential to consider all of the reactions that occur, not just the HDS reaction. As already discussed, HDN, HDA, HGO, and HCR must be considered as they occur simultaneously and compete for the catalytic active sites. It is worth noting that these reactions also consume hydrogen to different extents, which causes the partial pressure of the hydrogen gas to decrease along the entire transverse axis of the reactor. If only the HDS reaction is considered in the kinetic modeling, the hydrogen partial pressure profile and the estimation of the total hydrogen consumption will not be accurately predicted.

Hydrocracking reactions are particularly important in HDT because the degree of disintegration must be carefully controlled. Increasing the temperature to improve sulfur removal from the feedstock can also lead to a higher degree of hydrocracking and the formation of unwanted lower molecular weight species. However, a non-destructive approach to hydrogenation of the feedstock is required to ensure that the average molecular weight of the gas oil at the inlet and outlet has a similar molecular weight but with lower levels of impurities. This is because increasing the temperature can lead to increased production of naphtha and light hydrocarbon gases, resulting in a loss of yield of the target product. In addition, raising the temperature increases coke formation, which is also undesirable in hydrotreating processes, mainly because it leads to premature catalyst deactivation. For these reasons, if only the HDS reaction is considered in the kinetic modeling, these issues cannot be accurately addressed, and increasing the severity of the operating conditions, such as the start-of-run temperature, with the aim of reducing the S content in the end product could negatively affect the hydrotreating process.

On the other hand, an important aspect of the two main reactions during HDT, i.e., HDS and HDN, is their competition for the catalytic active sites. As reported by Junior et al.,⁹⁴ most studies regarding the kinetic modeling of both HDS and HDN reactions use power-law kinetic models

due to their simplicity in analyzing highly sophisticated reaction schemes. However, L–H type models consider the adsorption of reactants and products on the surface of the used catalyst. In this way, the competitiveness of the reactions for the active sites of the catalyst can be explained; nevertheless, the estimation of the kinetic parameters in these models may require detailed experimental data.

Also, Dorneles de Mello et al.⁹⁵ investigated the competitiveness of both HDS and HDN reactions in the presence of phosphorus using a series of NiMoP/Al₂O₃ catalysts. The results obtained by the authors showed that, in fact, an inhibition occurs between both HDS and HDN reactions. The HDS of 4,6-DMDBT was highly inhibited at concentrations of 90 ppm N, mainly by the HYD route, confirming that the sulfur compound competes for the same hydrogenation active sites as the products of nitrogen compounds. This confirms that when HDS and HDN reactions occur simultaneously, competition for the active sites of the catalyst is present. In addition, HDS reaction kinetics alone does not accurately predict the ULSD production.

Therefore, it is crucial to consider all reactions in the HDT process to ensure that the kinetic model is accurate for a wider range of operating conditions and experimental settings and provides useful results for the production of ULSD.

8.1. Numerical Algorithms and Methods for Parameter Estimation. Since the manner to represent the kinetic modeling and estimate the kinetic parameters of reactions is through ordinary/partial differential equations that are solved by numerical methods and linear/nonlinear optimization techniques, it is crucial to discuss some of the most popular and useful methods used worldwide to carry out parameter estimations, as well as their advantages and disadvantages.^{96,97}

Alcázar and Ancheyta⁹⁸ proposed a methodology based on sensitivity analysis to estimate the kinetic parameters of heterogeneous kinetic models. This methodology consists of three main steps: initialization of parameters (with the Monte Carlo method), nonlinear optimization (using the Levenberg–Marquardt algorithm), and sensitivity analysis. The main advantage of this methodology is that the optimal values of kinetic parameters can be obtained by minimizing the objective function that assures the global minimum. Other techniques have been used in recent years, such as simulated annealing (SA), which is a global stochastic optimization method that consists of randomly generating new configurations, and if this new configuration obtained presents a lower value of the objective function used, then this newly generated configuration will be the actual configuration, and so on. This process is repeated *n* times until the probability of the worse configuration is reduced.^{99,100}

Lakshmanan et al.¹⁰¹ proposed the grid search technique, which preserves the true nonlinearity of the model when estimating its parameters. This method consists of defining a region for grid search by specifying the upper and lower limits of the values of the parameters. Then, the number of grid points in each direction has to be specified, and the sum of squares of residuals (SSR) between predicted and experimental values is obtained by using the parameters that characterize the grid points. This process is repeated until the SSR is obtained for each grid point.

