Journal of Mines, Metals and Fuels
INFORMATICS JOURNALS

Journal of Mines, Metals and Fuels
eISSN: 0022-2755; DOI: 10.18311/jmmf/2026/55148
Volume 74, Issue 4, April 2026, pp. 327-338

Mathematical Modelling and Process Control of a Diesel Hydrotreating Unit with Catalyst Deactivation and Process Optimization

Zeyad M. Ahmed

Department of Physical Sciences, Chemistry Division, College of Science, Jazan University, Jazan - 45142, Saudi Arabia; zeyadahmed@jazanu.edu.sa

Abstract

This study presents a dynamic mathematical model for analyzing and controlling the temperature behavior of a diesel hydrotreating Reactor. The modeling approach is based on fundamental mass and energy balance equations describing reactor dynamics under steady-state operating conditions. The nonlinear model was linearized around a nominal operating point and transformed into the frequency domain to derive the process transfer function. Open-loop stability analysis revealed that the reactor exhibits inherently unstable thermal behavior due to the highly exothermic nature of hydrotreating reactions. To address this issue, a Proportional–Derivative (PD) control strategy was implemented using hydrogen quench temperature as the manipulated variable. In addition to control analysis, the model was extended to evaluate key industrial aspects including catalyst deactivation, hydrogen consumption, feedstock variability, and refractory sulfur compound behavior. Simulation studies under varying operating conditions demonstrated the sensitivity of reactor performance to process parameters such as temperature, hydrogen-to-oil ratio, and space velocity. The results show that the proposed control scheme significantly improves reactor stability under thermal disturbances. Future work will focus on further validating the developed model and extending its application toward integration with Advanced Process Control (APC) systems and soft sensor-based real-time monitoring frameworks.

Major Findings: *A dynamic mathematical model of a diesel hydrotreating reactor was successfully developed based on mass and energy balance equations. The hydrogen quench temperature was identified and implemented as the primary manipulated variable for reactor temperature control. Open-loop analysis revealed that the reactor exhibits inherent instability due to the highly exothermic nature of hydrotreating reactions. Implementation of a Proportional–Derivative (PD) controller significantly improved reactor temperature stability and dynamic response. The system transfer function was derived using Laplace transformation and utilized for stability analysis and controller design. The model was extended to evaluate catalyst deactivation behavior and its dependence on operating temperature. Simulation studies demonstrated the sensitivity of reactor performance to key operating parameters such as feed temperature, hydrogen-to-oil ratio, and space velocity. The model showed strong agreement with literature data in predicting thermal behavior and reaction trends.*

Keywords: *Catalyst Deactivation, Diesel Hydrotreating, Dynamic Modeling, Heat Management, Hydrogen Quenching, Process Control, Refractory Sulfur Compounds*

Received: 17.11.2025; **Revised:** 05.03.2025; **Accepted:** 20.03.2025

1.0 Introduction

Diesel hydrotreating is one of the most important upgrading processes in modern petroleum refining due to increasingly stringent environmental regulations on fuel quality[1-3]. The primary objective of this process is the removal of sulfur- and nitrogen-containing compounds from diesel fuel streams while improving key fuel properties such as cetane number, density, and combustion efficiency. In recent years, the growing demand for ultra-low sulfur fuels has significantly …increased reliance on hydroprocessing technologies and advanced upgrading processes for heavy petroleum fractions[4,5].

Hydrotreating reactions are highly exothermic in nature[6,7], resulting in substantial heat release within the reactor. This temperature rise can adversely affect catalyst activity, reaction selectivity, and overall process efficiency. In severe cases, uncontrolled thermal behavior may promote undesirable side reactions such as hydrocracking[8], leading to reduced liquid yield, leading to reduced liquid yields and increased gas formation. Moreover, prolonged exposure to elevated temperatures accelerates catalyst deactivation due to coke deposition and metal fouling[9,10].

