Analysis of sulfur removal in gasoil hydrodesulfurization process by application of response surface methodology

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Abstract−To investigate the efficiency of a Co-Mo catalyst in HDS process, a set of experiments were designed and carried out based on central composite design (CCD) methodology in an HDS pilot plant. The designed variables included temperature, LHSV and pressure. However, the hydrogen over fresh feed ratio remained constant. The ranges of these variables were, respectively, equal to 335-361 °C, 1.06-1.8 1/hr and 46.8-53.2 bar. The outcomes of experiments were employed to determine the coefficients of statistical models. For the clarification of the accuracy of the model, several statistical tests like ANOVA (Analysis of Variance), Lack-of-Fit test and residual squares were carried out. To optimize the operating conditions to achieve maximum sulfur removal, an optimization algorithm was employed. The outcomes revealed that the minimum sulfur content, which is 23.65 ppm in the final product, is attained at 355 °C, 1.2 1/hr and 49.2 bar.

Key words: HDS, Experimental Design, CCD, Catalyst, Sulfur Removal, Gasoil, Optimization

INTRODUCTION

The hydrodesulfurization (HDS) of oil cuts containing sulfur is one of the vital catalytic units in refinery complexes. They become more crucial by strict official rules concerning the environment which are approved and run in different countries. The main focus is on reducing sulfur, nitrogen and metal components in fuels which can be performed in hydro treating units. Obviously, HDS units are hydrotreating units which are used for sulfur reduction.

Most HDS units employ fixed bed reactors with high active catalysts (which in most cases are Co-Mo/Al$_2$O$_3$ catalysts). Hence, enhancements in HDS technology have focused on developing high active catalyst and also designing an advanced reactor for multiple bed systems [1,2]. Where the main mass-transfer resistance is placed is subject to two kinds of three phase catalytic fixed beds. The first is the trickle bed reactor which has a continuous gas phase and distributed liquid phase, and the second is bubble bed reactors with distributed gas and a continuous liquid phase. Due to various advantages, the trickle bed reactors are widely used in large-scale units [3].

Since the sulfur removal reactions are strongly limited by competitive adsorption of H$_2$S at active sulfided sites of catalysts, the trickle beds of commercial HDS reactors are usually designed to have concurrent downward flow of gas and liquid over a randomly filled fixed bed catalytic reactor [4].

Due to the great importance of HDS units, different researchers have concentrated on various aspects of this process [5-11]. As kinetic and conversion determination studies, Feredous et al. [5] studied

the hydrodenitrogenation and hydrodesulfurization of heavy gasoil derived from bitumen by employing NiMo/Al$_2$O$_3$ catalyst containing boron (B). In the research, temperature, pressure and liquid hourly space velocity (LHSV) were considered as experimental variables. An experimental design methodology was used to design proper set of experiments and also statistical tests were used for analyzing the accuracy of experiments. They also determined sets of kinetics for HDS and HDN reactions at the presence of the selected catalyst. HDS reactions of different sulfuric species were studied by different researchers [6-9]. The hydrodesulfurization reactions of 4,6-Dimethylbenzo thiophene were studied by Fanga et al. [6]. The HDS reactions of this species were carried out in the presence of Mo/γ-Al$_2$O$_3$ and NiMo/γ-Al$_2$O$_3$. The investigation results revealed that the hydrogenation step of dimethylbenzothiophene is the slowest step over the selected catalysts. Kabe et al. [7] studied the HDS of benzothiophene (BT) and dihydrobenzothiohene (DHBT) over Mo/γ-Al$_2$O$_3$. Also, different steps of reactions as hydrogenation and hydrogenolysis of these species were determined. Moreover, the effects of the presence and the absence of H2S on hydrodesulfurization of species were investigated. The hydrodesulfurization rate equation of dibenzothiophene as the only sulfuric component in a model feed has been reported by Broderick and Gates [8] and by Edvinsson and Irandoust [9]. Broderick et al. [8] neglected the hydrogenation of biphenyl into cyclohexylbenzene. Also, Edvinsson and Irandoust [9] did not determine the influence of H$_2$S concentration on the reaction rates.

