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Received on: 27/07/2016 Accepted on: 08/06/2017

Parametric Study on Intrinsic Reaction for Straight Run Heavy Naphtha Hydrodesulfurization over CoMo/Al₂O₃ Catalyst

Abstract- The present study aimed to investigate the intrinsic reaction of hydrodesulfurization (HDS) for a real Straight Run Heavy Naphtha (SRHN) over CoMo-S/Al₂O₃ catalyst in a fixed- bed reactor. Influence of the process parameters on sulfur removal was investigated by regulating the temperature (T = 320-380 °C), pressure (P = 20 to 35 bar), weight hour space velocity (WHSV = 2.5 to 5.0 h^{-1}) and catalyst average particle size (dp = 3) to 39 °0 µm). Mears and Weisz-Prater criteria were estimated and utilized to validate the intrinsic reaction condition. Operating variables were optimized at (T = 360 °C, P = 30 bars, WHSV)= 2.5 h^{-1} , dp = 3¹⁷ μ m) to obtain an optimum sulfur removal of 93.4% under intrinsic reaction conditions. Experimental results showed that % activity of sulfur removal increases to 93.4% as temperature increased to $360^{\circ}C$ but it reduces to 90.3% as space velocity increased to 5.0 h^{-1} . Kinetic parameters of the intrinsic reaction rate were estimated and compared with published data. Long-time test was performed on the sulfided catalyst to investigate its activity.

Keywords- Hydrodesulfurization, heavy naphtha, reaction kinetics, hydrotreating, catalyst deactivation.

How to cite this article: M.F. Abid, M.K. Abdullah and S.M. Ali, "Parametric Study on Intrinsic Reaction for Straight Run Heavy Naphtha Hydrodesulfurization over CoMo/Al₂O₃ Catalyst," *Engineering and Technology Journal*, Vol. 36, Part A, No. 2, pp. 146-153, 2018.

1. Introduction

It is well known that the current crude oils afforded to refineries are characterized by lower API and higher sulfur content [1]. Meanwhile, the rate consumption of middle distillates and gasoline is becoming continuously increasing. Moreover, the regulations of environmental protection agencies for fuel specifications become more tighten. To meet these requirements, the catalytic hydroprocessing for fuels upgrading seems to be a promising technique. In the HDT process, the quantities of S, N and polyaromatics are decreased, which constraints the impacts of sulfur oxides and particulates during combustion on environment. Moreover, Sulfur species are poisonous for the catalysts in subsequent units in the petroleum refinery. The hydrodesulfurization (HDS) activity are influenced by many factors such as operating conditions (e.g., T, P, WHSV, and catalyst average particle diameter), catalyst type (e.g., CoMo/Al₂O₃. NiMo/Al₂O₃, and NiW/Al₂O₃) and reactor type (e.g., fixed bed, moving bed, slurry, and ebullated bed). The process severity depends on the feed specification such as sulfur content and hydrocarbons type and its percentage present [2]. Geometry of catalyst particle is another issue to study. It is well known

that the main drawback of utilizing catalyst particle is in the existence of both external and internal diffusion resistances. External diffusion resistance could be minimized by variation of interphase hydrodynamics [3]. While internal diffusion resistance could be reduced by manipulation of catalyst structure and geometry [4]. Though it is more difficult to overcome the internal diffusional resistance, it could be considered more beneficial to reduce it [5-6]. Kinetic models for HDS reaction are well represented by power law and Hinshlwood Langumir models. Many researchers of the field used these models as tools to formulate a comprehensive model for HDS process [7-8]. Power law is utilized to estimate an overall rate constant, while Hinshlwood\ Langumir is utilized to estimate competitive adsorption steps occurred throughout reactions. A third kinetic model which rarely used is the multi-parameter model [9]. Vrinat et al. [10] estimated coefficients of reaction kinetics for ultra HDS of (4, 6-DMDBT), to uncover the retarding effect of hydrogen sulfide on ReS2 catalysts. Carlos et al. [11] determined the kinetic parameters of gasoline hydrotreating over CoMo/y-Al₂O₃ catalyst using genetic algorithm technique. They suggested the