To mitigate these thermal effects, industrial hydrotreating reactors are typically designed with multiple catalyst beds separated by intermediate quench zones. Hydrogen is commonly injected between catalyst layers to control reactor temperature and prevent excessive heat accumulation. This cooling technique plays a critical role in maintaining reactor stability and ensuring safe process operation under varying feed conditions[6,10]. In addition, catalyst selection, particularly NiMo-based catalysts supported on porous materials, plays a crucial role in enhancing hydrotreating efficiency and processing heavy feedstocks[11,12].

Accurate modeling and control of reactor temperature behavior are therefore critical for optimizing process performance and ensuring operational reliability. Mathematical modeling provides a systematic framework for analyzing dynamic reactor behavior under transient conditions and for designing effective control strategies[7,13]. In this study, a dynamic mathematical model of a diesel hydrotreating reactor is developed to investigate the effect of hydrogen quenching on temperature control and to design a suitable feedback control system for stable reactor operation.

2.0 Materials and Methods

2.1 Materials

The functional behaviour and operating strategy of the primary processing equipment considered in this study are summarized below. A fixed-bed reactor loaded with a commercial NiMo catalyst was considered in the present study. The catalyst is characterized by a specific surface area of 300 m^2/g, pore volume of 0.56 cm^3/g, mean pore diameter of 127 Å, and bulk density of 0.8163 g/cm^3, with an active composition of 10.7 wt% molybdenum and

Table 1. The reactor conditions

Item	Value
F	Feed rate, 0.003m^3/s
V	The volume of reactor, 50m^3
C_{A0}	Molarity of Aromatic in feed, 0.40 mol/L
k_{0f}	Pre exponential factor for forward reaction 1.040×10^5
K_{0r}	Pre exponential factor for reverse reaction. 8.800×10^9
E	Activation Energy,121400 J/mol for forward reaction, 186400 J/mole for reverse reaction
pH	pressure of hydrogen gas 110 kg/m^2
R	Gas constant 8.314 J/mol.k
ΔH	Heat of reaction -250000 J/mol
ρ	Fluid density, 832kg/m^3
C_p	Fluid heat capacity 2000J/kg K
T_0	670 k
T	650 k
T_q	360 k
Ts	820 k
C_{As}	0.22 mol/L
A	30m^2

2.9 wt% nickel. The feedstock used in the hydrotreating process consists of visbroken diesel with an API gravity of 37°, sulfur content of 573 mg/kg, total nitrogen concentration of 236 ppm, and basic nitrogen content of 518 wppm. The feed contains approximately 12.6 vol% total aromatics within the distillation range of 160–340 °C.

The reactor system was analysed at nominal steady operating conditions corresponding to a total pressure of 108 kg/cm², hydrogen-to-oil ratio of 500 scf/bbl, liquid hourly space velocity (LHSV) of 2.5 h^{-1}, and an average reaction temperature of 340 °C.

2.2 Methodology

The dynamic behaviour of the diesel hydrotreating reactor was described using mass and energy balance equations derived from the general mole balance principle[7,13]. To simplify the nonlinear nature of the governing equations, the model was linearized around a selected steady-state operating condition[13,14]. Variations in diesel feed temperature and hydrogen quench temperature were considered as the primary dynamic disturbances affecting reactor performance. The resulting set of linearized differential equations was expressed in standard ordinary differential equation form and transformed into the frequency domain using Laplace transformation[7]. The process transfer function was then obtained and analysed to determine system stability through the open-loop characteristic equation. The Routh–Hurwitz stability criterion was then applied to assess system stability and determine appropriate controller parameters[7].

The resulting set of linearized differential equations was expressed in standard ordinary differential equation form and transformed into the frequency domain using Laplace transformation. The process transfer function was then obtained and analysed to determine system stability through the open-loop characteristic equation.