On the other hand, the flow pattern and specification of trickle beds were studied by other researchers too [10,11]. Gunjal et al. [10] focused on CFD modeling of laboratory and commercial scale of trickle bed reactors to design a satisfactory model for the study of flow patterns in these reactors. Nigam et al. [11] focused on the

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trickle bed reactors to intensify the HDS process units innovatively. They determined that improvement of liquid distribution and wetting efficiency by cycling liquid feed could be beneficial for improvement of the efficiency of trickle bed reactors.

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.

EXPERIMENTAL

1. Characteristics of Selected Catalyst and Feedstock

The selected catalyst is Co-Mo hydrodesulfurization catalyst which is provided by Bandar Abbas refinery complex. The catalyst has the characteristics which are demonstrated in Table 1.
Feedstock which is selected for HDS investigation is gasoil with

Table 1. Characteristics of selected catalyst

Chemical composition, wt% dry basis	
Cobalt	3.4
Molybdenum	13.6
Physical properties	
Surface area, m²/gr	235
Pore volume, cc/gr (H_2O)	0.53
Flat plate crush strength, N/cm (lb/mm)	200
Attrition index	99
Compacted bulk density, g/cc	0.72 (45)

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.

2. Pilot Plant Setup

The experiments were performed 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 that 55 bar. Fig. 1 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.

There are twelve thermocouples along the reactor for determin-

Table 2. Characteristics of selected gasoil

	Temperature (ºC)	Fraction (volume%)
Distillation curve	158	0
	242	5
	254	10
	266	20
	275	30
	283	40
	292	50
	349	90
	360	95
	361	100
Specific gravity (gr/cm³)		0.865
Total sulfur (ppm)		11000

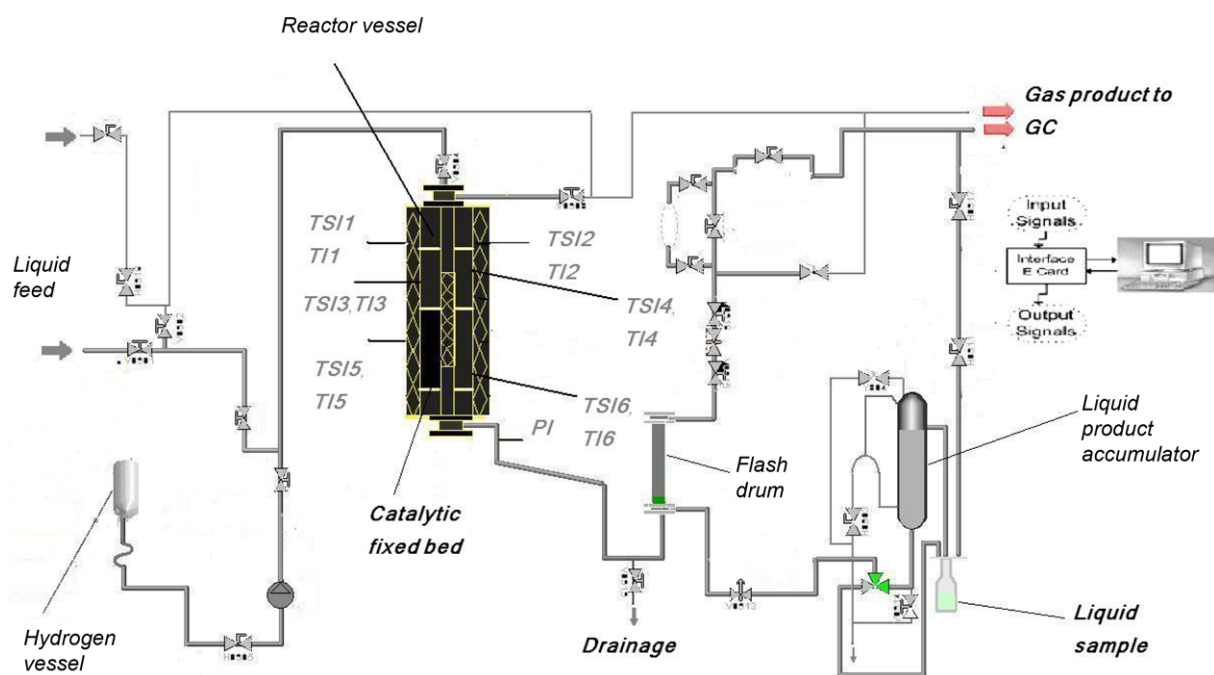**Fig. 1. Schematic process flow diagram of HDS pilot plant.**