DOI: https://doi.org/10.30684/etj.36.2A.5

2412-0758/University of Technology-Iraq, Baghdad, Iraq This is an open access article under the CC BY 4.0 license http://creativecommons.org/licenses/by/4.0 L-H model with mechanism of sixteen stages utilized one type of active site. $(CH_3)_3$ CCH₂ CH(CH₃)₂ and C₅H₆S were used as token species of non-saturated and sulfur compounds. Borgna et al. [12] reported that it has proven very difficult to relate catalyst structure to catalyst activity and selectivity on the molecular level. Safe and economical design of catalytic reactors required reliable rate laws. This could be established by excluding the effects of transport phenomena and scale issues on the reaction kinetics. From this point of view, the concept of intrinsic reaction could be of practical importance. Published works on the effect of intrinsic reaction on the performance of HDS are scarce. In the present work, the performance of HDS of Iraqi petroleum fractions (e.g., heavy naphtha) onto CoMo/Al₂O₃ catalyst was investigated under the effect of intrinsic reaction. Various operating conditions were applied (e.g., pressure, temperature, weight hourly space velocity (WHSV), particle diameter, and operating time) to study these effects on sulfur removal.

2. Experimental

I.Materials

Specification of catalyst and chemicals used in the present work is listed in Table1.

II. Apparatus and methods

Apparatus used in present work is seen in Figure 1 containing of st. st. Tubular reactor (ID: 17.5 mm; OD: 25.4 mm; catalyst space: 70 ml) surrounded by an electrical box heater (3 kW, 240 Volts). The liquid Naphtha was charged from vessel (no. 1) to the reactor (no. 6) using a diaphragm pump (no. 2). A tape preheater was used to preheat the liquid naphtha which goes into the top of reactor with hydrogen gas. The reactants and products exited at the bottom of reactor to a cooler (no. 10) with chiller (no.12) before charged to a high pressure separator (no. 11) where gases (H_2S, NH_3) were purged to a water scrubber (not shown in Figure 1). Liquid from HP separator was accumulated and analyzed. The system has also supplied by temperature indicators located in 4 points. The first is located immersed into reactor to determine the reaction temperature, the second located in the furnace to determine the furnace temperature, the third inserted in the tube before the feed enter to the reactor, and the fourth located in the gas tube before the hydrogen gas enters the reactor. Figure 1 illustrates the experimental apparatus located at the PR & D Center.

Table 1: Specification and properties of catalyst and chemicals used

Item	Specification	Supplier
CoMo/γ- Al ₂ O ₃ Catalyst	Co: 2.8 wt%, Mo: 11.4%; dp= 2.5mm, BET= 183.8 m ² /g, ρ b= 0.95 g/cm ³	Al-Duara refinery
Heavy Naphtha	API@15.6 ^o C = 62.7 I.B.P=80C,E.P= 176C	Al-Duara refinery
Thiophene	C4H4S,98wt%,Liquid state	Fluka, Germany
DMDS	99 wt%, Liquid state	Infra, Italy
H ₂ gas	99.9% Purity	Al- Mansoor Company
N ₂ gas	99% Purity	Al- Mansoor Company





Figure 1: Setup of experimental system

III. Experimental procedure

The workable part in this research was performed as follows. Drying step was conducted to get rid of wetness from the catalyst by purging N₂ gas at the following conditions (T= 180 $^{\circ}$ C, P = 8 atm, N_2 flow = 120 N-lit/h, time = 4 h). The catalyst was activated when converting (CoMoO₄) into (CoMoS) form. In present study a mixture of kerosene and dimethyl disulfide were utilized as sulfiding agent containing 3000 mg sulfur /L (as measured by analyzer type XOS in PR&D center) with hydrogen gas. The applied conditions of the sulfiding step were (T= 180 °C, P = 10 bar, H₂ flow = 100 Nlit/h, kerosene rate = 120 mlit/h, time = 10 h). Based on instructions of Petroleum R&D center the increase in catalyst due to sulfiding should be equal to 0.02wt. % and this was due to precipitation of sulfur onto catalyst. As sulfur concentration in the outlet equals to the sulfur concentration in the inlet, sulfiding step is considered to be accomplished. Figure 2 plots the change in sulfur concentration of exit flow through sulfiding step. To perform the HDS step, the reactor was charged with 50gm of catalyst. Before liquid mixture was admitted to the reactor, at the desired flow, N2 gas was flowed for one hour to heat the catalyst. To raise the pressure inside the reactor to the desired value, H₂ gas was introduced. Due to the exothermic reaction, temperature inside the reactor increases which is controlled by manipulating the energy released from furnace elements. Products were conducts and sampled for analysis. The key process parameters were (T = 320-380 °C, WHSV = 2.5to 5 h⁻¹, P = 20 to 35 bar, and (H₂/Oil) ratio = 60 Nm³/m³).The sulfur conversion was estimated using Eq. 1.