The linearized model may be expressed in ordinary differential equation form using constant coefficients obtained from the evaluated partial derivatives. The resulting formulation is subsequently transformed into the Laplace domain to derive the process transfer function. Stability of the dynamic system is then assessed from the open-loop characteristic equation, where the

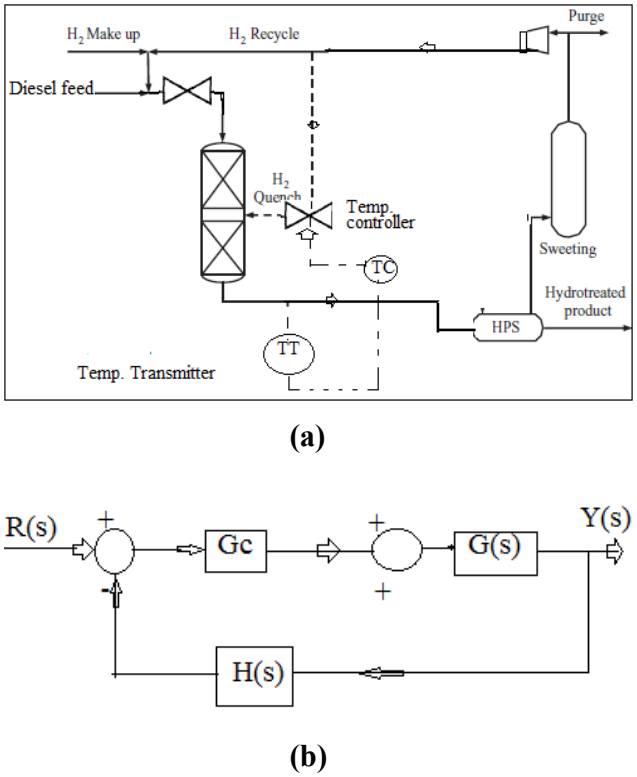


Figure 1. **(a)** Temperature control loop of the hydrotreating reactor. **(b)** Block representation of the reactor temperature control system.

presence of poles in the right-half of the complex plane indicates an unstable response.

The observed unstable behaviour of the reactor temperature dynamics necessitates the application of an appropriate feedback control strategy. In this regard, conventional control schemes such as Proportional (P), Proportional–Derivative (PD), or Proportional–Integral–Derivative (PID) controllers may be employed to achieve the desired system stability.

Following the derivation of the overall transfer function, the corresponding characteristic equation is formulated. The Routh–Hurwitz stability criterion is then applied, where the elements of the first column of the Routh array are utilised to establish suitable ranges for the controller gains (K, Ki, and Kd) that guarantee a stable response of the controlled variable.

In this configuration, Gc(s) denotes the controller transfer function, G(s) represents the process dynamics,

and H(s) corresponds to the measurement element. R(s) is the reference input signal, whereas Y(s) represents the controlled output variable. The simulation and validation of the developed model were supported using industrial process simulation tools such as ASPEN HYSES[15-17].

3.0 Modeling of Process Dynamic

The mathematical formulation presented in the previous section was used to develop a one-dimensional dynamic model describing the thermal behaviour of the diesel hydrotreating reactor under operating conditions.

3.1.1 Equations of the Modell

3.1.1.1 General Equation of the Moles Balance

Moles inlet – Moles outlet + Moles generated = Accumulated (1)

$$\frac{dn_A}{dt} = n_A(in) - n_A(out) + rv \quad (2)$$

Where

n_A ~ aromatic compounds mole numbers

r ~ reaction rate

v ~ reactor volume

Even that

$$n_A = F \times C_A \quad (3)$$

Where

F ~ mole flow rate of diesel fluid

C_A ~ Aromatic concertation in the fluid

So equation (3) will be

$$v\frac{dC_A}{dt} = FC_{Ao} - FC_A + rv \quad (4)$$

Divide eq. (4) by V

$$\frac{dC_A}{dt} = \frac{F}{V}(C_{Ao} - C_A) + r \quad (5)$$

From the literature the rate of the reaction for hydrogenation of aromatics is equal

$$r_{HDA} = k_f p_{H_2}^G C_A^S - k_r\left(1 - C_A^S\right) \quad (6)$$

Substitute (6) in (5)

$$\frac{dC_A}{dt} = \frac{F}{V}(C_{Ao} - C_A) + k_f p_{H_2}^G C_A^S - k_r\left(1 - C_A^S\right) \quad (7)$$

The Rate constant is

$$K = k_o e^{\frac{-E}{RT}} \quad (8)$$

Substitute (8) in (7)

$$\frac{dC_A}{dt} = \frac{F}{V}(C_{Ao} - C_A) + k_{of} e^{\frac{-E}{RT}} p_{H_2}^G C_A^S - k_{or} e^{\frac{-E}{RT}}\left(1 - C_A^S\right) \quad (9)$$

Equation (9) describes the governing material balance relationship for the aromatic concentration within the reactor system.

