

Hydrodesulfurization of gas condensate containing di-sulfide oil: Catalyst synthesis and evaluation

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Hydrodesulfurization
(HDS).

Abstract

In this research, a catalyst based on design parameters of molybdenum percentage, Co/Mo and Urea/Co ratios by applying the Response Surface Methodology (RSM) was synthesized, characterized and optimized for the Hydrodesulfurization (HDS) process. The catalyst decreased sulfur content in the gas condensate from 2200 to 19 ppm wt. Then, various operating conditions such as temperature range of 320-340°C, reactor pressure range of 30-40 barg, Liquid Hourly Space Velocity (LHSV) range of 2-3h⁻¹ and H₂/Oil ratio range of 150-250 ml/ml were applied. Finally, the sulfur content in the gas condensate was found at 8 ppm wt. (<10 ppm wt.) at the optimum operating conditions when the synthesized catalyst with characteristics of 18% MoO₃, Co/Mo molar ratio of 0.48 and Urea/Co volume ratio of 5 was used.

1. Introduction

Sulfur is as a major impure component in crude oil and its derivatives. It may form in the various sulfur types. These are responsible for a lot of environmental problems [1,2]. The amount of sulfur in crude oil generally depends on its source. This usually varies from 0.025 to 7.89 weight percent. Burning of fossil fuels produces the sulfur oxide compounds which their emission should strictly be controlled due to the environmental regulations [3-5]. Because Novaes et al. [6] scrutinized global crude oil production has increased around 12–13 million barrels from 2008 to 2017. So hence it's a great challenge to derive facile rate laws and in recent years, extensive research has been done in this regard by many researches including Wu et al. [7]. As the sulfur content of diesel fuel in the Euro-V emission standard is limited to less than 10 ppm [8,9].

There are various methods for desulfurization of crude oil and its derivatives [10-15]. Although Tanimu and Albooshani

[15] generally reviewed the Hydrodesulfurization (HDS) process which is the most efficient commercial technique but, the other researchers focused on the Co (Ni) Mo/Al₂O₃ as catalyst for the HDS process [16-19]. In fact, the HDS is a reaction between sulfur compounds and hydrogen. The reaction products are a saturated hydrocarbon with H₂S. This reaction is carried out in the presence of heterogeneous catalysts under extreme conditions such as high temperature and pressure. Saturated hydrocarbon molecules remain with sulfur compounds. This is main advantage of hydrogen desulfurization process compared to the other ones. Sometimes there are several active sites which promote some reactions. Topsøe et al. [20] claimed that edge and corner sites work for hydrogenation and direct removal of sulfur, respectively. Furthermore, the basic mechanism for the activation of organic sulfur compounds by HDS catalyst was the formation of a chemical bond with the metal site located

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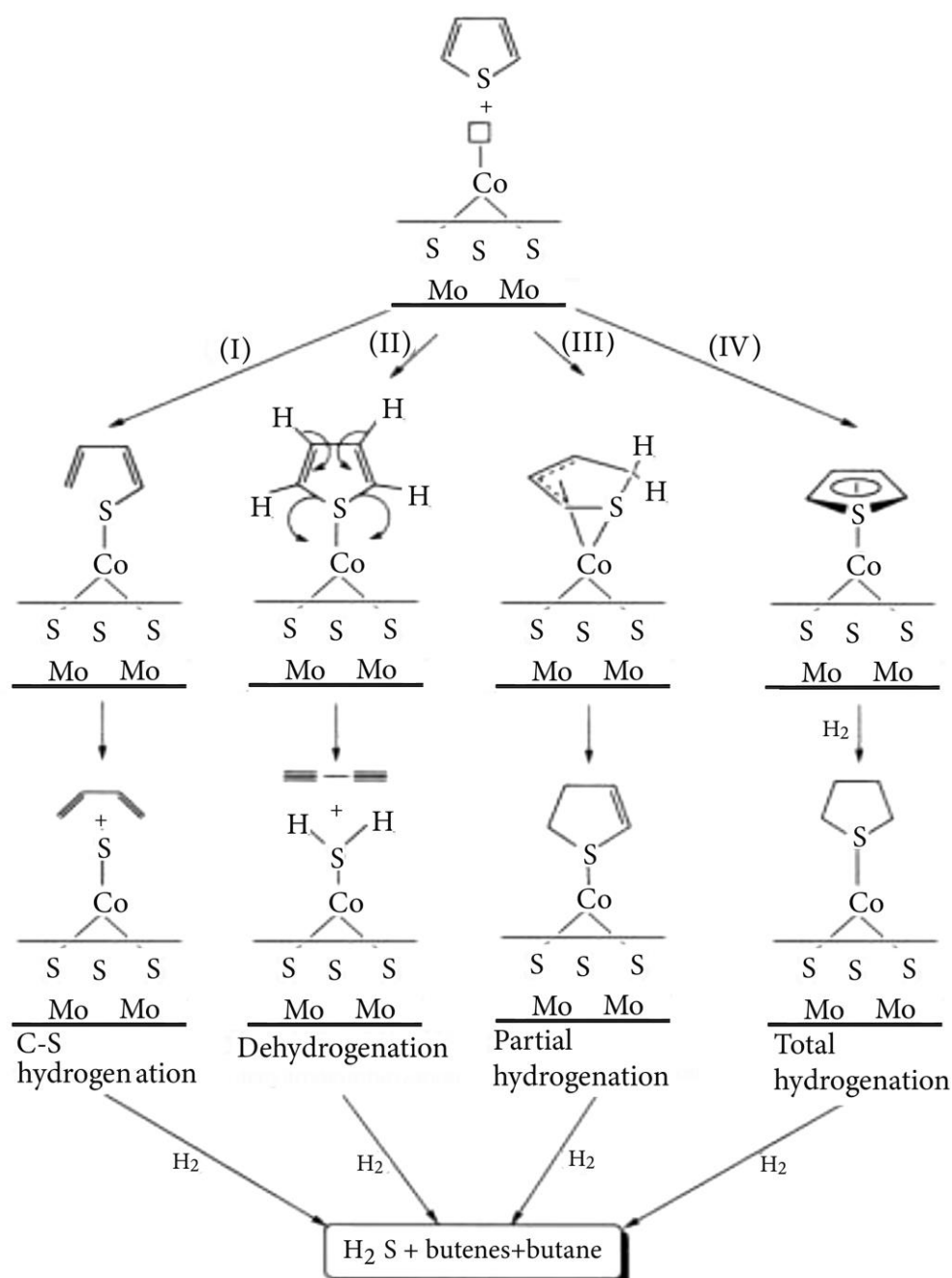


