

Non-catalytic oxidative desulfurization of gas condensate by ozone and process optimization using response surface methodology

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(Received 27 October 2019 • Revised 28 May 2020 • Accepted 31 May 2020)

Abstract—This study modelled and optimized the oxidative desulfurization of gas condensate with ozone, as a gaseous oxidant. Experiments in this study were non-catalytic, and sulfone extraction was done by acetone. Response surface methodology was applied for the experimental design, mathematical modeling, and optimization using Design-Expert® software. The influence of effective variables and their interaction on the response was also investigated. For the first time, non-catalytic ozonation of this feed was performed on the oxidative desulfurization process. The developed model properly fitted the experimental results. The accuracy of the model was confirmed, while this model predicted 95% desulfurization would result in the optimized conditions, and the actual value of desulfurization obtained was 95.8%. Further, the results indicated interaction between the superficial gas velocity of ozone and coefficient of oxidant-to-sulfur molar ratio. GC-SCD revealed that DBT was the most refractory component in comparison with the other sulfur components in the gas condensate. It was also found that 84.3% desulfurization occurred just with oxidation and sedimentation of sulfones and without solvent extraction.

Keywords: Oxidative Desulfurization, Gas Condensate, Ozone, Response Surface Methodology

INTRODUCTION

Air pollution is a serious threat to the environment. There are numerous air contaminants, and the sulfur content in fuel oils can be considered as an example of them. These destructive substances not only pollute the air but also can cause engine corrosion and poisoning of catalysts [1,2]. Thus, restrictions have been regulated for the sulfur compounds allowed in the fuel [3,4]. Various desulfurization methods, such as hydrodesulfurization (HDS), adsorptive desulfurization (ADS), extractive desulfurization (EDS), biodesulfurization (BDS), and oxidative desulfurization (ODS) are being used for reducing sulfur components in the hydrocarbon [5-7]. Although among these methods HDS is applied in industry as a conventional and the most common way of desulfurization, HDS has some drawbacks. Thiophenic compounds and their derivatives, which are abundant in hydrocarbon fuels, are difficult to be deeply treated with HDS. Since for removing of these substances via HDS, high pressure, high temperature, and too much hydrogen is needed [3,8,9]. The solution to this problem is ODS. Because reactivity of these refractory compounds in ODS is inverse of HDS. Likewise, mild operational conditions are the benefit of ODS [3,7].

ODS process is divided into two steps: oxidation and extraction. Various oxidants are used to oxidize sulfur components to its sulfones, where subsequent extraction of sulfones occurs through different solvents or absorbents. The common oxidants of ODS can be categorized into liquid phase oxidants and gaseous phase oxidants. Hydrogen peroxide, tert butyl hydroperoxide, and cumene

hydroperoxide are the common liquid oxidants used in the oxidation process with different homogeneous and heterogeneous catalysts [10-12]. Hydrogen peroxide, which is the most common oxidant for oxidation in the ODS process, has the problem of being biphasic [13,14]. Hydrogen peroxide is in the aqueous phase, while sulfur components are in the organic phase. Therefore, in this oxidation reaction, a phase transfer agent is used for enhancing the rate of reaction. In addition to the mass transfer problem, due to the production of water as a by-product in the oxidation reaction, this product negatively affects the quality of oil and complicates the recovery of oil [15,16].

This biphasic problem does not exist in gaseous oxidants such as air, molecular oxygen, and ozone. Gaseous oxidants are mostly accommodated with heterogeneous catalysts [17-19]. The heterogeneous catalysts used with air and molecular oxygen have numerous problems, such as rise in the cost of the process, catalytic pollution, and further complicating the reaction. Furthermore, these catalysts need high temperature, and oxidation at high temperature contributes to more cost and difficulty for light products of crude oil [1,8,20]. Ozone can be used in ODS without any catalyst

Table 1. The oxidation potential of some of the common oxidant's in ODS process [21,22]

Oxidant	Oxidation potential (V)
Hydroxyl radical	2.86
Oxygen atom	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Oxygen molecule	1.23

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Table 2. A review of the relevant recent works in the ODS

Feedstock	Oxidizing agent and operating conditions	Desulfurization (%)	Reference
Model oil (974 ppm)	Oxidant: Ozone and hydrogen peroxide Extracting solvent: ionic liquid Temperature: 60 Time: 150	64.3%	21
Diesel (1,450 ppm)	Oxidant: Ozone Extracting solvent: Acetonitrile Temperature: 25 °C Time: 60 min	97%,	23
Model fuel (500 ppm)	Oxidant: Ozone Catalyst: TiO ₂ /MCM-41 Extracting solvent: ionic liquid Temperature: 25 Time: 30 min	95.2-98.6%	24
Sour gas condensate (2,300 ppm)	Oxidant: HNO ₃ , H ₂ SO ₄ , and NO ₂ Temperature: 50 Time: 30 min	95.56%	25
Naphtha (3,010 ppm)	Oxidant: Ozone Catalyst: transition metal salts Adsorbing agent: silica gel Temperature: 80 Time: 60 min	74.4%	26
Model oil (500 ppm)	Oxidant: Tert-butyl hydroperoxide Catalyst: Polyoxometalate based catalysts Temperature: 60 Time: 120 min	50%	27
Model diesel oil	Oxidant: Ozone Catalyst: FeCl ₃ -SiO ₂ Adsorbing agent: FeCl ₃ -SiO ₂ Temperature: 25 Time: 30 min	98.4%	28
Model fuel (500 ppm)	Oxidant: air Catalyst: Platinum nanoparticles Temperature: 130 Time: 360 min	85.9-98.3%	29

due to its high potential oxidation. Table 1 indicates the potential oxidation for common oxidants in ODS.