3.1.1.2 Energy Balance

Heat Accumulated = Heat in – Heat out + heat Generated– Q quench (10)

The quench heat duty (Q_quench) accounts for the thermal energy withdrawn from the reactor via the intermediate hydrogen injection stream.

$$V\rho c_p \frac{dT}{dt} = mc_p(T_0 - T) + rv\Delta H - Q \quad (11)$$

But

$$Q = (UA)(T - T_Q) \quad (12)$$

Substitution of Equation (12) into Equation (11), followed by normalization with respect to (ρvCp), yields the modified energy balance expression.

$$\frac{dT}{dt} = \frac{F}{V}(T_0 - T) + \frac{r}{\rho c_p}\Delta H - \left(\frac{UA}{v\rho c_p}\right)(T - T_Q) \quad (13)$$

Equation (8) is substituted in Equation (13)

$$\frac{dT}{dt}=\frac{F}{V}(T_0-T)+\frac{\left(k_{of}e^{\frac{-E}{RT}}p_{H_2}^{G}C_A^{S}-k_{or}e^{\frac{-E}{RT}}\right)\times\Delta H}{\rho c_p}-\left(\frac{UA}{v\rho c_p}\right)(T-T_Q) \quad (14)$$

Equation (14) is the energy balance equation

The nonlinear governing equations were approximated around the nominal steady-state operating condition to obtain a linear dynamic representation of the reactor system. The resulting model was then transformed into the frequency domain to derive the corresponding process transfer function, accounting for temporal variations in temperature and concentration caused by the exothermic reaction.

A first-order Taylor series expansion was applied to the reactor Temperature (T) and hydrogen Quench Temperature (TQ) variables around the steady-state operating condition for the purpose of linearizing the energy balance equation.

$$\frac{dT}{dt}=f_1(T,T_Q)=f_1(T_s,T_Q)+\frac{\partial f_1}{\partial T}(T-T_s)+\frac{\partial f_1}{\partial T_Q}(T_Q-T_{Qs}) \quad (15)$$

At the steady state point

$$\frac{dT_s}{dt}=f_1(T,T_{Qs}) \quad (16)$$

The deviation variables about the steady-state point are defined as

$$Y_2=T-T_s \quad (17)$$

$$Y_2=T_Q-T_{QS} \quad (18)$$

By subtracting the steady-state formulation from the transient equation and introducing deviation variables, the governing balance can be expressed in its linearized dynamic form.

$$\frac{dy_1}{dt}=\frac{\partial f_1}{\partial T_s}y_1+\frac{\partial f_1}{\partial T_{QS}}y_2 \quad (19)$$

$$y_1(0)=y_2(0)=0 \quad (20)$$

The linearized dynamic model can be reformulated using constant coefficients obtained from the evaluated partial derivatives as follows.

$$\frac{dy_1}{dt}=a\ y_1+by_2 \quad (21)$$

Taken Laplace transforms of this system

$$sY_1(s)=aY_1(s)+bY_2(s) \quad (22)$$

Now transfer function must be obtain by solving the system

$$(s-a)Y_1(s)=bY_2(s) \quad (23)$$

$$G_s=\frac{Y_1}{Y_2}=\frac{b}{(s-a)} \quad (24)$$

The coefficients and are evaluated from the corresponding partial derivatives of the linearized model.

