

Experimental Analysis of Diesel Hydrotreating Reactor to Development a Simplified Tool for Process Real- time Optimization

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Abstract—In this research, a systematic investigation was carried out to determine the optimum conditions of HDS reactor. Moreover, a suitable model was developed for a rigorous RTO (real time optimization) loop of HDS (Hydro desulfurization) process. A systematic experimental series was designed based on CCD (Central Composite design) and carried out in the related pilot plant to tune the develop model. The designed variables in the experiments were Temperature, LHSV and pressure. However, the hydrogen over fresh feed ratio was remained constant. The ranges of these variables were respectively equal to 320-380°C, 1-21/hr and 50-55 bar. a power law kinetic model was also developed for our further research in the future. The rate order and activation energy, power of reactant concentration and frequency factor of this model was respectively equal to 1.4, 92.66 kJ/mol and $k_0 = 2.7 \times 10^9$.

Keywords—Statistical model; Multiphase Reactors; Gas oil; Hydrodesulfurization; Optimization; Kinetics

I. INTRODUCTION

THE increasing competition in refinery industries, reducing refinery plant's costs, minimizing measurement errors and environmental issues lead to growing interest in modeling, simulation and optimization of refineries.

Real time optimization (RTO) of the process units is one of the most effective ways for enhancing economic performance and reducing overhead costs of chemical plants (fig.1).

This method has a fully automated system, which intelligently collects and processes main outputs of the plant. [1, 2]

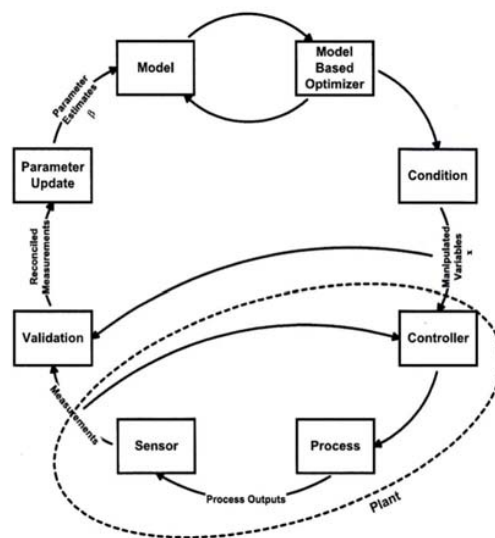


Fig. 1 Real time optimization loop

Modeling of a process is one of the vital steps in RTO (Real Time Optimization) loop and determination of the optimum conditions is very important for this purpose. In this article we studied upon the RTO model block and suitable model was developed for a rigorous RTO loop of HDS (Hydro desulfurization) process.

Presence of sulfur compounds in crude oil and heavy fractions is an undesirable issue. Sulfur compounds are one of the most important impurities in various petroleum fractions that cause many problems. For example, in the case of fuels they cause environmental pollution, and in the refining and petrochemical industries they poison catalysts. It can lead to corrosibility in oils and lubricants and poisonous emissions such as SO₂ and H₂S when the fuel is burned.

Several processes have been proposed to deal with the problem of removing these compounds. Hydrodesulfurization technique is very effective in sulfur removal from fuel oil, where the molecules that contain sulfur lose that atom by hydrogenation reactions.

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The sulfur containing components are converted to H₂S and Hydrocarbons in presence of Hydrogen on solid catalyst. Hydrodesulfurization process is mostly carried out in trickle bed reactors.

Sulfur is one of the pollutants in fossil fuels. It contents in crude oil which may be categorized in the following groups:

1. Free elemental sulfur
2. Mercaptans & tiols (R-SH)
3. Hydrogen sulfide
4. Sulfides
5. Disulfides (R-S-S-R')
6. Poly sulfides (R-Sn-R')
7. Thiophenes and their derivatives such as BT (benzothiophene) and DBT (dibenzothiophene)

With reference to recent investigations on hydrodesulfurization reactions, it can be understood that sulfur removal from mercaptans, sulfides and disulfides are easily done and free sulfur hydrocarbon and H₂S are produced as a result, while thiophenes and particularly benzothiophenic and dibenzothiophenic derivatives are difficult to desulfurize. But, if deep hydrodesulfurization of diesel fuel is concerned, removing benzothiophenic and dibenzothiophenic compounds is important. Most of industrial hydrodesulfurization methods are similar, and there are only minor differences in their details.