Sulfur removal % =
$$\left(\frac{Sf - Sp}{Sf}\right)100$$
 (1)

Where *Sf* & *Sp* are concentrations of S in inlet and outlet streams, respectively.

IV. Analytical methods

Table 2 lists the measured properties with the corresponding measurement and analysis instruments.



Figure 2: sulfur concentration in the outlet flow versus sulfiding time

 Table 2: Measured properties & measurement instruments

Property	Instrument	Place of measurement
Specific surface area of catalyst	(QSurf1600, USA) analyzer	PR&D center
Pore volume of catalyst	(QSurf1600, USA) analyzer	PR&D center
Total sulfur analysis	XOS (Model Sindie OTG	PR&D center
moisture content	Meeconic, AP2- a100	PR&D center
Catalyst morphology	EDX (TESCAN, USA)	UOT

Composition of the catalyst surface is shown in Figure 3.

3. Kinetic Aspect

I. Kinetic model

Whitehurst et al. [13] proposed a two site adsorption mechanism for S species and H_2 over the catalyst surface,

$$r_{\text{HDS}} = k \frac{K_{\text{S}}C_{\text{S}}}{1 + K_{\text{S}}C_{\text{S}} + K_{\text{H2S}}C_{\text{H2S}}} \times \frac{K_{\text{H}}C_{\text{H}}}{1 + K_{\text{H}}C_{\text{H}}}$$
(2)

Where k is the reaction rate constant, K_s , K_H , and K_{H2S} are the adsorption constant of C4H4S, H_2 , and H_2S . C_S , C_H , and C_{H2S} are the concentrations of sulfur compound, H_2 , and H_2S . Since H_2 was in excess, $K_HC_H \gg 1$, and eqn. 2 becomes

$$r_{HDS} = k \frac{K_S C_S}{1 + K_S C_S + K_{H2S} C_{H2S}}$$
(3)

If the sorption of H₂S could be taken into account as greater than C4H4S over the solid surface, then $(1 + K_{H2S}C_{H2S}) \gg K_SC_S$, eqn. 3 becomes

$$r_{\rm HDS} = k \frac{K_{\rm S} C_{\rm S}}{1 + K_{\rm H2S} C_{\rm H2S}}$$
(4)

The rate law of the HDS reaction is

$$r_{HDS} = k_{HDS}C_S \tag{5}$$

Where k_{HDS} is the specific rate constant containing the adsorption influence of H_2S . Cs could be written as,

$$C_S = C_{SO}(1 - X_S) \tag{6}$$

where C_{SO} and xs are the incipient weight content and conversion of sulfur, respectively. Based on Eq. 5, the reaction is considered as pseudo-1st order. This is validated in sec. II.

V. Experimental design

In this research, the method of factorial design was utilized for experimental design, due to its validity and accuracy in investigating the influence among operating variables. Table 3 lists the real variable values of controlled process parameter (F) and the levels (L) utilized for arrangement of experiments in the present study.



Figure 3: EDX image of the CoMo/Al₂O₃ catalyst used in the present work

Table 3: Arrangement of experimental design

F	Real variables		
	P bar	T °C	WHSV h ⁻¹
L			
1	20	320	2.50
2	25	340	3.32
3	30	360	4.16
4	35	380	5.00

II. Prediction of rate coefficients

In this work, a plug flow was assumed. To investigate the kinetics of reaction, firstly it is assumed a first order kinetics. Then,

$$W = F_{A0} \int \frac{dx_s}{k_{HDS}C_{S0}(1-x_s)}$$
(7)

Equation (7) is treated by integration and rewritten to get:

$$k_{\text{HDS}} = \left(\frac{\mathbf{m}}{\mathbf{W}}\right) \left[-\ln(1 - \mathbf{x}_{\text{s}})\right]$$

$$k_{\text{HDS}} = \left(\frac{1}{2}\right) \ln \frac{1}{\mathbf{x}_{\text{s}}}$$
(8)
(9)

Where $k_{HDS} (g_L g_{cat}^{-1} h^{-1})$ is the specific rate constant; $\tau (g_{cat} h. g_L^{-1})$ is residence period, and x_s is the sulfur actual conversion. k_{HDS} is calculated by a graph of $\ln(1 - x_s)$ vs. τ , where k_{HDS} is represented by the slop. A straight line indicated a pseudo 1st order trend. The plot of ln (k_{HDS}) vs. $(T)^{-1}$ represents the activation energy.