Figure 1. Mechanism of the desulfurization of thiophene [21].

on the catalyst surface. According to the literature, sulfur with organic compounds can highly be adsorbed on the sites of some promoter atoms such as cobalt and nickel compared with molybdenum. In order to investigate the mechanism of hydrogen desulfurization with Co (Ni) Mo/ γ -Al₂O₃ catalyst, the desulfurization of thiophene as a simple model is shown in the Figure 1. Moreover, the other models for HDS mechanism of benzothiophene and dibenzothiophene compounds are shown in Figure 2. However, according to studies conducted by Sánchez-Delgado [21] disulfides react and form hydrogen sulfide and mercaptans but, mercaptans can be converted to hydrocarbons and hydrogen sulfide. Along with the increase in the consumption of natural gas resources, the production of gas condensate as a cost-effective hydrocarbon feedstock

increased, too. Heavy hydrocarbon compounds as gas condensate will be extracted from the natural gas. gas condensate is mainly containing pentane and heavier liquid hydrocarbons (C₅⁺). It is free of metals and usually contains large amounts of naphtha and gasoil cuts. According to a traditional process, after stabilizing the vapor pressure, adjusting the dew point and removing some corrosive sulfur compounds (such as mercaptans) and/or oxidizing them (Merox), the corrosive mercaptans removal and/or oxidation will conduct this valuable fuel source to the storage tanks. Each of the fractionated products will be refined after distillation process. Kidnay and Parrish [22] studied on a large-scale undesirable by product such as Disulfide Oil (DSO). In order to improve the quality of gas condensate as a

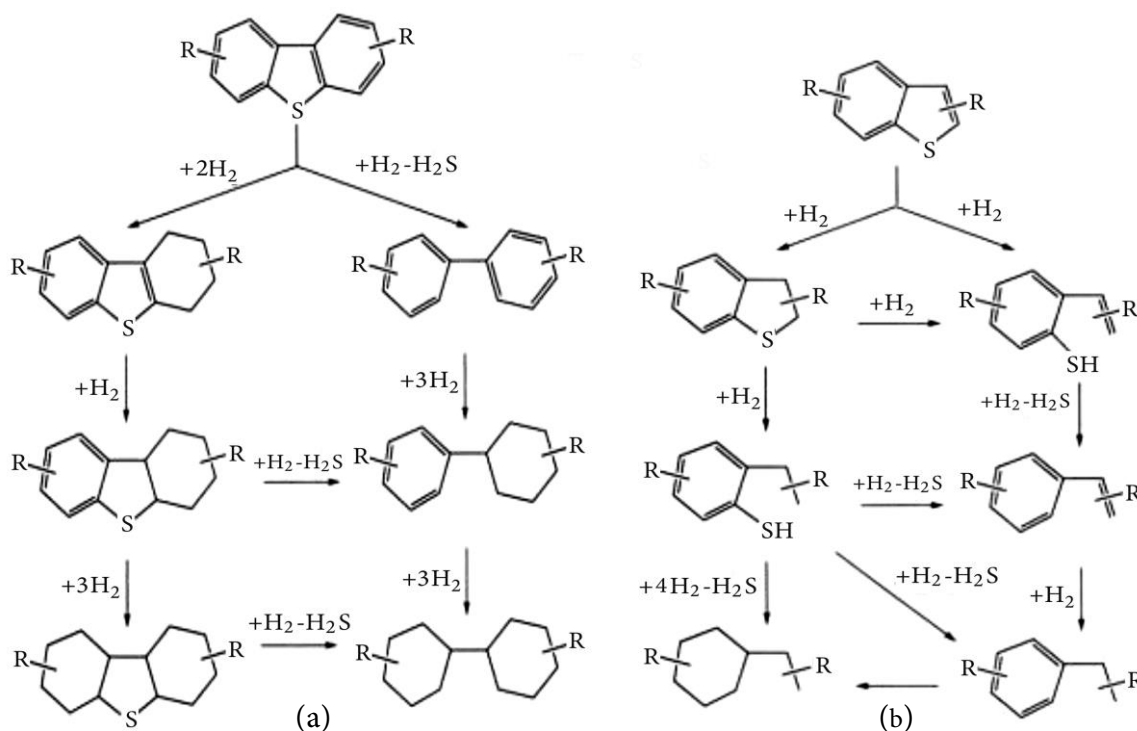


Figure 2. Main reactions of HDS for benzothiophene (a); and dibenzothiophene (b) [21].

valuable hydrocarbon source, it is necessary to investigate removal of undesirable sulfur compounds from the gas condensate. On the other hand, simultaneous HDS of mercaptan and other sulfur compounds will prevent the DSO by product formation. Shabani and Royaei [23] showed that presence of DSO compounds during the HDS process will enable the purification of produced DSOs.

In the current research, CoMo/Al₂O₃ catalyst was synthesized, characterized and tested to apply it for the gas condensate feedstock under various operating conditions. For this, the synthesized catalyst in the HDS reactor was loaded to investigate the optimum conditions. Finally, a deep HDS of gas condensate containing DSO with the synthesized catalyst under the optimized operating conditions was carried out.