Table 3. Coded level and natural value of design factor

Design factor	−1.6818	−1	0	1	1.6818
X1: Flow rate (gr/hr)	106.36	120	150	180	194
X2: Temperature (°C)	335	341	351	361	367
X3: Pressure (bar)	46.8	48	50	52	53.2

ing 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 Fig. 1, TSI's refer to skin temperature indicator and TI's refer to inside reactor temperature indicator). A quarter of the total reactor volume (100 cm^3) 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 H_2S and H_2 content of stream.

Before the main experiments, after the catalytic bed is filled with catalyst, a presulfiding procedure is carried out to strengthen the activity and selectivity of catalyst. To execute the procedure, an inert gas followed by a pure H_2 stream is fed to the reactor. Then the reactor temperature is raised to a certain value. At the end, the H_2 gas stream contaminated with H_2S (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 carried out to investigate the reproducibility of pilot plant setup and to find 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 showed 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.

STATISTICAL DESIGN OF EXPERIMENTS

A central composite design [12,13] was applied with three design factors: the feed flow rate (gr/hr)(X_1), temperature (°C)(X_2) and pressure (bar)(X_3). 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.

The number of trials, which is based on the number of design factors, is equal to 18 experiments (15 combinations with 3 replications). The following full quadratic model was obtained by a multi-

Table 5. 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
X1xX1	0	0.397	0.7
X2xX2	0.2	3.231	0.009
X3xX3	0.9	0.626	0.545
X1xX2	−0.1	−3.965	0.003
X1xX3	−0.0	−0.087	0.932
X2xX3	−0.2	−0.671	0.517
R-squared	94.73%		
P-value of lack-of-fit	0.565		

ple regression technique for three factors (Table 3). To calculate the coefficients of the model, MINITAB software (Release 13.2) was used:

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

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 are shown. The derived coefficients which are demonstrated in Table 5 are adapted to Eq. (1) and show the general form of a quadratic equation.

The P-value column in Table 5 demonstrates the crucial parameters in statistical analysis aspect. Regarding statistical concepts [14], the effects of parameters with a p-value 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.

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].

The most significant parameters in Table 5 are X1 (feed flow rate), X2 (temperature), X1xX2 (interaction of feed flow rate and temperature) and X2xX2 (square temperature).

Table 4. Design matrix and results of experiments

Rec	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Feed flow (cc/hr)	−1	−1	1	1	−1	−1	1	1	0	0	−1.682	1.6818	0	0	0	0	0	0
T (°C)	−1	−1	−1	−1	1	1	1	1	−1.6818	1.6818	0	0	0	0	0	0	0	0
P (bar)	−1	1	−1	1	−1	1	−1	1	0	0	0	0	−1.6818	1.6818	0	0	0	0
Sulfur content (ppm)	68	81	170	200	38	55	67	62	180	39	17	130	44	55	38	41	47	45

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 Figs. 2 to 4. The effects of feed flow rate and pressure are demonstrated in Fig. 2. As shown, an increase in feed flow rate at constant pressure results in an increase in sulfur content of the product. On the other hand, increasing the pressure at constant feed flow makes a varied trend. At first, increasing the pressure decreases the sulfur content of the product. But, applying more pressure raises the sulfur content. However, increasing both feed flow rate and pressure simultaneously at constant temperature increases the sulfur content of the 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.