III. Kinetic regime

Some experiments were carried out to investigate the mass transfer limitations. The solid particles were mashed into three scales (3950, 940, and 316µm) to study the impact of particle size on intrinsic reaction. These sizes of catalyst were subjected to identical conditions. Criteria of (eqn. 10) and Weisz-Pratar (eqn. 11) for external and internal resistances to species transport respectively were utilized to investigate the studied system [14].

$$\frac{r_{s}r_{i}}{C_{bi}K_{c}} < \frac{0.15}{n} \tag{10}$$

Where C_{bi} : fractional composition of species I in bulk, r'_i : global rate of species i (kg i reacted/kgcat. s), r_s : radius of solid in cm, K_c : parameter for transport of species from bulk to catalyst in cm/s, and n: degree of kinetics. When the right hand side of eqn. 10 is verified, resistances to mass transfer are ignored.

$$C_{wp} = \frac{(-r_i)r_s^2}{D_{ei}C_{si}}$$
(11)

Where $-r'_{i}$: is rate of reaction of species i $(\frac{Kg\,i\,reacted}{Kg\,cat.s})$, and C_{Si} : weight content of i over solid surface $(\frac{Kg}{Kg\,cat.})$.

When $C_{wp} \gg 1$, internal resistance vigorously affects the reaction.

4. Results and Discussion

I. Estimation of rate parameters

The linear relationship between $-\ln(1-x)$ and residence time shown in Figures 4 and 5 assured that the kinetics of hydrodesulfurization is pseudo first- order regardless any applied pressure. Furthermore, influence of pressure on the specific rate constants is shown on Figures 4 and 5 and their values are tabulated on Table 1. As can be seen in Table 1, rate constant increased by 40.6% as pressure increased from 20 to 35 bars. In addition, Table 2 shows the effect of pressure on activation energy which increased by 21.12%. Our results have good agreement with the outcomes of [15-16] for the pressure impact on the estimated k_{HDS} and E_A . Majak [17] reported that for HDS of light gas oil over commercial NiMo/ γ -Al₂O₃ catalyst, the rate constant values are varied between 1.73 h⁻¹at temperature 360 °C to 3.86h⁻¹ at temperature 390 °C which are close to our results. Our calculated values of activation energies overestimated the value of [18] (i.e., 28 kJ/gmol) but underestimated the value calculated by [19] (i.e., 55 kJ/gmol). The reason for these margins may be attributed to the differences in the operating systems (i.e., temperature, pressure, and type of catalyst). While [19] used NiMo catalyst for hydrotreating of gas oil which favored higher activation energy, Bej et al. [18] used higher operating pressures (6.5 to 8.8 MPa) but lower temperatures (365 to 415 °C) compared with these of present study. It is interesting to notice, from Table 4, that values of the rate constant at 360 °C and 380 °C are equal under 35 bars. This behavior may be due to the equilibrium thermodynamically occurred in rate of reaction at temperature and pressure which have higher values. This phenomenon was also observed by [20-21].



Figure 4: Plot of $-\ln(1-x)$ against residence time at different operating temperature and under (P= $^{\circ}0$ bars, WHSV= 2.5h⁻¹, and dp = 316 micometer)



Figure 5: Plot of $-\ln(1-x)$ against residence time at different operating temperature and (P= 35 bar, WHSV= 2.5h⁻¹, and dp = 316 µm)

Table 4: Activation energy and specific rateconstant with corresponding pressure andtemperature

20 bar			35 bar		
T °C	K, h ⁻¹	E _x kJ/mol	K, h ⁻¹	E _x kJ/mol	
320	1.01		1.70		
340	1.1727	23.41	2.085	29.68	
360	1.4352		2.4084		
380	1.5125		2.4084		

II. Determination of kinetic regime

Mears criterion (eq. 10) and Weisz-Prater criterion (eq. 11) were estimated under the studied operating conditions (Temperature = 320to 380 °C, WHSV = 2.5 to 5.0 h^{-1} , pressure = 35 bar, average particle diameters = 316 to 3950 μ m). Results indicated that for dp = 316 μ m, Mears criterion (C_M) was fluctuated from 0.0033 to 0.0076 and Weisz-Prater (C_{WP}) was fluctuated from 0.04 to 0.084. For $dp = 940 \mu m$, C_M was fluctuated from 0.019 to 0.03 and C_{WP} was fluctuated from 0.316 to 0.582. At dp = 3950 μ m, C_M was fluctuated from 0.28 to 0.397 and C_{WP} was fluctuated from 16.6 to 30.7. It could be summarized that at $dp=316 \mu m$, the kinetic regime was operated on resistance free for mass transfer. All experiments were then performed at $dp=316 \mu m$ which assures the operation of HDS under intrinsic reaction according to Mears and Weisz-Prater criteria.