2. Materials and methods

2.1. Materials

Aluminum sulfate [Al₂O₃ (SO₄)₃ · 18 H₂O], ammonia (NH₃ 25 wt. %), nitric acid (HNO₃ 65 wt. %), ammonium heptamolybdate tetrahydrate [(NH₄)₆Mo₇O₂₄ · 4H₂O > 0.994 g/g in purity], Co(II) nitrate hexahydrate [Co(NO₃)₂ · 6H₂O, analytical grade] and citric acid were supplied by Merck KGaA. Sodium aluminate (Na₂O 41%, Al₂O₃ 53% and H₂O 6%) was supplied by Van Waters and Rogers Company. All chemicals were used without further treatments.

2.2. Catalyst support preparation

γ-Al₂O₃ support was prepared by peptization of boehmite powder synthesized through precipitation method. Then, the

catalyst was synthesized by the dry impregnation technique.

2.3. Catalyst characterization

The synthesized catalyst was analyzed through X-ray diffractometer (EQUINOX3000, France), High Resolution Transmission Electron Microscopy (HRTEM) and X-ray Photoelectron Spectroscopy (XPS) (with K-Alpha⁺, Thermo Co.). HRTEM analysis was performed by FEI 200 kV (TEC9G20, USA). The extrudates were powdered and dispersed in ethanol to take the Transmission Electron Microscopy (TEM) images.

Temperature Programmed Reduction (TPR) analysis was carried out to determine the active sites of catalyst. The TPR was obtained on a Micromeritics-2900 device. TPR profiles were exposed to gaseous mixture flow (5% hydrogen in Ar) with a flow rate of 151 ml/min to stabilize the baseline of Thermal Conductivity Detector (TCD). Temperature increased with a rate of 10°C/min from ambient temperature to 800°C and the hydrogen consumption was reported based on the calibration curve. The pyrolysis method (multi-EA[®] 5000 for micro-elemental analysis) was applied to measure the sulfur content of products when the reactor was filled by the synthesized catalyst.

2.4. Catalyst activation

Yamada et al. [24] employed H₂S utilized to a gaseous mixture containing 10 wt.% of H₂S and 90 wt.% of H₂ with a flow rate of 30 ml/min was used to activate the fresh catalyst under the atmospheric pressure and temperature program according to Figure 3.

Table 1. Experimental design for the synthesized catalysts.

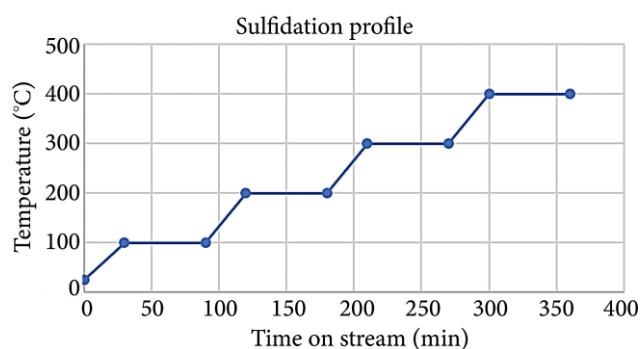
Run	No	MoO ₃ (wt. %)	Co/Mo (molar ratio)	Urea/Co (molar ratio)	Total sulfur (ppm)
1	Cat 01	20	0.5	0	43
2	Cat 02	12	0.2	5	64
3	Cat 03	16	0.5	5	20
4	Cat 04	20	0.8	5	45
5	Cat 05	20	0.2	5	47
6	Cat 06	16	0.8	10	29
7	Cat 07	16	0.2	0	51
8	Cat 08	16	0.5	5	22
9	Cat 09	16	0.5	5	21
10	Cat 10	12	0.5	0	61
11	Cat 11	20	0.5	10	37
12	Cat 12	16	0.2	10	35
13	Cat 13	12	0.5	10	48
14	Cat 14	16	0.8	0	45
15	Cat 15	12	0.8	5	56

Table 2. Specification of gas condensate.

Specification	Unit	Result	Method
Specific gravity @ 15.56 /15.56°C	-	0.7451	ASTM D4052
API	-	58.4	ASTM D4052
Total sulfur content	ppm	2200	ASTM D5453
Molecular weight	g/mole	110	IP 86

Table 3. Various models obtained from the statistical software.

Model	Sum of squares	F-value	p-value prob>F	R-squared	Adj R-squared	Suggestion
Linear	142.52	2.04	0.0058	0.0956	0.0666	No adequate
2FI	185.31	13.59	0.0039	0.8702	0.2708	No adequate
Quadratic	236.54	167.11	0.000106	0.9138	0.9826	Suggested
Cubic	239.29	58.92	0.2206	0.946	0.9934	Aliased

**Figure 3.** Catalyst activation pattern (temperature versus time).

3. Synthesis of catalyst

CoMo/Y-Al₂O₃ catalyst was produced by inoculation of ammonium hepta-molybdate (dissolved in ammonia) on the dry support (with surface area of 250 m²/g, pore volume of 0.63 cm³/g and pore diameter of 10.5 nm). Then, the support was dried at 60°C for 4h. Cobalt nitrate and urea solution were then inoculated on the dry support surface. It was dried for 3h at 60°C followed by 10 hours in a furnace with temperature of 120°C with a rate of 3°C/min. Finally, the catalyst was calcined with the same rate for 4 h at 500°C. Three factors involving MoO₃ content (12-20 wt.%), Co/Mo

molar ratio (0.2-0.8), and Urea/Co ratio (0-10) was studied on the sulfur content in a fixed bed reactor filled by the activated catalyst under temperature of 320°C, pressure of 35 barg, and H₂/Oil ratio of 200 Nml/ml, and Liquid Hourly Space Velocity (LHSV) of 3 h⁻¹. The operating conditions were extracted from the literature for naphtha and gasoil [25,26]. According to the Box-Behnken Design (BBD), fifteen runs were designed and 15 catalysts were synthesized to desulfurize gas condensate in a reactor. The results of experimental design and data were summarized in Table 1.