There have been reported many works on hydrodesulfurization. Song [3] reviewed both catalyst and process of desulfurization of fuels. Korsten and Hoffman [4] made a model for desulfurization of vacuum gas oil in a trickle bed reactor. They used Langmuir –Hinshelwood kinetics for rate equations. Yamada and Goto [5] compared counter - current and co-current operations for hydrodesulfurization.

Chowdhury et al. [6] expanded Korsten's models and applied it to desulfurization and dearomatization of the diesel oil. Inert particles were put on the catalyst to transfer hydrogen from gas to liquid. Dearomatization reaction and gas liquid mass transfer in nonactive zone were added to Korsten's model. Simulation results of desulfurization and dearomatization agreed with the experimental data.

Thiophenic components are known to be the most refractory organic sulfur-containing components. Rigorous kinetics for the hydrodesulfurization (HDS) of thiophene and benzothiophene has already been derived [7,8]. For dibenzothiophene, hydrodesulfurization rate equations have been reported by Broderic and Gates [9] and by Edvinsson and Irandoust [10]. Broderic and Gates [9] neglected the hydrogenation of biphenyl into cyclohexylbenzene, while Edvinsson and Irandoust [8] did not determine the influence of H₂S concentration on the reaction rates.

Recently kinetic modeling of hydrodesulfurization of oil fraction was introduced by Froment et al. [11]. Their work was proceeded by developing rate equations for all reactions in the network for the hydrodesulfurization of dibenzothiophene on the commercial CoMo/Al₂O₃ catalyst by Vanrysselberghe and Froment [12]

The proposed model is validated by the pilot data. Based on the reactor model, a hydrodesulfurization process is being simulated. In addition, a parametric sensitivity analysis on the process performance being put forward in order to estimate the optimum operating conditions for the HDS reactor and process.

In this research the ability and capability of a selected catalyst to remove sulfur from Gasoil feed is investigated. Consequently, some experiments are designed based on central composite design method. In the set of designed experiments, pressure, temperature and LHSV are considered as experimental parameters and the sulfur content of product is determined as a response variable. To clarify the maximum conversion of hydrodesulphurization reactions over the selected catalyst, a statistical model together with SQP (Sequential Quadratic Programming) optimization algorithm is used.

I. EXPERIMENTAL SECTIONS

A. Feed & Catalyst Characteristics

The Characteristics of used catalyst are listed in Table 1.

TABLE I THE CHARACTERISTICS OF SELECTED CATALYST

Specific Area(m ² /g)	200
Catalyst size(inch)	1.16
Catalyst shape	Cylindrical
Co content (mass %)	2.7
Mo content (mass %)	20-25
Al ₂ O ₃ (mass%)	60-80

Feedstock which is selected for HDS investigation is gasoil with the characteristics demonstrated in table 2. As it is shown the total sulfur of feedstock is 1.1 wt%, which is in the range of industrial feedstock for gasoil HDS unit.

TABLE II CHARACTERISTICS OF SELECTED GASOIL

Specification	Value
Feed:	
Total.SULPHUR	1.1wt%
SP.GR@60F	0.865
IBP	158 °c
5 vol. %	242 °c
10vol. %	254 °c
20 vol. %	266 °c
30 vol. %	275 °c
40vol. %	283 °c
50 vol. %	292 °c
90vol. %	349 °c
95vol. %	360 °c
FBP	361 °c

B. Operating Conditions

The LHSV, reactor temperature and pressure were determined as the experimental variables. The ranges of these variable were, respectively equal to 1-2l/hr, 320-380°C and 50-55 bar.