The effects of temperature and feed flow rate are shown in Fig. 3. As shown, raising the feed flow rate at constant temperature increases the sulfur content of the 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
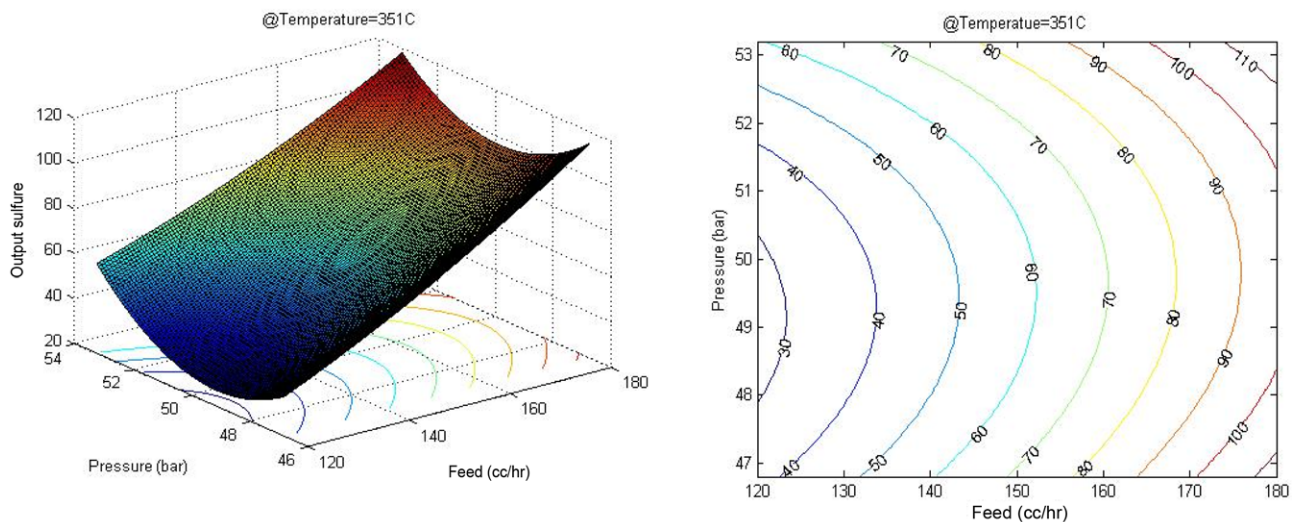

Fig. 2. Effects of feed flow rate and pressure on sulfur content of product at temperature=351 ºC.
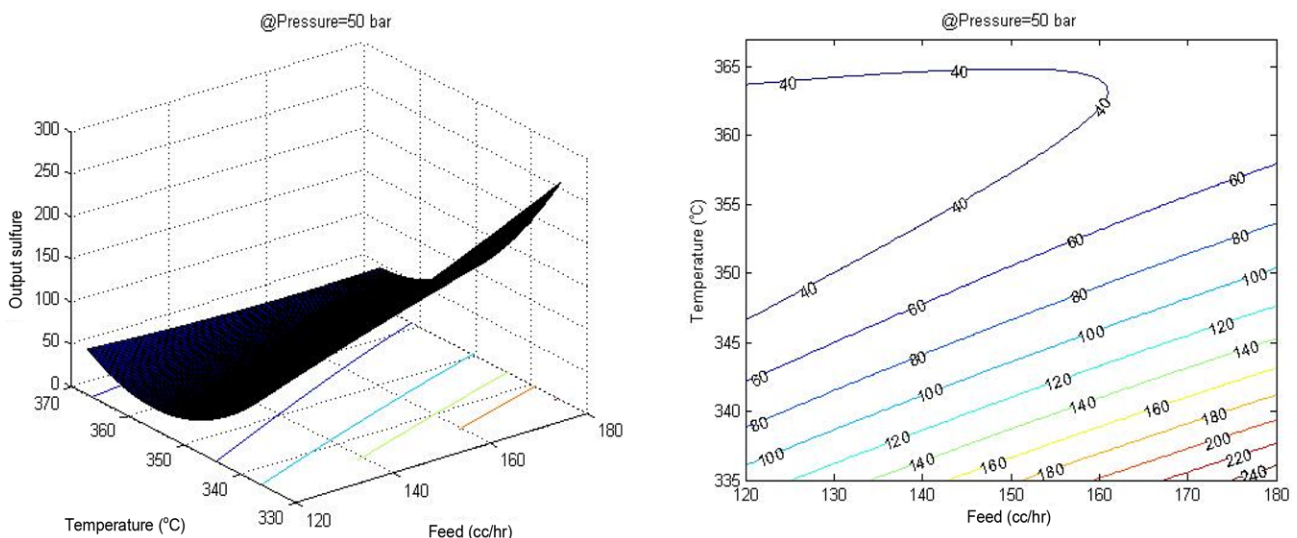