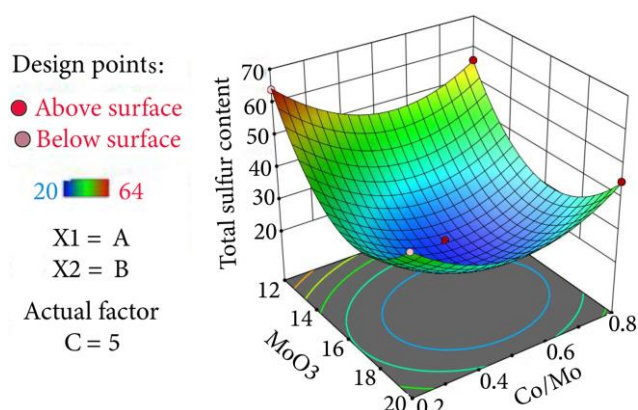
Table 2 shows the gas condensate specification. As shown in Table 3, interaction between the parameters can be studied by a second-order model.

Although R² value for a good model is around 0.8 but, adj-R² value for the developed model is 0.98 (with R² = 0.91). A high F-value (167) and low p-value (0.0001) indicates that the model components are significant, as well. Table 4 shows Analysis of Variance (ANOVA) for the proposed second-order model (large F-values and low p-values can be observed for various parameters).

As shown in Table 4, quadratic model as a proposed one could predict the experimental data with a high accuracy (with large F-value and small p-value).

Table 4. Analysis of variance.

Source	Sum of squares	Degrees of freedom	Mean square	F-value	p-value	Description
Model	2743.85	9	304.87	64.18	0.0001	Significant
A:Mo	406.13	1	406.13	85.50	0.0002	-
B:Co/Mo	60.50	1	60.50	12.74	0.0161	-
C:Urea/Co	325.13	1	325.13	68.45	0.0004	-
AB	9.00	1	9.00	1.89	0.2271	-
AC	12.25	1	12.25	2.58	0.1692	-
BC	0.0000	1	0.0000	0.0000	1.0000	-
A ²	1422.06	1	1422.06	299.38	< 0.0001	-
B ²	565.44	1	565.44	119.04	0.0001	-
C ²	162.06	1	162.06	34.12	0.0021	-
Residual	23.75	5	4.75	-	-	-
Lack of fit	21.75	3	7.25	7.25	0.1236	Not significant

Figure 4. Effect of Co/Mo ratio and MoO₃ on the catalyst activity.

Results indicated the effective interactions between the parameters which can be better observed by investigating the three-dimensional diagrams of the effect of parameters on each other. Figures 2-4 reveal the effect of different parameters, Elsayed et al. [27] presented those elliptical lines in Figure 4 indicate a distinct interaction while the circular contours show a small effect.

As shown in Figure 4, the maximum catalyst activity (total sulfur content) can be observed in the Co/Mo range of 0.35-0.55 and in MoO₃ of 15-17%. It seems that an increase in Co/Mo ratio can enhance the active sites. Furthermore, the catalytic activity may be declined in the presence of Co/MoS species in the molar ratios more than 0.55. These results support the data reported in previous studies by Zhang et al. [28]. Moreover, the catalyst showed a reduction in efficiency at Co/Mo ratios less than 0.35. This may be due to piling of MoS₂ layers on each other.

Figure 5 shows effect of Urea/Co and MoO₃ on the total sulfur content as a symbol of catalyst activity. Co/Mo molar ratio enhancement (with optimum value of 0.45) would improve the catalyst activity because the active sites would increase although an increase in Co-promoter amount can highly break C-S bonds. Molybdenum oxide loading increment (from 12 to 16%) would increase the catalyst activity although a decreasing in the catalyst activity was also observed. According to the obtained results by Zhang et al. [29] this may be due to overlapping the layers which can

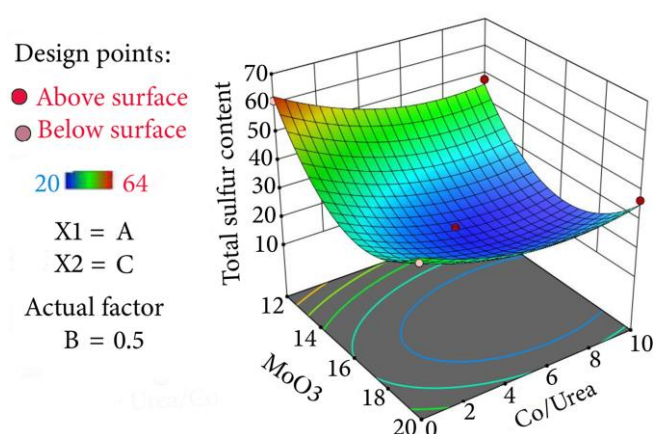
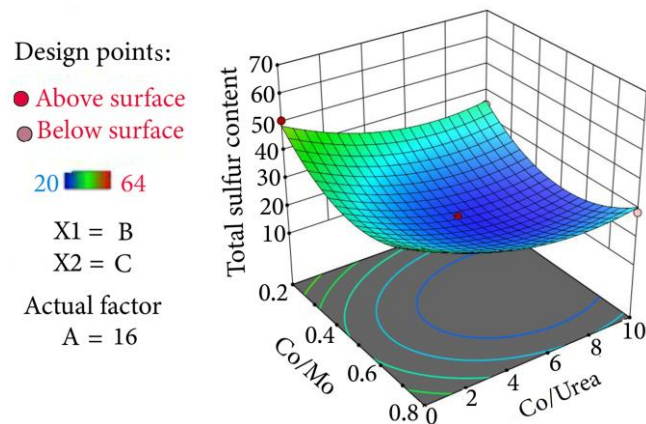
Figure 5. Effect of Urea/Co and MoO₃ on the catalyst activity.

Figure 6. Effect of Co/Mo and Urea/Co on the catalyst activity.

limit the active sites access. Figure 6 shows effect of Co/Mo and Urea/Co on the catalyst activity, as well. The sulfidation reaction would increase with increasing Urea/Co molar ratios. In fact, urea amount increment can substantially increase the reaction molar enthalpy which will increase the catalyst porosity and decline the interactions between the alumina support and active phase [30-33]. Van Haandel et al. [34] scrutinized that this will result in the formation of type-II desirable active sites. Moreover, over-consumption of urea can lead to the accumulation of MoS₂ and lower dispersion.