II. PILOT PLANT SETUP

The experiments have been carried out in a pilot plant that was designed and assembled to perform HDS experiments at high pressure. The reactor of this pilot plant is a 400 cm³ vessel which can operate at pressure less than 55 bar. Figure (2) demonstrates the schematic process flow diagram (PFD) of this pilot. As it is shown in this figure, the feed and hydrogen are mixed with a certain ratio before flowing into the reactor. The mixed feed enters to the reactor with definite pressure to achieve a predetermined temperature for performing the HDS reactions.

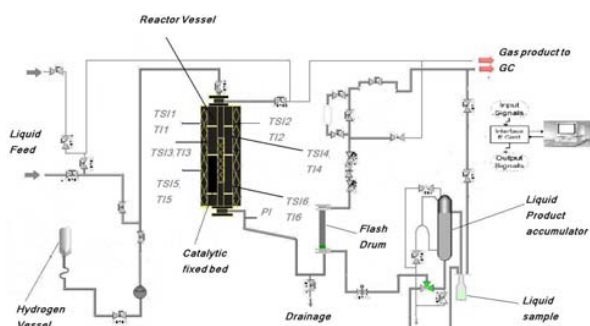


Fig. 2 Schematic process flow diagram of HDS pilot plant

There are twelve thermocouples along the reactor for determining the skin and the inside reactor temperature. Six thermocouples are specified to determine the skin temperature and the others are for inside reactor temperature (In figure 2, TSI's refer to Skin temperature indicator and TI's refer to inside reactor temperature indicator). A quarter of total reactor volume (100 cm³) which is located in the middle of reactor vessel is specified for catalytic fixed bed. This is normally operated at isothermal conditions. The reactor product stream is fed to a flash drum to separate gas and liquid products. The liquid product is accumulated in a drum and the gas product is transferred for online analysis to determine the H₂S and H₂ content of stream.

In addition to feed preparation, the catalyst should be presulfided before using it with actual feed. Presulfiding of catalyst is done by dimethyl disulfide (DMDS), which is added to the Isomax gas oil, and circulated through the reactor bed.

This is performed to strengthen the activity and selectivity of catalyst. To execute the procedure, an inert gas followed by a pure H₂ stream is fed to the reactor. Then the reactor temperature is raised to a certain value. At the end, the H₂ gas stream contaminated with H₂S (2-5 mol %) or liquid streams like Carbon sulfide, Dimethyl sulfide or Dimethyl disulfide

which can lose their sulfur species more easily is injected to the reactor.

Presulfiding procedure was followed by a set of experiments which was carried out to investigate the reproducibility of pilot plant setup and to find out a suitable procedure for carrying out the main set of experiments. The liquid samples were analyzed by Raney nickel method to determine the total sulfur content. The results elucidated that for improvement of reproducibility of experimental results, twelve hours should pass to attain steady state of pilot plant system. By passing each six hours the liquid sample is collected to analyze. The average total sulfur content for each experiment is calculated by averaging the set of results which are attained during the experiment. By passing one day the operating condition can be changed to carry out another experiment.

III. STATISTICAL DESIGN OF EXPERIMENTS

A Central Composite Design [13, 14] was applied with three design factors: the Feed Flow rate (gr/hr)(X₁), Temperature (°C)(X₂) and Pressure (bar) (X₃). The coded levels and the natural value of mentioned factors are shown in Table 3. The sulfur content of product is considered as response variable.

TABLE III CODED LEVEL AND NATURAL VALUE OF DESIGN FACTOR

Design Factor	-1.68	-1	0	1	1.68
X ₁ :Flow rate(gr/hr)	106.36	120	150	180	194
X ₂ :Temperature(°C)	335	341	351	361	367
X ₃ :Pressure(bar)	46.8	48	50	52	53.2

The number of trials which is based on the number of design factors is equal to 20 experiments (15 combinations with 3 replications). The following full quadratic model was obtained by a multiple regression technique for three factors (Table 3). In order to calculate the coefficients of the model, MINITAB software (Release 13.2) has been used:

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

The result of experiments and the design matrix are shown in Table 4. In Table 5 the significance of different factors and their interactions, the related coefficients, the ANOVA results for lack-of-fit and the results of R-squared tests have been shown. The derived coefficients which are demonstrated in Table 5 are adapted to equation (1) and show the general form of a quadratic equation.