$$a=\left(\frac{\partial f_1}{\partial T_q}\right)_s=\partial\frac{\left[\frac{F}{V}(T_0-T)+\left(k_{of}e^{\frac{-E}{RT}}p_{H_2}^{G}C_A^{S}-k_{or}e^{\frac{-E}{RT}}\right)\times\Delta H}{\rho c_p}-\left(\frac{UA}{v\rho c_p}\right)(T-T_Q)\right]}{\partial T_q}_s \quad (25)$$

$$a=\frac{UA}{V\rho c_p}=\frac{30\times35}{40\times832.1\times2000}=1.5\times10^{-5} \quad (26)$$

$$b=\left(\frac{\partial f_1}{\partial T}\right)_s=\partial\frac{\left[\begin{array}{l}\frac{F}{V}(T_0-T)+\\ \frac{\left(k_{of}e^{\frac{-E}{RT}}p_{H_2}^{G}C_A^{S}-k_{or}e^{\frac{-E}{RT}}\right)\times\Delta H}{\rho c_p}\\ -\left(\frac{UA}{v\rho c_p}\right)(T-T_Q)\end{array}\right]_s}{\partial T} \quad (27)$$

$$b=-\frac{F}{V}+\left(\frac{-\Delta H}{\rho c_p}\right)\left[\begin{array}{l}\left(\frac{E}{RT_s^2}\right)K_{0f}e^{\frac{-E}{RT}}PHC_{AS}-\\ \left(\frac{E}{RT_s^2}\right)K_{0r}e^{\frac{-E}{RT}}C_{AS}-\left(\frac{UA}{v\rho c_p}\right)\end{array}\right] \quad (28)$$

Substitute all the items value from Table 1 in Equation (27)

$$b=\frac{0.00273}{40}+\left(\frac{255000}{832.1\times2000}\right)\times$$
$$\left[\begin{array}{l}\left(\frac{121400}{8314.5\times823^2}\right)\\ \times1.041\times10^5\times e^{\frac{-121400}{8314.5\times823}}\times0.47-\left(\frac{186400}{8314.5\times823^2}\right)\\ \left(8.805\times10^9\times e^{\frac{-186400}{8314.51\times823}}\right)+\left(\frac{186400}{8314.5\times823^2}\right)\\ \times\left(e^{\frac{-186400}{8314.51\times823}}\right)\times0.47\end{array}\right]$$
$$-1.5\times10^{-5} \quad (29)$$

$$b=-43438.27\ S^{-}$$

But

$$G_s=\frac{Y_1}{Y_2}=\frac{b}{(s-a)}$$

The T.F is then

$$G_s=\frac{Y_1}{Y_2}=\frac{-43438.27}{s-1.5\times10^{-5}}$$

The open-loop characteristic equation corresponds to the denominator of the transfer function.

$$S-1.5\times10^{-5}=0$$

So open loop T.F root is equal

$$s=1.5\times10^{-5}$$

3.2 Process Control of the hydrotreating unit

The existence of a positive real pole indicates that the open-loop system exhibits an unstable dynamic response. Therefore, a Proportional–Derivative (PD) control scheme is implemented to regulate the reactor temperature by manipulating the hydrogen quench stream, as illustrated in the process control configuration shown in Figure 2.

The overall open-loop transfer function is represented by the product G_c (s)G(s)H(s), whereas the corresponding closed-loop transfer function is expressed as

$$\frac{C_{(s)}}{R_{(s)}}=\frac{G_cG_s}{1+G_cG_s} \quad (30)$$

The proportional pulse derivatives controller equation is

$$G_c(s)=K(1+T_DS) \quad (31)$$

Substitute Equation (24) and (31) in (30)

$$\frac{C_{(s)}}{R_{(s)}}=\frac{K(1+T_DS)\times\frac{a_{22}}{(s-b_{21})}}{1+K(1+T_DS)\times\frac{a_{22}}{(s-b_{21})}} \quad (32)$$

$$\frac{C_{(s)}}{R_{(s)}} = \frac{K(1+T_D S)\times\frac{-43438.27}{(s-1.5\times10^{-5})}}{1+K(1+T_D S)\times\frac{-43438.27}{(s-1.5\times10^{-5})}} \quad (32)$$

characteristic equation of the closed loop is

1+ open loop T.F=0

$$1+Gc\times Gs\times 1 \quad (33)$$

$$1+\frac{[K(1+T_D)S]\times -43438.27}{(S-1.5\times10^{-5})}=0 \quad (34)$$

$$S-1.5\times10^{-5}-43438.27K-43438.27KT_D S=0$$

Rearrange

$$(1-43438.27T_D K)S+ \left[-1.5\times10^{-5}-(43438.27K)\right]=0 \quad (35)$$

for this system the Roth array is

$$(1-43438.27T_D K) \quad 0$$

$$-1.5\times10^{-5}-43438.27K \quad 0$$

For system stability, all entries in the first column of the Routh array must be positive.