Figure 7 shows a good matching between the total sulfur content experimental data with the predicted ones by model for the gas condensate.

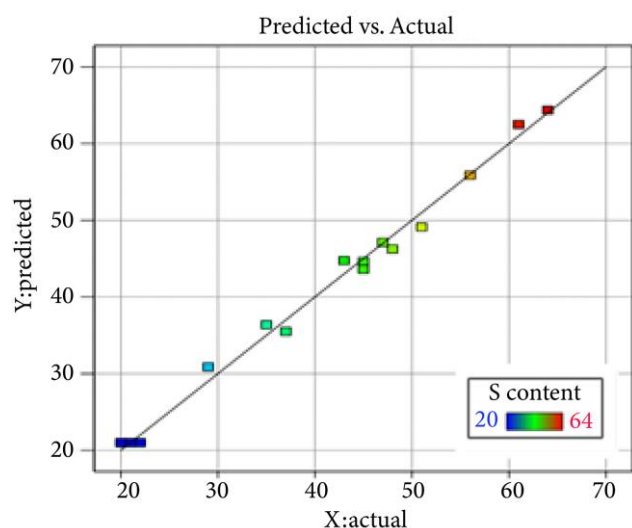


Figure 7. Predicted total sulfur content data versus experimental ones.

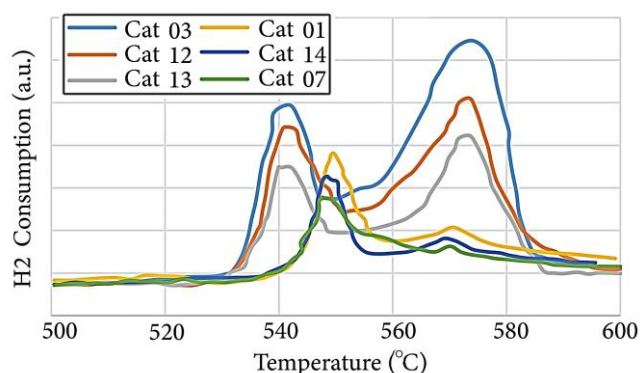


Figure 8. TPR diagrams for various synthesized catalysts.

3.1. Catalyst optimization

The catalyst activity would be optimized by minimizing the sulfur content in the product (from 20 to 64 ppm). So, the molybdenum oxide percentage, Co/Mo molar ratio and Urea/Co molar ratio should respectively vary from 15.2 to 15.8, from 0.41 to 0.48 and from 5.1 to 5.6. The catalyst with molybdenum oxide of 15.5%, Co/Mo ratio of 0.45, and Urea/Co ratio of 5 showed the best efficiency compared with the others in this study.

3.2. TPR analysis

Figure 8 shows TPR analysis for the various catalysts. According to this figure, urea-containing catalysts show lower temperatures in comparison with the urea-free ones. Therefore, urea consumption will lead more interaction between the active phase and support, and better dispersion of catalyst particles. The higher chart area (more hydrogen consumption) of the catalyst indicates stronger active sites and more probability of the formation of Co-Mo-S-II active sites which have higher efficiency in the desulfurization process. According to the literature, urea consumption results in the formation of type-II Co-Mo-S active phase on

support [35-37]. Co/Mo ratio increment (up to the optimal value) will show no reverse effect in overlapping of layers. Therefore, an increase in Co/Mo ratio up to the optimal value will increase the active sites (promoter effect of Co can highly break the C-S bonds).

3.3. HRTEM analysis

Some microstructural properties of catalyst can be studied by HRTEM. Figure 9 shows the HRTEM images with different magnifications along with the histogram of particle size distribution and the SAED diffraction pattern. Therefore, an image was used to measure particle size, atomic spacing, and ring diameter in the SAED diffraction pattern. The HRTEM images of CoMoAl₂O₃ sample at three different magnifications (a)-(c), the particle size distribution histogram (d), and the corresponding SAED diffraction pattern (e) are presented in Figure 9. The clustered agglomerates of CoMoAl₂O₃ particles with various sizes (from 100 to 500 nm) are visible in Figure 9(a). The agglomerates have formed due to the small size of CoMoAl₂O₃ particles and their tendency for the surface energy reduction through agglomeration. Since the particles size decreases and the ratio of surface to volume and surface energy increase, the aggregation minimizes the energy. Figure 9(b) shows the CoMoAl₂O₃ nanoparticles. The size distribution histogram was obtained for 100 particles using Image J processing software (open source) and depicted in Figure 9(d). According to the histogram, 22 particles (from 100 measured particles) had sizes of 4 to 4.5 nm. The average particle size and standard deviation from these measurements were around 4.29 and 1.04 nm, respectively. These indicate the particles ultrafine size and monodispersity with a normal distribution. Furthermore, the smallest and largest particles were at 2.20 and 6.45 nm, respectively.

According to Figure 9(e), the SAED pattern of sample shows bright rings corresponding to the crystal planes (111), (311), (400), (511), and (440) of the alumina structure with the reference code JCPDS No. 00-029-0063, which has a cubic crystal structure with an Fd3m space group. The absence of secondary phases of cobalt and molybdenum in the SAED pattern indicates an appropriate placement in the crystalline structure of alumina. This confirms high purity of the synthesized catalyst. Figure 9(c) shows a magnified micrograph revealing visible atomic rows of the crystal structure. As shown in Figure 9(e), atomic rows of crystal planes (400) and (311) can be observed at atomic row distances of 1.98 and 3.70 nm, respectively.