P-value column in Table 5 demonstrates crucial parameter in statistical analysis aspect. Regarding to statistical concepts [14], the effects of parameters with a p-value was higher than 0.05 were insignificant. Therefore, they could be discarded with the confidence level of 95%. The lack-of-fit test was used to determine whether or not the constructed model was appropriate to describe the observed data. When the p-value for the lack-of-fit is less than 0.05, there is a statistically significant lack-of-fit at the 95% confidence level, which means that the model does not adequately represent the data.

TABLE IV DESIGN MATRIX AND RESULTS OF EXPERIMENTS

Rec	1	2	3	4	5	6	7	8	9
Feed Flow (cc/hr)	-1	-1	1	1	-1	-1	1	1	0
T (°C)	-1	-1	-1	-1	1	1	1	1	-1.68
P (bar)	-1	1	-1	1	-1	1	-1	1	0
Sulfur Content (ppm)	68	81	170	200	38	55	67	62	180

Rec	10	11	12	13	14	15	16	17	18
Feed Flow (cc/hr)	0	-1.68	1.68	0	0	0	0	0	0
T (°C)	1.68	0	0	0	0	0	0	0	0
P (bar)	0	0	0	-1.68	1.68	0	0	0	0
Sulfur Content (ppm)	39	17	130	44	55	38	41	47	45

The R-squared statistic indicates the variability percentage of the optimization parameter explained by the model [12-14]. The "T" column in Table 5 demonstrates the t-value for each factor which generally measures the difference between an observed statistic and its hypothesized population parameter in units of standard error [14].

TABLE V TEST OF SIGNIFICANCE OF FACTORS AND INTERACTIONS FOR MODELS OF SELECTED PARAMETERS, R-SQUARED AND LACK-OF-FIT

Fraction or Interaction	Output Sulfur Content		
	Coefficient	T	P-Value
Constant	25905	2.207	0.052
X1	29.1	3.143	0.01
X2	-154.6	-2.80	0.019
X3	-11.7	-0.066	0.948
X1*X1	0	0.397	0.7
X2*X2	0.2	3.231	0.009
X3*X3	0.9	0.626	0.545
X1*X2	-0.1	-3.965	0.003
X1*X3	-0.0	-0.087	0.932
X2*X3	-0.2	-0.671	0.517
R-Squared	94.73%		
P-Value of Lack-of-fit	0.565		

The most significant parameters in table 5 are X1(feed flow rate), X2(temperature), X1*X2 (interaction of feed flow rate and temperature) and X2*X2 (square temperature).

To examine the precision of developed statistical models, a kinetic model was also developed. It is based on Arrhenius

kinetics which has the general form as follow: [18]

$$r_A = -kC_A^n \quad (2)$$

In order to solve the above equation for the discussed pilot reactor, a plug flow patterns was assumed and an integral model was developed. An optimization algorithm was utilized to determine the constants of the above rate. Table 6 demonstrates the amount of rate constants.

TABLE VI RATE CONSTANTS

n	E(kJ/mol)	k ₀
1.4	92.66	2.7*10 ⁹

IV. RESULTS AND DISCUSSION

The surface and contours of the sulfur content of product were sketched according to the developed statistical model and are shown in figures 2 to 4. The effects of feed flow rate and pressure are demonstrated in figure 3. As it is shown, an increase in feed flow rate at constant pressure results in an increase in sulfur content of product. On the other hand, increasing the pressure at constant feed flow makes varied trend. At first, increasing the pressure decreases the sulfur content of product. But, applying more pressure raises the sulfur content of product. However, increasing both feed flow rate and pressure simultaneously at constant temperature increase the sulfur content of product. In this figure, the minimum sulfur content is obtained at the minimum allowable feed flow rate and at approximate average operating pressure. Moreover, this trend can be observed in table 4 too. Experiments 11 and 12 have the same temperature and pressure but with different feed flow rate. The results show that with increasing feed flow rate from -1.6818 in coded levels to 1.6818, the sulfur content is raised from 17 ppm to 130 ppm. But in experiment 15 where the feed flow rate changes to level 0 (in comparison with experiments 11 and 12), the sulfur content reaches to 38 ppm. The effect of pressure among the operating domain can also be observed by the comparison between experiments 13, 14 and 15. It is clear that a change in pressure from -1.6818 in coded levels to 1.6818 increases the sulfur content from 44 ppm to 55 ppm. However, changing the pressure to level 0 reduces the sulfur content to 38 ppm which is in minimum level in comparison with experiments 13 and 14.