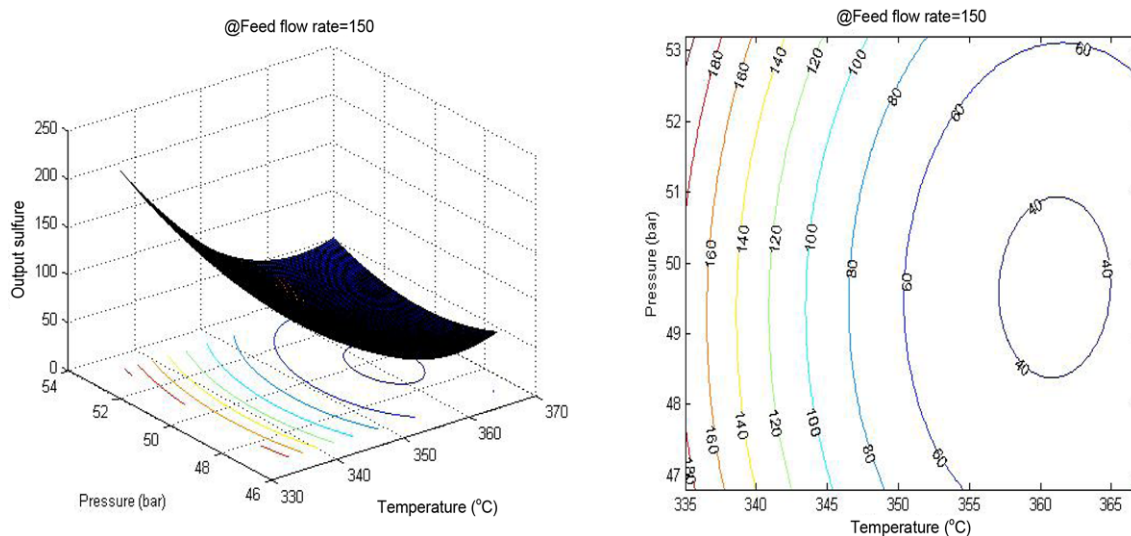Fig. 3. Effects of temperature and feed flow rate on sulfur content of product at pressure=50 bar.

Fig. 4. Effects of pressure and temperature on sulfur content of product at feed flow rate=150 cc/h.

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. Moreover, Table 4 is approved of the fact which is demonstrated in Fig. 3. The comparison among experiments number 11, 12 and 15 expresses that growth in feed flow rate from −1.6818 in coded levels to 1.6818 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. 4 demonstrates the effects of temperature and pressure on sulfur content of product. As it is revealed, for a steady feed flow rate and temperature a rise in pressure plunges the sulfur content of product at first, but furthermore an increase in pressure causes the sulfur content to soar gradually. On the other hand, a rise in temperature with constant pressure decreases 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 is prolonged, 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 limits the reaction rate of hydrodesulfurization and consequently decreases the HDS conversion. These can interpret the phenomenon which is demonstrated in Fig. 3. On the other hand, the growth in pressure could increase the concentration of hydrogen and H_2S 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 concentrations are declined

Table 6. 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

near the catalyst surface so the hydrodesulfurization rates are dipped. This can explain the effects of pressure which are demonstrated in Figs. 2 and 4.

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

As can be seen in Table 6, the 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.

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 an 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 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 the reactor, so it lowers 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 hydrocracking reaction rates so the conversion of sulfur removal dips.

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 bar and 1.2 1/hr.

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

ACKNOWLEDGEMENT

NOMENCLATURE

X_1 : experimental design parameter (feed flow rate (cc/hr))
X_2 : experimental design parameter (temperature (°C))
X_3 : experimental design parameter (pressure (bar))
α : constant coefficient for quadratic statistical model
β_i : coefficient for quadratic statistical model

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