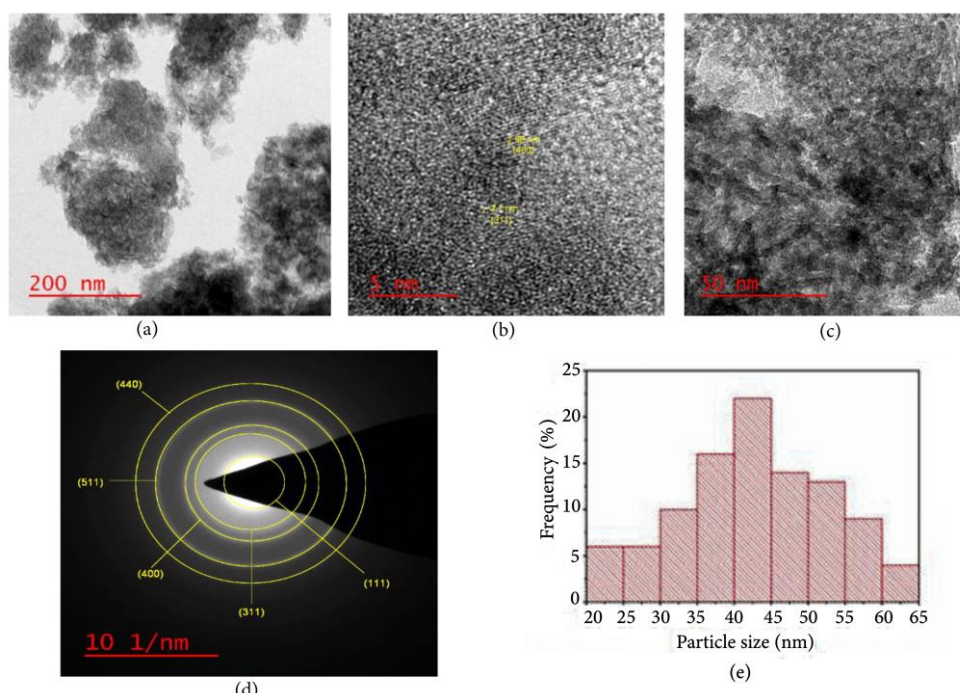


Figure 9. (a)-(c) HRTEM images of CoMoAl₂O₃ catalyst with various magnifications, (d) Histogram of particles size distribution, and (e) SAED diffraction pattern of the catalyst.

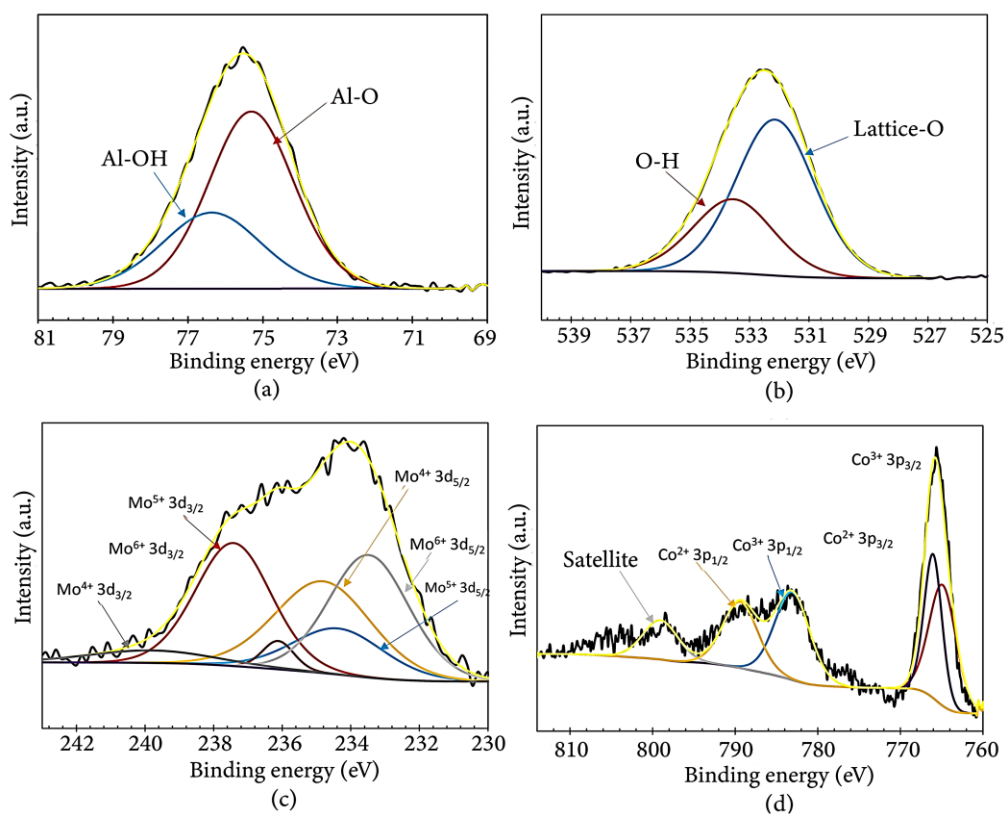


Figure 10. XPS spectra of the catalyst with various peaks: (a) Al 2p, (b) O 1s, (c) Mo 3d and (d) Co 3p.

3.4. XPS analysis

The presence of Al 2p, Al 2s, and O 1s peaks indicates aluminum and oxygen elements in the structure of alumina. Moreover, the peaks corresponding to Co 3p, Co 3s, Mo 3p, and Mo 3d demonstrate successful doping of alumina structure by cobalt and molybdenum elements. Figure 10 (a)-(d) show high-

resolution spectra of Al 2p, O 1s, Co 3p, and Mo 3d. Table 5 shows the atomic percentage values of each bond.

According to Figure 10 and Table 5, O 1s peak has been resolved into two peaks at 532.13 and 533.54 eV corresponding to the oxygen bonds with a metallic network structure (such as aluminum), and oxygen bond to hydrogen,

Table 5. Atomic percentage values of each bond extracted from the XPS analysis.