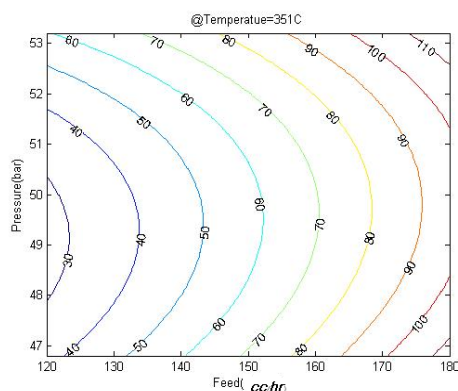
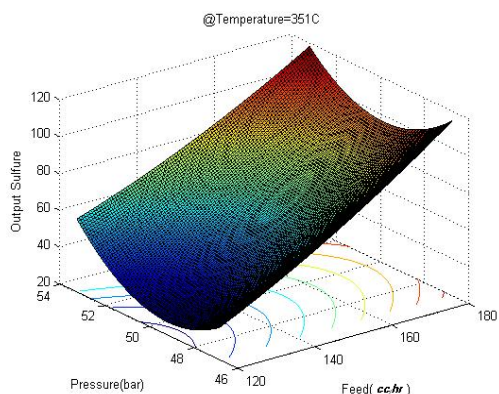


Fig. 3 Effects of feed flow rate and pressure on sulfur content of product at temperature=351°C

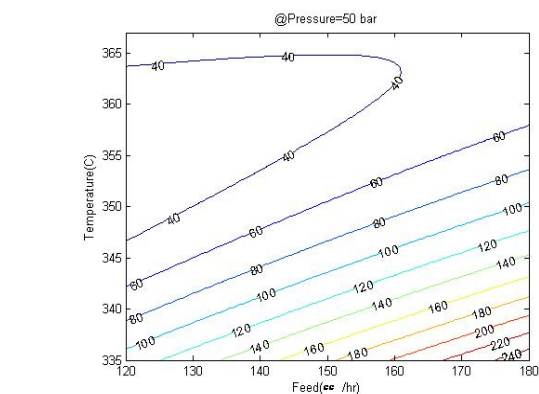
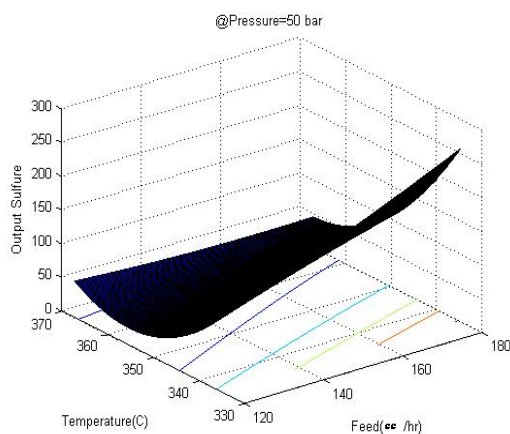
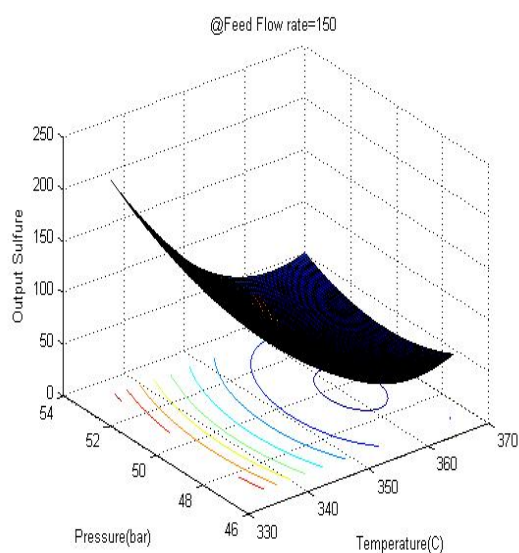