All of these approaches highlight the importance of selecting appropriate techniques to estimate kinetic parameters for heterogeneous reactions based on the complexity of the

reaction schemes and kinetic models with the aim of assuring the achievement of optimal parameter values.

8.2. Comparison of Kinetic Parameter Values. As previously mentioned, HDS is the most critical reaction in hydrotreating, as it removes sulfur from the feedstock. The HDS reaction is typically described by a L–H mechanism in which adsorption of the sulfur-containing species onto the catalyst surface is followed by dissociation of the S–H bond and formation of hydrogen sulfide (H₂S). Recent studies have shown that the activation energy for HDS reactions is typically between 60 and 120 kJ/mol, while the frequency factor for pseudo-first-order reactions is between 10⁷ and 10⁹ s^{−1}. However, it can be misleading to compare pre-exponential factors estimated in different studies, as the kinetic model has a large influence on the units and magnitudes of the factor. In addition, the reaction order for HDS is usually between 0.5 and 2, indicating that the reaction rate is directly proportional to the concentration of S-containing species.

Hydrodenitrogenation is another important reaction in hydrotreating, as it removes nitrogen from the feedstock. The HDN reaction is similar to HDS and is also described by a L–H mechanism. The activation energy for HDN reactions is typically in the range of 80–120 kJ/mol, while the frequency factor ranges from 10⁶ to 10⁸ s^{−1}. The reaction order for HDN is commonly between 0.5 and 1. HDA, HGO, and HCR also play a key role in hydrotreating, as these reactions account for most of the hydrogen consumed and have an impact on operating costs.

Lump kinetic models for HDS, HDN, HAD, HGO, and HCR reactions for ULSD production have some advantages over single-lump kinetic models, single-component kinetic models, and detailed kinetic models, as follows:

- Improved accuracy: Lump kinetic models account for the different reactivities of chemical species more accurately than models based on the total content of sulfur, nitrogen, or aromatics, or even individual model compounds. The lumping approach takes into account the differences in the chemical structure and reactivity between different compounds, resulting in better prediction of kinetic parameters and selectivity.
- Better representation of real feedstocks: These models take into account the complexity of the mixture of unwanted compounds present in real feedstocks. This approach is particularly relevant to ULSD production, where conventional and unconventional feedstocks contain a wide range of impurities. By lumping similar compounds together, the kinetic model can represent the behavior of the complex mixture and provide more accurate predictions of product quality and optimum operating conditions at an industrial scale.
- Increased flexibility: Lumped kinetic models can be easily modified to incorporate new compounds or operating conditions. Since the lumping approach is generally based on the chemical structure and reactivity, new compounds can be easily incorporated into the model by carefully assigning them to the appropriate lump.
- Reduced computational complexity: In lumping kinetic models, similar compounds are grouped into families or lumps. The reaction rate equation and kinetic parameters of a lump account for all of the compounds grouped within it. This approach reduces the number of species

to be considered in the kinetic model and simplifies the reaction network, reducing computational complexity and simulation time, especially when compared with detailed kinetic models.

8.3. Kinetics on Sequential Catalytic Beds. Sequential catalytic bed technology, also known as stacking technology, can significantly benefit the hydrotreating process by using different catalysts stacked in different beds throughout the reactor, while the global process uses each catalyst type to remove impurities according to its selectivity.¹⁰²

Different catalytic beds for heterogeneous catalysts in the same reactor were first used in hydrotreating to prevent catalyst deactivation by coke deposition and metal poisoning during heavy oil upgrading. The upper catalytic bed in the reactor enhances metal and asphaltene removal, while the second section tends to remove heteroatoms such as sulfur and nitrogen.⁴

Regarding the HDS process, the reactor (typically a three-phase reactor) contains two or more catalysts packed in different beds, with each catalyst selected to achieve different objectives depending on the operating conditions and the properties and type of feedstock. For instance, in the HDT of gas oil, the common catalysts used are CoMo/Al₂O₃ and NiMo/Al₂O₃, where each catalyst possesses different properties. First, it is important to remark that the HDS occurs simultaneously via two routes: (a) direct desulfurization, also known as hydrogenolysis, consisting of the direct adsorption of the S atom on the active sites of the catalyst in just one step, and (b) hydrogenation of one of the neighboring aromatic rings for refractory sulfur compounds. Therefore, this consideration helps choose the right catalyst by understanding its properties. For example, the CoMo catalyst has the DDS route as the main HDS pathway due to its higher activity for reactive sulfur compounds (the HDS reactivity of sulfur compounds is inversely proportional to their boiling point, whereas the boiling point increases as the compounds are more refractory). In addition, it is not severely affected by the inhibition of the compounds such as H₂S, NH₃, N, and aromatics and is only slightly dependent on H₂ consumption and partial pressure. On the other hand, NiMo catalyst promotes the HYD in the HDS reaction pathway having greater activity for refractory sulfur compounds. By-products such as H₂S and NH₃ affect its activity, and it is highly dependent on hydrogen consumption.^{103,104}