Peak	Bonds	Peak position (eV)	Peak area (CPS. eV)	%At.
O1s	O-Lattice	532.13	103288.5	67.32
	O-H	533.54	50173.7	32.68
Al2p	Al-O	75.31	9894.0	66.76
	Al-OH	76.36	4929.1	33.24
Mo3d	Mo ⁶⁺ 3d _{5/2}	233.47	2993.3	28.40
	Mo ⁵⁺ 3d _{5/2}	234.36	1273.6	12.08
	Mo ⁴⁺ 3d _{5/2}	234.81	2692.2	25.53
	Mo ⁶⁺ 3d _{3/2}	263.11	272.2	2.58
	Mo ⁵⁺ 3d _{3/2}	237.42	2843.4	26.94
	Mo ⁴⁺ 3d _{3/2}	239.82	473.0	4.48
Co3p	Co ³⁺ 3p _{3/2}	764.87	6573.7	26.03
	Co ²⁺ 3p _{3/2}	766.04	5203.5	20.58
	Co ³⁺ 3p _{1/2}	783.09	6235.9	24.37
	Co ²⁺ 3p _{1/2}	789.38	4697.3	18.27
	Satellite	799.05	2781.3	10.74

respectively. Furthermore, Al 2p peak has been convoluted into two peaks at 75.31 and 76.36 eV corresponding to the aluminum-oxygen bond in the alumina structure and aluminum-hydroxide bond on the surface that presented by Batra et al. [38]. Since XPS is a surface analysis technique and about 30% of tests belong to the sample surface, the last peak would belong to hydroxide.

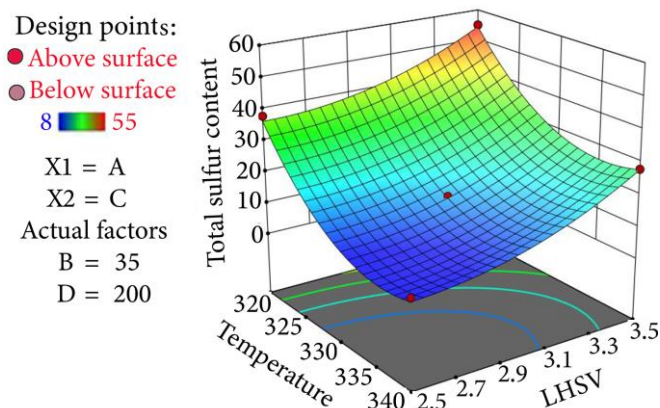
According to the results related to convolution of Co 3p and Mo 3d peaks, the structure will be compatible with Co in both divalent (38.85%) and trivalent (50.4%), as well as Mo in hexavalent (30.98%), pentavalent (39.02%), and tetravalent (30.01%), as reported in Table 5.

4. Operating conditions of gas condensate

4.1. Effect of operating parameters on the catalyst activity

Temperature, pressure, H₂/Oil ratio and LHSV are the operating variables for the HDS process. The desulfurization efficiency and hydrogen consumption increased with temperature and pressure increment although high temperatures may produce coke and decrease the catalyst lifetime [39-42]. Furthermore, the space velocity increment can reduce conversion rate, hydrogen production and coke formation.

According to the boiling range of gas concentrates (as a combination of naphtha and gasoil boiling points), the operating conditions were chosen, accurately. The temperature and pressure ranges were chosen as 320-340°C and 30-40 barg, respectively. H₂/Oil ratio and LHSV ranges were selected as 250-350 Nml/ml and 2.5-3.5 h⁻¹, respectively. Therefore, twenty-seven runs were proposed under BBD through Design of Experiments (DoE) software (Version 13) and illustrated in Table 6.

**Figure 11.** Effect of temperature and LHSV on the catalyst activity.

A second-order equation considering the inter-parametric interactions was proposed as a proper model by the software. As shown in Table 6, temperature and LHSV had the maximum impacts on the HDS. Figure 11 indicates the effects of temperature and LHSV on the total sulfur content. As shown in this figure, desulfurization should be in maximum at higher temperatures due to the energy elevation. Since the feedstock had enough time to contact with the catalyst, lower LHSV had a positive impact on the desulfurization. Therefore, temperature and LHSV had direct and indirect relation with the sulfur content. High temperature and low LHSV can promote the cracking reaction with adverse impact on the process.

Since temperature increment was more effective parameter than pressure enhancement on sulfur content, desulfurization process was achieved at temperature and pressure ranges of 332-340°C and 33-35 barg, respectively. According to the studies conducted by Pal et al. [43] temperature had higher effect on HDS than H₂/Oil ratio when the other parameters were fixed as constant values. Furthermore, maximum HDS was observed at maximum temperature and minimum H₂/Oil ratio. Since LHSV was more effective parameter than pressure on the sulfur content, maximum HDS was achieved at pressure and LHSV ranges of 35-40 barg and 2.5-3 h⁻¹ when the other parameters were fixed as constant values.

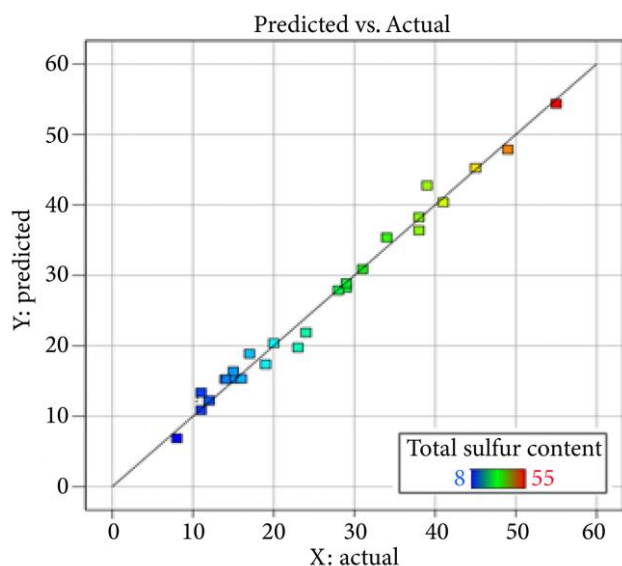
The pressure was more effective parameter than H₂/Oil at constant temperature and LHSV. The maximum HDS was found at maximum pressures and at minimum H₂/Oil ratio.