Fig. 4 Effects of temperature and feed flow rate on sulfur content of product at pressure=50 bar

The effects of temperature and feed flow rate are shown in figure 4. As it is shown, raising the feed flow rate at constant temperature increases the sulfur content of product. However, increasing the temperature at constant feed flow rate and pressure divides the surface into two different regions. In the first region (with a borderline which is approximately begun at 355°C and 120 cc/hr and ended to 365°C and 180 cc/hr), an increase in temperature results in a decrease in sulfur content of product. On the contrary, having higher temperature in the second region increases the sulfur content of product. Moreover, table 4 is approved of the fact which is demonstrated in figure 4. The Comparison among experiments number 11, 12 and 15 expresses that growth in feed flow rate from -1.68 in coded levels to 1.68 at steady pressure and temperature surges the sulfur content from 17 ppm to 130 ppm, but a decrease in feed flow rate from 1.6818 to 0 in coded level dipped the sulfur content to 38 ppm.



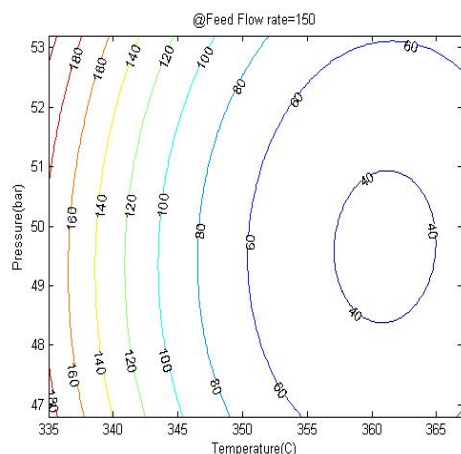


Fig. 5 Effects of pressure and temperature on sulfur content of product at feed flow rate=150 cc/hr.

Figure 5, demonstrates the effects of temperature and pressure on sulfur content of product. As it is revealed, in case of steady feed flow rate and temperature a rise in pressure plunges the sulfur content of product at first, but further more an increase in pressure causes the sulfur content to soar gradually. On the other hand, a rise in temperature with constant pressure plummeted the sulfur content of product to less than 40 ppm followed by a gradual increase to higher levels. In addition, the variation of response variable has the same trend if equal growth happens in temperature and pressure.

Every trend of the contour lines and surfaces can be interpreted with regard to the nature of hydrodesulfurization reactions of different oil cuts. The main parameters which can directly affect the conversion of the hydrodesulfurization reaction network are temperature, residence time and mass transfer [15-17]. As the residence time prolongs, reactions have more times for evolution so the conversion improves. Feed flow rate relates to the residence time directly. If the feed flow rate is decreased, the residence time rises as well and if it falls the residence time soars. Moreover, temperature has positive effects on the reaction rates. Increasing the temperature in a definite span raises the hydrodesulfurization reaction rates [16]. But, more growth increases other reaction rates as hydrocrackings which limit the reaction rate of hydrodesulfurization and consequently decreases the HDS conversion. These can interpret the phenomenon which is demonstrated in figure 3. On the other hand, the growth in pressure could increase the concentration of hydrogen and H₂S in liquid phase near the catalyst surfaces. In the high pressure spans, it can weaken the mass transfer rate of sulfuric species. Consequently, these species concentration are declined near the catalyst surface so the Hydrodesulfurization rates are dipped. This can interpret the effects of pressure which are demonstrated in figures 2 and 4.