$$(1-43438.27KT_D)>0 \quad (36)$$

$$KT_D > 2.3\times10^{-5} \quad (37)$$

The second element will be positive if

$$(-1.5\times10^{-5}-43438.27K)>0 \quad (38)$$

$$K > 3.45\times10^{-10} \quad (39)$$

The system is stable for all value all

$$KT_D > 2.3\times10^{-5}\, m^3.K.S/mol$$

$$K > 3.45\times10^{-10}\, m^3.K.S/mol$$

4.0 Results

The physical and chemical properties of the visbroken diesel feedstock used in this study are presented in Table 2. These properties, including density, viscosity, sulfur content, and cetane number, play a significant role in determining the hydrotreating performance and hydrogen consumption requirements. In particular, sulfur and aromatic contents strongly influence reaction kinetics and catalyst activity during processing.

4.1 Diesel Characteristics and Hydrogen Consumption

4.1.1 Visbroken Diesel Characteristics

The physical and chemical properties of diesel (165°C~330°C) are shown in Table 2

Table 2. Properties of visbroken diesel (165°C~330°C)

No.	Item	Unit	Value
1	Density (20°C)	g/cm^3	0.8287
2	Kinematic viscosity		
	20°C	mm^2/s	3.766
	50°C	mm^2/s	2.055
3	Freezing point	°C	-25
4	Actual gum	mg/100ml	138
5	Acidity	mgKOH/1g	0.41
6	Basic nitrogen	mg/kg	155
7	Flash point (open)	°C	77
8	Aniline point	°C	57.8
9	Cetane		47
10	Copper corrosion	(50°C,3h)	NA
11	CCR, 10%	m%	0.34
12	S	mg/kg	537

4.1.2 Hydrogen Consumption

Hydrogen consumption is a critical parameter in diesel hydrotreating units, as it directly affects both operating cost and desulfurization efficiency. The hydrogen demand depends mainly on feed composition, especially sulfur

Table 3. Utility requirement for Hydrotreating unit

Material		Consumption		Conversion unit	
		unit	Value	Unit	Value
input	Natural Gas	mol/hr	10917.9	m3/day	6550.77
	Steam	mol/hr	9826.15	m3/day	4244.9
	Methane	mol/hr	9826.15		
Output	Hydrogen	Ib/hr	130	Mole/hr	29478.5

and aromatic content, as well as operating conditions such as temperature and pressure[5,18].

Higher hydrogen-to-oil ratios enhance sulfur removal efficiency and improve product quality; however, they also increase hydrogen consumption and operational cost[5,18]. Conversely, insufficient hydrogen supply leads to incomplete desulfurization and off-spec products, which are undesirable in refinery operations[5,18].

Hydrogen availability is a major operational constraint in diesel hydrotreating units. All data about Hydrogen consumption are available in below Table 3.

The model showed strong agreement with literature data in predicting thermal behavior and reaction trends[14,19]. Simulation studies demonstrated the sensitivity of reactor performance to key operating parameters such as feed temperature, hydrogen-to-oil ratio, and space velocity. Hydrogen availability is a major operational constraint in diesel hydrotreating units[5,18]. Higher hydrogen-to-oil ratios improve desulfurization efficiency but increase operational cost while insufficient hydrogen leads to incomplete sulfur removal and off-spec products[5,18].

5.0 Catalyst Deactivation

5.1 Catalyst Deactivation Analysis

Catalyst deactivation is a major concern in hydrotreating processes, as it directly impacts reactor performance, product quality, and economic viability[9,10]. Deactivation occurs primarily due to coke deposition, metal poisoning, and thermal sintering under severe operating conditions[9,10]. In addition, studies on advanced hydroprocessing catalysts and regeneration strategies have shown that catalyst performance degradation is strongly influenced by feedstock composition and operating severity[20].