For these reasons, a stacked-bed or sequential-bed reactor is often recommended and used to carry out these reactions, as hydrogenation is more prone to increase the desulfurization of the refractory sulfur species. Conversely, this catalytic function is more susceptible to inhibition caused by organonitrogen compounds. Hydrogenolysis sites are less active for the desulfurization of refractory sulfur compounds, but they are more resistant to the inhibitory effects of organonitrogen compounds. In this way, it is possible to remove both types of sulfur compounds by exploiting the properties of each catalyst, with the main objective being focused on obtaining ULSD.

From a kinetic point of view, when modeling an HDT reactor with more than one catalyst inside, the kinetics must be determined individually for each catalyst. The reaction rate equations can be the same; however, the values of reaction rate coefficients, activation energies, and other involved parameters would be different. All of the derived kinetic models must be

incorporated into a reactor model according to the position of each catalyst to carry out simulations.

8.4. Generalization of a Kinetic Model for ULSD Production. The following kinetic models must be considered for each of the reactions to adequately predict the production of ULSD. It is important to note that a set of equations or a group of models would be considered as the general kinetic model of ULSD due to the need to include each reaction that takes place in the HDT process.

Based on all of the previously discussed kinetic models, the minimum set of reaction rate equations that need to be used for modeling reactors for producing ULSD is

- HDS reaction

$$r_{S_1} = k_{f,S_1} C_{S_1} P_{H_2}^{n_1} \quad (124)$$

$$r_{S_2} = k_{f,S_2} C_{S_2} P_{H_2}^{n_2} \quad (125)$$

$$r_{S_3} = k_{f,S_3} (C_{S_3} - C_{S_e}) P_{H_2}^{n_3} + \frac{k'_{f,S_3} (C_{S_3} - C_{S_e})}{(1 + K_{BN} C_{BN} + K_{NBN} C_{NBN})^{n_3} (1 + K_{H_2S} C_{H_2S})} P_{H_2}^{n_5} \quad (126)$$

$$r_{S_T} = r_{S_1} + r_{S_2} + r_{S_3} \quad (127)$$

- HDN reaction

$$r_{N_{BN}} = \frac{k_{BN} C_{BN}^{n_6} P_{H_2}^{n_8}}{(1 + K_{BN} C_{BN})^2 (1 + K_{H_2S} C_{H_2S})} \quad (128)$$

$$r_{N_{NBN}} = \frac{k_{NBN} C_{NBN}^{n_7} P_{H_2}^{n_9}}{(1 + K_{NBN} C_{BN})^2 (1 + K_{H_2S} C_{H_2S})} \quad (129)$$

$$r_{N_T} = r_{N_{BN}} + r_{N_{NBN}} \quad (130)$$

- HDA reaction

$$r_{Poly} = k_{Poly} C_{Poly} - k_{Poly} C_{Di} \quad (131)$$

$$r_{Di} = k_{Di} C_{Di} - k_{Di} C_{Mono} \quad (132)$$

$$r_{Mono} = k_{Mono} C_{Mono} - k_{Mono} C_{Naph} \quad (133)$$

$$r_{Naph} = -k_{Mono} C_{Mono} + k_{Mono} C_{Naph} \quad (134)$$

- HGO and HCR reactions

$$r_O = k_O C_O \quad (135)$$

$$r_{GO} = (k_1 + k_2) C_{GO}^s \quad (136)$$

$$r_{Naph} = -k_2 C_{GO}^s + k_3 C_{Naph}^s \quad (137)$$

$$r_{LG} = -k_1 C_{GO}^s - k_3 C_{Naph}^s \quad (138)$$

These reaction rate equations cover a wide group of impurities in the gas oil, such as those containing sulfur and nitrogen, other hydrogen-consuming reactions, such as the hydrogenation of aromatics and olefins, and hydrocracking that impacts the diesel yield. By incorporating all of these rate equations in a reactor model, a more accurate representation of all of the reactions and inhibition effects that occur during the production of ultralow sulfur diesel can be achieved.