Determination of the optimum conditions is one of the vital challenges in chemical processes. Regarding to optimization

goal, it can be carried out for maximization of the process benefit or minimization of a definite variable. In this research, the optimization is utilized for minimization of sulfur content of product. The SQP optimization algorithm was applied to determine the optimum point. Table 6 demonstrates the optimum conditions which are calculated by the optimization algorithm. The optimization is carried out in the range of operating conditions which is clarified in Table 3.

TABLE VI OPTIMUM OPERATING CONDITION FOR MINIMIZATION OF PRODUCT SULFUR CONTENT

Temperature(°C)	Pressure(bar)	LHSV(1/hr)	sulfur content(ppm)
355	49.2	1.2	23.65

As it can be seen in the table 6, optimum feed flow rate is at minimum allowable value in the operating span. On the other hand, the optimum pressure and temperature are placed within the permitted zone. This is due to the effects of different variables which are discussed above.

V. CONCLUSION

Based on central composite design method, 18 experiments (15 experiments combined with three replications) were designed to determine the effects of pressure, temperature and feed flow rate and their interactions on the sulfur removal in HDS reactor. A quadratic statistical model was developed and evaluated. The results of experiments and statistical model were analyzed by some statistical tests to determine the significance of parameters and their interactions. Regarding to the results, the flow rate, temperature and the interaction of these two parameters are the most significant factors in the HDS reactor. The surfaces and contours which are sketched from the model results show the effects of different variables in the response surface. As it is shown, raising the feed flow rate decreases the residence time in reactor, so it dips the conversion of hydrodesulfurization reactions. Also, temperature growth surges the reaction rates which makes the conversion of HDS reactions increase in definite span. Having more temperature accelerates the hydro cracking reaction rates so the conversion of sulfur removal is dipped.

For better investigation of response surface of sulfur content of product, an optimization is carried out to determine the optimum operating condition to achieve maximum conversion of sulfur removal reactions. At the optimum conditions, temperature, pressure and LHSV for the selected catalyst are respectively equal to 355°C, 49.2 bars and 1.2 1/hr.

The obtained experimental and modeling results can be used for development of a kinetic model for HDS reactions.

The results of this research reveal that statistical models have good accuracy in the ranges of operating conditions which are validated. To accelerate the convergence of the model in RTO loop, we will use the statistical model in ordinary operating conditions and in startup and shutdown conditions we use kinetic based model.

To predict the output sulfur content and the conversion of catalyst, some statistical models were tuned based on the

results of conducted experiments. The models were evaluated with lack of fit and residual tests. The results prove that the model fitted well with experimental results.

Utilizing an optimization tool shows that for $n=1.4$, $E=92.66$ kJ/mol and $k_0=2.7 \times 10^9$ minimum model error from experimental data was obtained.

The results of this research reveal that statistical models have good accuracy in the ranges of operating conditions which are validated. To accelerate the convergence of the model in RTO loop, we will use the statistical model in ordinary operating conditions and in startup and shutdown conditions we use kinetic based model.

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NOMENCLATURE

X1: Experimental design parameter (Feed flow rate (cc/hr))

X2: Experimental design parameter (Temperature (°C))

X3: Experimental design parameter (Pressure (bar))