The LHSV was more effective parameter than H₂/Oil ratio. The maximum HDS was obtained at the LHSV range of 2.5-3, H₂/Oil range of 150-230 at constant temperature of 330 and at pressure of 35 barg.

Figure 12 shows the experimental and predicted data which show good agreement with each other when all operating conditions were considered together.

Table 6. Sulfur content of the product under various operating conditions.

Run	Factor 1 Temperature (°C)	Factor 2 Pressure (barg)	Factor 3 LHSV (h ⁻¹)	Factor 4 H ₂ /Oil (ml/ml)	Predicted values Sulfur content (ppm)
Cat 01	320	30	3	200	45
Cat 02	340	35	2.5	200	8
Cat 03	340	35	3	250	17
Cat 04	330	35	2.5	250	14
Cat 05	330	40	3.5	200	31
Cat 06	330	35	3.5	250	38
Cat 07	330	35	3.5	150	29
Cat 08	330	30	2.5	200	15
Cat 09	320	35	3	250	49
Cat 10	330	40	3	150	19
Cat 11	330	30	3.5	200	34
Cat 12	340	35	3	150	11
Cat 13	330	40	3	250	24
Cat 14	330	35	3	200	15
Cat 15	320	35	3	150	41
Cat 16	320	35	3.5	200	55
Cat 17	340	35	3.5	200	28
Cat 18	330	30	3	150	20
Cat 19	320	35	2.5	200	38
Cat 20	340	30	3	200	23
Cat 21	340	40	3	200	12
Cat 22	330	35	2.5	150	12
Cat 23	330	35	3	200	16
Cat 24	330	35	3	200	15
Cat 25	330	30	3	250	29
Cat 26	320	40	3	200	39
Cat 27	330	40	2.5	200	11

**Figure 12.** Predicted total sulfur content data versus experimental ones when all parameters were considered together.

4.2. Optimization of the operating parameters

As the software dramatically proposed the following equation, it was applied to investigate the optimum conditions. According to the software output, temperature range of 330-338, pressure range of 32-37 barg, LHSV range of 2.6-2.9, and H₂/Oil ratio range of 160-195 were found.

Total sulfur content of product was at 8 ppm wt. when the optimum conditions were applied with an optimal catalyst.

$$\begin{aligned}
 \text{Sulfur content} = & 12971.75 - 75.575 T \\
 & - 1.08333 P - 160.5 \text{ LHSV} \\
 & - 0.228333 \left(\frac{H_2}{\text{Oil}} \right) \\
 & + 0.025 (T \times P) + 0.15 T \\
 & \times \text{LHSV} - 0.001 \left(T \times \frac{H_2}{\text{Oil}} \right) \\
 & + 0.1 P \times \text{LHSV} \\
 & - 0.004 \left(P \times \frac{H_2}{\text{Oil}} \right) \\
 & + 0.07 \left(\text{LHSV} \times \frac{H_2}{\text{Oil}} \right) \\
 & + 0.11333 T^2 + 0.13333 P^2 + 18.8333 \text{LHSV}^2 \\
 & + 0.01383 \left(\frac{H_2}{\text{Oil}} \right)^2.
 \end{aligned} \quad (1)$$

4.3. Desulfurization of gas condensate containing DSO

There were two traditional techniques [Demercaptanization (DMC) process through sodium hydroxide solution consumption for the light mercaptans extraction and mercaptans oxidation (Merox) with air and catalyst for the heavier mercaptans] for desulfurization of gas condensate containing DSO. Since some big oil countries such as Iran, Qatar, and Saudi Arabia produce disulfide oil and its

Table 7. Typical DSO composition.

Parameter	Quantity (wt.%)
Sulfur content	51.2
Dimethyl disulfide	46–58
Diethyl disulfide	32
Diethyl sulfide	10–20
Dipropyl sulfide + methyl propyl disulfide + di-isopropyl + disulfide	<2

derivatives (such as gas condensate), a novel efficient technique for their sweetening has been encouraged. For this, 250 ppm disulfide oil was added to the gas condensate to make a feedstock with 115 ppm total sulfur content which most of it was DSO. Composition of a typical DSO is shown in Table 7.

The desulfurization of the gas condensate was carefully examined under the optimized operating conditions with the selected catalyst proposed in this research. The sulfur content was reduced to 53 ppm by increasing temperature from 330 to 345 although further increment in temperature will restrict the desulfurization due to the cracking process.

Therefore, the proposed catalyst reduced the total sulfur content of product to 8 ppm wt. under the optimized operating conditions at temperature of 330°C.

5. Conclusions

In this research, a novel efficient catalyst (instead of Demercaptanization (DMC), distillation, Hydrodesulfurization (HDS) processes for desulfurization of naphtha and gasoil) was synthesized, characterized and applied for desulfurization of a gas condensate under the optimum operating conditions. The statistical results obtained from the Design of Experiments (DoE) showed that the Mo content in the synthetic catalyst and temperature as a parameter of operating conditions had the most effect on the desulfurization of gas condensate. MoO₃ ratio increment had the maximum effect on the catalyst synthesis. Then, a DSO was added to the Gas Condensate and its desulfurization was investigated under the optimum conditions using the catalyst proposed in this research.

Nomenclature

API	American Petroleum Institute
BBD	Box Behnken Design
Co	Cobalt
DSO	Disulfide Oil
DMC	Demercaptanization of Condensate
HDS	Hydrodesulfurization
LHSV	Liquid Hourly Space Velocity
Mo	Molybdenum
RSM	Response Surface Methodology
S	Sulfur
TPR	Temperature Programmed Reduction

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Declarations

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors contribution statement

Mozhgan Rostami: Formal analysis; Methodology; Writing-original draft.

Reza Davarnejad: Supervision; Conceptualization; Writing-review and editing

Sayed Javid Royae: Supervision; Methodology; Resources; Data curation; Project administration; Validation; Visualization; Conceptualization.

Reza Seif Mohadessi: Supervision; Methodology; Resources; Data curation; Project administration; Validation; Visualization; Conceptualization.

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