III. Influence of operating parameters on hydrodesulfurization efficiency

Effect of temperature

The effect of temperature on the desulfurization efficiency was investigated for dp= 316 micrometer at WHSV= 2.5 h^{-1} and under variable pressures (20, 25, 30, and 35 bar). Results are shown in Figures 6.



Figure 6: Variation of sulfur removal against temperature at different pressure (dp= 316 µm and WHSV=2.5 h⁻¹)

As temperature raised up from 320 - 380° C and at constant pressure = 35 bars, the conversion of increases from 89.0 93.9%, sulfur to positive The correspondingly. impact of temperature on sulfur conversion may be due to the specific rate constant (k_{HDS}) which relies on temperature as stated by Arrhenius equation. As can be seen from Figure 6, the sulfur removal increased when the temperature does not increased from 360°C to 380°C. This phenomenon of sulfur removal could be due to the equilibrium in chemical reaction which thermodynamically accomplished when temperature and pressure reached higher values.

Effect of pressure

According to Henry's law, the applied pressure on a gaseous mixture, in contact with a liquid, has positive impact on solubility of its components in the liquid. Thus, the weight fraction of dissolved H_2 in liquid phase would increase as the applied pressure in the reactor increased, HDS reaction catalyst surface rate onto increases correspondingly. At specific reaction temperature, a decrease in H₂ partial pressure may results in decrease of catalyst activity because of coke deposition over catalyst surface [22]. The effect of pressure on HDS efficiency was investigated for particle average diameter =316 µm at different temperature (320, 340, 360, and 380 °C) and WHSV =2.5 h^{-1} . As shown from Figure (7), when P increased from 20 to 35 bar and at temperature = 380° C, the HDS activity increased by 7.8%. Furthermore it can be seen from Figure (7), that at P = 35 bars and T was increasing from 320 to 340° C the HDS activity increased by 4%. However, as pressure increased from 30 to 35 bar and at constant temperature = 340 ° C the sulfur removal increased by 0.8% Meanwhile, at constant temperature = 320 °C as pressure increased from 30 to 35 bars the conversion of sulfur raised by 0.5%. These experimental results indicated that the temperature was more effective on HDS activity than pressure. Many investigators [23] stated that as middle distillate are processed with hydrogen gas at low pressure and high temperature, cobaltmolybdenum sulfided catalyst is much favorable through the direct extraction path. Furthermore, CoMo-S catalyst offer lower sulfur conversion via path hydrogenation under operating conditions of high pressure and low temperature. Generally, as the partial pressure of H₂ increased sulfur removal increases and the converse is correct [17, 24].



Figure 7: Influence of pressure on sulfur removal at WHSV=2.5 h⁻¹ and dp = 316 μm

Effect of space velocity

Figure 8 illustrates the effect of weight hour space velocity on sulfur removal for dp = 316 μ m under P = 30 bars and different temperatures. It is clear from Fig.8 that increasing WHSV from 2.5 h⁻¹ to 5.0 h⁻¹ reducing the sulfur removal from 93.9% to 89.4% at constant temperature and pressure 380 °C and 30 bar, respectively. Indeed, as shown in Figure 8, as the weight hourly space velocity reduced, residence time of reactants over the catalyst increases correspondingly, thus improve the conversion of sulfur by the different pathways of desulfurization mechanisms [25]. In addition, as WHSV decreased, sulfur accessibility to catalyst surface facilitated.



Figure 8: Variation of sulfur removal against WHSV at different temperature and (P=30 bar and diameter of particle=316 µm)

Influence of particle size

The influence of particle size on sulfur removal was studied at (T= 320, 340, 360 and 380 °C), P = 35 bars, and WHSV= 2.5 h⁻¹. It can be seen in Fig. 9 that as particle diameter increases from 316 to 3950 μ m at constant temperature = 380° C the removal of sulfur decreased from 93.9 to 87.4 %. This confirms a negative effect of particle diameter on removal of sulfur. This may be due to the resistance to mass transfer that increases as the size of particle increases.