9. CONCLUDING REMARKS

The production of ultralow sulfur diesel requires considering all of the reactions that occur during the hydrotreating process of gas oil to adequately predict the reaction rates and reactor performance. The main reactions that must be considered in the kinetic modeling of ULSD production are the hydrodesulfurization, hydrodenitrogenation, hydrodearomatization, hydrogenations of olefins, and hydrocracking.

According to the values of the kinetic parameters reported, it is concluded that the activation energies ranged between 60–120 and 80–120 kJ/mol for HDS and HDN, respectively. For parameters like the frequency factor and reaction order, the average values for the HDS reactions are between 10^7 and 10^9 s⁻¹ of frequency factor and reaction order from 0.5 to 2, whereas for HDN, the frequency factors are in the range from 10^6 to 10^8 s⁻¹ and reaction orders from 0.5 to 1. These ranges of kinetic parameter values can be used for the initialization of proposed kinetic model parameters when developing modeling studies with their own experimental data.

In terms of kinetics, it has been found that in recent years, models have become more sophisticated by taking into account refractory compounds, while computational techniques have reduced the time needed to solve the models, giving high accuracy. Thus, the consideration of more detailed reactions occurring in the HDT process is a crucial and important task once an extended set of reactions is considered, where inhibitory and competitive effects on active sites are taken into account.

Finally, it can be concluded that the use of appropriate kinetic models for representing all of the reactions that take place in the HDT process is mandatory to define proper operating conditions to produce ULSD at a commercial scale.

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Notes

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ABBREVIATIONS

1-M-3-(3-MCH)B = 1-methyl-3-(3-methylcyclohexyl)-benzene
 3,3-DMBPH = 3,3-dimethylbiphenyl
 3-CHT = 3-cyclohexyltoluene
 3-MBPH = 3-methylbiphenyl
 3-MCHB = 3-methylcyclohexylbenzene
 4,6-DMDBT = 4,6-dimethyldibenzothiophene
 4,6-DMHHDBT = 4,6-dimethylhexahydrodibenzothiophene
 4-MDBT = 4-dimethyldibenzothiophene
 ACD = acridine
 ALA = aliphatic amine
 ANL = aniline
 APPI = atmospheric pressure photoionization
 ASCAR = alkyl-substituted carbazoles
 BCH = bicyclohexyl
 BCHA = bicyclohexylamine
 BPH = biphenyl
 BT = benzothiophene
 CAR = carbazole
 CGO = coker gas oil
 CHB = cyclohexylbenzene
 CHCH_e = cyclohexyl-cyclohexene
 DBT = dibenzothiophene
 DDS = direct desulfurization
 DHBT = dihydrobenzothiophene
 DHC = dihydrocarbazole
 ESI = electrospray ionization
 FD = field desorption/ionization
 FT-ICR MS = Fourier transform ion cyclotron resonance mass spectrometry
 GC = gas chromatography
 H₂S = hydrogen sulfide
 HCR = hydrocracking
 HDA = hydrodearomatization
 HDN = hydrodenitrogenation
 HDS = hydrodesulfurization
 HDT = hydrotreating
 HGO = hydrogenation of olefins
 HGOSB = heavy gas oils from oil sands bitumen
 HHC = hexahydrocarbazole
 HHDBT = hexahydrodibenzothiophene
 HTCT = high-temperature coal tar
 HYD = hydrogenation
 IND = indole
 LCGO = light cracked gas oil
 LCO = light cycle oil
 L-H = Langmuir–Hinshelwood
 LHHW = Langmuir–Hinshelwood–Hougen–Watson
 MDSO = middle distillates from shale oils
 MLCT = middle-low temperature coal tars
 MS = mass spectroscopy
 NTL = nitrile
 OCHA = orthocyclohexylaniline
 PAH = polycyclic aromatic hydrocarbons
 PDN = pyridine
 PFR = plug-flow reactor
 PYR = pyrrole
 QNL = quinoline
 SA = simulated annealing
 SQP = sequential quadratic programming

SRGO = straight-run gas oil
SSR = sum of squares of residual
TBR = trickle-bed reactor
THC = tetrahydrocarbazole
THDBT = tetrahydrodibenzothiophene
TP = thiophene
ULSD = ultralow sulfur diesel
VGO = vacuum gas oil

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