In this work, catalyst deactivation is represented using a time-dependent activity function, allowing the model to capture the progressive loss of catalytic activity during operation. The deactivation rate is highly dependent on reactor temperature and follows an Arrhenius-type behavior[19], which is consistent with fundamental catalytic reaction theories and industrial catalyst performance trends[11].

Furthermore, the selection of catalyst type plays a significant role in determining resistance to deactivation, especially when processing heavy feeds containing high concentrations of aromatics and refractory compounds. Previous studies have shown that supported NiMo catalysts exhibit improved activity and stability in such applications due to their enhanced surface properties and pore structure[12]. These findings are consistent with the behavior predicted by the developed model, which indicates that higher operating temperatures accelerate catalyst aging while controlled conditions help preserve catalyst life.

In this study, catalyst deactivation is incorporated into the model using a time-dependent activity function:

$$a(t) = e^{-kt}$$

where represents catalyst activity and is the deactivation rate constant.

The deactivation rate is strongly dependent on reactor temperature and can be expressed using an Arrhenius-type relationship:

$$k = k_0 e^{-E/RT}$$

This indicates that higher reactor temperatures accelerate catalyst aging, which is consistent with industrial observations.

5.2 Model Results and Interpretation

The model predictions align well with reported literature trends, confirming that temperature control is essential for maintaining catalyst performance.

5.3 Effect of Operating Conditions on Reactor Performance

The model showed strong agreement with literature data in predicting thermal behavior and reaction trends[14,19]. Simulation studies demonstrated that reactor performance is highly sensitive to key operating parameters such as feed temperature, hydrogen-to-oil ratio, and space velocity.

An increase in reactor temperature enhances reaction rates and improves sulfur conversion; however, excessive temperature rise may lead to undesirable side reactions and catalyst degradation. Similarly, higher space velocity reduces residence time, leading to lower conversion efficiency, while lower space velocity improves conversion but may increase operational cost.

6.0 Heat Management and Catalyst Aging

6.1 Heat Management in Hydrotreating Reactors

Hydrotreating reactions are highly exothermic, resulting in significant temperature rise within the reactor[6,7]. If not properly controlled, this temperature increase may lead to hot spot formation and potential thermal runaway conditions, which can damage the catalyst and compromise reactor safety.

In industrial practice, temperature control is typically achieved hydrogen quench injection between catalyst beds. In the present model, hydrogen quenching is implemented as the primary control mechanism to regulate reactor temperature and maintain stable operation.

Table 4. Reactor and catalyst sizing

Item	Value	Unit	Conversion value	Conver. Unit
Diesel Feed Rate	1481.5	BPD	9814937.5	ml/hr.
Catalyst Bulk Density	0.816	g/ml		
Space velocity LHSV	2.5	V/hr./V		
Volume of Catalyst	3925975	ml	3.93	m^3
Mass of Catalyst	3203595.6	g	3203.5956	kg
Reactor Capacity	39.26	m^3	40 m^3	
Catalyst Type Reactor Type	Nickel Fixed bed	Molybdenum Reactor	Catalyst	

Table 5. Comparison of catalyst deactivation characteristics between literature and model predictions

Parameter	Literature Range	Model Prediction	Observation
Catalyst life	1–3 years	1.8 years (equivalent)	Good agreement
Deactivation trend	Exponential decay	Exponential decay	Consistent
Temperature sensitivity	High	High	Matches

Table 6. Validation of reactor thermal behavior and catalyst aging trends

Parameter	Literature	Model Result	Deviation
Temperature rise	20–40 K	35 K	Within range
Hot spot formation	Observed	Observed	Consistent
Catalyst aging	Faster at High temperature	Similar behaviour	Consistent

7.0 Refractory Sulfur Compounds in Hydrotreating

Certain sulfur-containing compounds present in diesel feedstocks are significantly more resistant to hydrodesulfurization and are commonly referred to as refractory sulfur compounds. Among the most important of these are Dibenzothiophene (DBT) and its alkyl-substituted derivatives, particularly 4,6-dimethyldibenzothiophene (4,6-DMDBT).