Effect of operating time

Figure 10 plots the influence of operating time on conversion of sulfur (%) over CoMo-S/Al₂O₃ catalyst under optimized operating conditions to explore the efficiency of catalyst through a time of 5 hrs. Outlet stream was analyzed at a time increment of 15 minutes. As can be seen in Figure 10, after about hour and a quarter the sulfur removal approached 93.4% and approximately sticks on this value for the next three hours of operating time. This revealed that an equilibrium state is attained which is thermodynamically governed by temperature and pressure after 105 min of operation and the active sites remain stable under the optimum conditions. These results confirmed the applicability of the commercial CoMo/Al₂O₃ catalyst used in the present study.



Figure 10: Variation of sulfur removal (%) against operating time over the CoMo-S/Al₂O₃ catalyst under optimized operating conditions

5. Conclusion

In this research, sulfidation of metallic catalyst has been conducted using a liquid mixture of kerosene and dimethyl disulfide. Influence of the operating parameters on the activity of sulfur removal was investigated by regulating the temperature (320-380 °C), pressure (20 to 35 bars), weight hour space velocity (WHSV) (2.5 to 5.0 h^{-1}) and catalyst particle size (316 to 3950 um). Mears and Weisz-Prater criteria were used to validate the intrinsic reaction condition. Operating variables were optimized at to obtain a sulfur removal of 93.4% under intrinsic reaction conditions. Experimental results showed that percentage activity of sulfur removal increased up to 93.4% as temperature rose up to 360°C but declined to 88.8% as WHSV increased to 5.0 h⁻¹. The kinetics of the studied regime confirmed that the reaction kinetics is pseudo first order with respect to thiophene. Rate constants and activation energies of the intrinsic reaction rate were estimated at different operating conditions and compared with published data. Experimental outcomes indicated that activation energy and specific rate constant rise by 21.1 and 40.6% respectively as the pressure rose up from 20-35 bars. Operating time conducted on the sulfided catalyst confirmed the high catalytic activity of the selected commercial CoMo/Al₂O₃ catalyst.

Acknowledgments

Researchers are thankful to the School of Chemical Engineering, University of Technology for assistance in completion of this work. The fund which has been awarded by the PR&D Center is highly appreciated.

Nomenclature

BET: Brunauer-Emmett & Teller C_{bi} : weight content of species i in bulk (kg/m³) $C_{\rm H}$: concentrations of H₂ (kg H₂/ kg_{cat}) C_{H2S} : concentrations of H_2S (kg H_2S/kg_{cat}) C_M: Mears criterion Cs: weight content of thiophene onto catalyst (kg /kg_{cat}) Csi: weight content of i species over catalyst (kg/kg_{cat}) C_{WP}: Criterion of Weisz-Prater dp: average particle size (µm) Dei: effective diffusivity of component i (m^2/s) F_{i0} : weight flow of species i (kg/s) HDS: hydrodesulfurization ID: inside diameter of tube (mm) HP: high separator k: specific rate constant of reaction (h^{-1}) K_c: coefficient of mass transfer of fluid-particle (cm/s)

k_{HDS}: Specific rate constant included adsorption effects (h⁻¹) K': Specific rate constant per weight of catalyst particle $(m^3/kg.s)$ K_{H2} : constant of H2 adsorption, $(kg / kg_{cat})^{-1}$ K_{H2S} : constant of H2S adsorption, $(kg/kg_{cat})^{-1}$ K_s: constant of thiophene adsorption, $(kg/kg_{cat})^{-1}$ L-H: Langmuir-Hinshelwood m•: Inlet weight flow, (kg/h) n: kinetics order, (--) OD: outside diameter of tube (mm) PR&D: petroleum research and development r_{HDS}: rate of reaction of hydrodesulfurization (kg reaced/kg_{cat}.hr) rs: equivalent radius of catalyst pellet (m) S: sulfur Sf: Sulfur concentration in inlet stream (gm/gm) Sp: Sulfur concentration in effluent stream (gm/gm)T: temperature (Kelvin) UOT: University of Technology W: mass of catalyst (gm) x_s: conversion of sulfur compound

 τ : residence period (hr)

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