α : Constant coefficient for quadratic statistical model

β_i : Coefficient for quadratic statistical model

REFERENCES

- [1] Forbes, J. F., & Marlin, T. E. "Design cost: a systematic approach to technology selection for model-based real-time optimization systems" *Computers and Chemical Engineering*, 20 (6/7), 717 (1996).
- [2] Yale Zhang, Dayadeep Monder, J. Fraser Forbes" Real-time optimization under parametric uncertainty: a probability constrained approach" *Journal of Process Control* 12, 373–389, (2002).
- [3] Song, C., "An overview of new Approaches to Deep Desulfurization for Ultra-Clean Gasoline, Diesel Fuel and Jet Fuel", *Catal. Today*, 86, 211(2003).
- [4] Hans. Korsten, U.Hoffmann "Three – Phase Reactor Model for Hydrotreating in Pilot Trickle – Bed Reactors" *AIChE. J.*, Vol, 42, No.5, May (1996).
- [5] H.Yamata, Sh.Goto"Advantages of Counter-Current Operation for Hydrodesulfurization in Trickle bed Reactors" *Korean J.Chem.Eng.* 21 (4), 773-776(2004).
- [6] Chowdhury, R., Pedernera, E. and Reimert, R., "Trickle Bed Reactor Model For Desulfurization and Dearomatization of Diesel," *AIChE J.*, 48, 126(2002).
- [7] Van Parys, I.A.; Froment, G.F. Kinetics of Hydrodesulfurization on a γ -Al₂O₃ catalyst. 1. Kinetics of the Hydrogenolysis of Thiophene." *Ind Eng. Chem. Prod. Res. Dev.* 25, 431, (1986).
- [8] Van Parys, I.A.; Hosten, L.H.; Froment, G.F. "Kinetics of Hydrodesulfurization on a γ -Al₂O₃ catalyst. 2. Kinetics of the Hydrogenolysis of Benzothiophene" *Ind Eng. Chem. Prod. Res. Dev.* 25, 437, (1986).
- [9] Broderick, D.H.; Gates, B.C. "Hydrogenolysis and hydrogenation of Dibenzothiophene Catalyzed by Sulfided CoO-MoO₃/ γ -Al₂O₃: The Reaction Kinetics". *AIChE J.* 27, 663, (1981).
- [10] Edvisson, R.; Irandost, S. "Hydrodesulfurization of dibenzothiophene in a Monolithic Catalyst Reactor." *Ind. Eng. Chem. Res.* 32, 391, (1993).
- [11] Gilbert, F. Froment, Guy A. Depauw, V. Vanrysselberghe "Kinetic modeling and reactor simulation in hydrodesulfurization of oil fractions." *Ind. Eng. Chem. Res.* 33, P.2975 – 2988 (1994).
- [12] V. Vanrysselberghe, G.F. Froment. "Hydrodesulfurization of dibenzothiophene on a CoMo/Al₂O₃ catalyst: reaction network and kinetics." *Ind. Eng. Chem. Res.* 3, 3311-3318, (1996).
- [13] Dimitrios G. Avraam, Iacovos A. Vasalos "HdPro: a mathematical model of trickle – bed reactors for the catalytic hydroprocessing of oil feedstocks" *Catalysis Today* 79-80; 275-283; (2003).
- [14] V. Vanrysselberghe, G.F. Froment "Kinetic Modeling of Hydrodesulfurization of oil fractions: Light cycle oil". *Ind. Eng. Chem. Res.* 37, 4231 – 4240, (1998).
- [15] 12. S.Z. Abghari, J. Towfighi, R. Karimzadeh, M. Omidkhan, *Scientia Iranica*, 15(4), 1112 (2008).
- [16] 13. L. Davies, *Efficiency in Research Development, and Production: The Statistical Design and Analysis of Chemical Experiments*, the Royal Society of Chemistry (1993).
- [17] S. Zahedi. Abghari, J. Towfighi, R. Karimzadeh, M. Omidkhan, "Application of Response Surface Methodology in Study of the Product Yield Distribution of Thermal Cracking of Atmospheric Gasoil", *Scientia Iranica* vol. 15, Nov. 4, pp1123-1135 (2008).
- [18] D. Ferdous, A. K. Dalai, and J. Adjaye; Hydrodenitrogenation and Hydrodesulfurization of Heavy Gas Oil Using NiMo/Al₂O₃ Catalyst Containing Boron: Experimental and Kinetic Studies. *Ind. Eng. Chem. Res.* 2006, 45, 544.
- [19] Botchewey, C.; Dalai, A. K.; Adjaye, J. Two-Stage Hydrotreating of Athabasca Heavy gas Oil with Interstage Hydrogen sulphide Removal: Effect of Process Conditions and Kinetic Analysis. *Ind. Eng. Chem. Res.* 2004, 43, 5854.
- [20] Yao Wang, Kinetics of Hydrodesulfurization of Dibenzothiophene catalyzed by sulfided Co-Mo/MCM-41, *Ind. Eng. Chem. Res.*, 2004, 43, 2324.