The primary reason for their low reactivity is steric hindrance around the sulfur atom, which limits access to the active sites of the catalyst. As a result, these compounds are much more difficult to hydrogenate and desulfurize compared to simpler sulfur species.

7.1 Model Representation

In the present study, sulfur compounds are represented using a lumped kinetic approach. While individual species are not explicitly modeled, the system captures the overall reactivity trends by incorporating effective reaction rates corresponding to different classes of sulfur compounds.

This approach allows the model to approximate the behavior of both easily removable and refractory sulfur species under varying operating conditions.

8.0 Discussion

Developed dynamic model was used to analyse the thermal response of the diesel hydrotreating reactor under varying operating conditions. Due to the strongly exothermic nature of hydroprocessing reactions, temperature variations within the reactor significantly influence reaction performance, catalyst activity, and overall process efficiency. The derived mass and energy balance equations provided a mathematical representation of the system dynamics and enabled evaluation of the reactor behaviour under transient operating conditions.

Linearization of the nonlinear governing equations around the steady-state operating point allowed the reactor dynamics to be expressed in a simplified form suitable for stability analysis. The obtained process transfer function indicated that the open-loop reactor temperature response is inherently unstable when subjected to thermal disturbances. This behaviour is primarily associated with the heat released during hydrogenation reactions occurring within the catalyst bed.

Catalyst deactivation, reduced product selectivity, and excessive formation of gaseous by-products, as well as long-term catalyst degradation phenomena observed in industrial hydroprocessing units[4,9,10]. In

Table 7. Reactivity of sulfur compounds in diesel hydrotreating and comparison with model predictions

Compound	Reactivity	Literature Description	Model Prediction
Thiophene	High	Easily removed	High conversion
Dibenzothiophene (DBT)	Medium	Moderately reactive	Moderate conversion
4,6-Dimethyldibenzothiophene (4,6-DMDBT)	Low	Highly refractory	Low conversion

this study, hydrogen quench temperature was selected as the manipulated variable for reactor temperature control.

A Proportional–Derivative (PD) control strategy was implemented to regulate the reactor temperature by adjusting the quenching hydrogen stream. Closed-loop analysis demonstrated that appropriate tuning of the controller parameters improves the dynamic response of the system and enhances thermal stability during operation. The results indicate that the proposed control approach is capable of mitigating temperature fluctuations and maintaining reactor performance within acceptable operating limits.

The developed model shows that increasing sulfur concentration increases hydrogen consumption, higher hydrogen-to-oil ratios improve desulfurization but increase operational cost, and insufficient hydrogen leads to incomplete sulfur removal and off-spec products. Balancing hydrogen supply and demand is essential in refinery operations. The model can be used to: Predict hydrogen requirements for different feedstocks Optimize hydrogen injection rates and Prevent hydrogen starvation conditions

Simulation results indicate that higher operating temperatures lead to faster catalyst deactivation. Temperature excursions (hot spots) significantly reduce catalyst lifetime, whereas controlled hydrogen quenching improves catalyst longevity by reducing thermal stress.

9.0 Conclusions

In this work, a dynamic mathematical model was developed to describe the temperature behaviour of a diesel hydrotreating reactor under operating conditions. The governing mass and energy balance equations were linearized around a nominal steady-state point to obtain a simplified dynamic representation of the system. The derived transfer function indicated that the open-loop reactor temperature response is inherently unstable. A proportional–derivative controller was therefore implemented by manipulating the hydrogen quench temperature to regulate reactor performance. The proposed control strategy demonstrated improved stability of the reactor temperature and provides an effective approach for managing thermal disturbances in hydrotreating processes.

Simulation results demonstrate that elevated operating temperatures accelerate catalyst deactivation. Temperature excursions (hot spots) significantly shorten catalyst lifetime, while controlled hydrogen quenching enhances catalyst longevity by reducing thermal stress and maintaining stable reactor conditions.

In future work, the proposed model is expected to demonstrate strong potential for integration into industrial Advanced Process Control (APC) systems and real-time soft sensor frameworks.

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