Table 2 lists a review of the relevant recent works on the ODS. Ozone has been used alone or together with other oxidizing agents. In addition, the gas condensate, as a feed of ODS, was included in the review.

The oxidative desulfurization of model oil (DBT) was developed by Wang et al. [21]. In this paper, two oxidants of ozone and hydrogen peroxide were used. In the desulfurization with ozone and ionic liquid, 64.3% desulfurization was reported with 41.9% out of 64.3% being related to extraction with ionic liquid. Thus, only 22.4% desulfurization was done with ozone and without the catalyst.

Non-catalytic ODS of diesel by ozone was investigated by Zhang et al. [23]. Although in this research, the influence of effective parameters was not considered, the sulfur removal reached 97%, and the

order of the oxidation reactivity of sulfur compounds was BT>4,6 DMDBT>DBT. Note, in this work, acetonitrile was used as both extractant and reaction medium.

Ma et al. evaluated the oxidative desulfurization of model fuel with ozone and TiO₂/MCM-41 catalyst and ionic liquid [24]. Although thiophene and benzothiophene were eliminated very well without catalyst, the reduction of dibenzothiophene and 4,6-dimethyldebenzothiophene was trivial. The sulfur removal of the four sulfur compounds was reported in the order of TS>BT>>DBT>4,6-DMDBT.

Pouladi et al. used multiple oxidizing agents such as HNO₃, H₂SO₄, and NO₂ for the oxidation of sulfur-containing compounds in a sour gas condensate [25]. The optimization was done via response surface methodology (RSM) approach. The effect of concentration of oxidants on the desulfurization was investigated as

effective variables. The interaction of the process variables (oxidant concentration) was also proven. This research was successful in addressing the drawback of NO_2 as an oxidant in the ODS process (low yield and poor selectivity) through a combination of HNO_3 , H_2SO_4 , and NO_2 , causing 95.56% desulfurization.

The catalytic oxidative desulfurization of naphtha with indirect ozonation was done by Akopyan et al. [26]. Transition metal salts were used as the catalyst and the adsorption of sulfones was done by silica gel. This method could reduce the sulfur from 703 ppm to 180 ppm (74% desulfurization).

Akbari et al. used polyoxometalate-based heterogeneous catalysts for oxidative desulfurization of dibenzothiophene [27]. The materials for these catalysts were synthesized via three different methods: reversed microemulsion, reversed emulsion, and co-precipitation. Tert-butyl hydroperoxide (TBHP) was used as oxidant, and the results proved that the method of reverse microemulsion led to the best catalytic activity.

Ban et al. examined the oxidative desulfurization of model diesel oil with ozone [28]. In this article, $\text{FeCl}_3\text{-SiO}_2$ was used as catalyst and adsorbent. The results indicated that different types of sulfur have different degrees of selectivity on the oxidation with 4,6-dimethyldibenzothiophene being the most refractory component.

Platinum nanoparticles have been regarded as catalysts for the ODS process of model fuel by Wu et al. [29]. The catalytic performance was boosted with strong metal-edge interactions between platinum nanoparticles and hexagonal boron nitride support. This novel catalyst successfully resulted in high sulfur removal with oxidation by air as the oxidant. Also, the catalyst could be recycled five times with no reduction in catalytic activity.

In previous research, ozone was seldom used as the oxidant and in most of the papers with ozone, the model fuel was desulfurized. The oxidative desulfurization of gas condensate with ozone has never been conducted so far. Desulfurization with ozone has been generally done with catalyst causing the regeneration of a catalyst, high cost of the process, and environmental problems. All of the experiments in the oxidative desulfurization with ozone have been investigated via the classic method, while the interaction of parameters has never been reported.

In the present study, the desulfurization of gas condensate, which contains thiophenic compounds which are tough to be deeply eliminated by HDS, was done via oxidative desulfurization. Ozone was used as oxidant due to its outstanding features. The great advantage of ozone in comparison with air and molecular oxygen is non-use of catalyst and in comparison with hydrogen peroxide is a single phase oxidation reaction. Acetone was used to extract generated sulfones and the feed in this research was gas condensate. The aims of this study were non-catalytic oxidative desulfurization with ozone and evaluating effective parameters with response surface methodology. In addition, a mathematical model was introduced for the explanation of the relationships between variables and the response. Finally, process optimization was accomplished.

EXPERIMENTAL

1. Materials

Sour gas condensate from a gas refinery of Iran South Pars with

Table 3. The specification of South Pars gas condensate

Specification	Result
SPECIFIC GRAVITY @ 15.56/15.56 °C	0.7454
API	57.7
SULPHUR CONTENT wt%	0.37

Table 4. Boiling points of gas condensate

Boiling point (°C)	Cutting range (vol%)
IBP-15	2
175	55
275	79
350	96
350+	100

3,700 ppm initial total sulfur was provided, with its specification presented in Table 3. In addition, the distillation of feed was according to ASTM D2892 with the results shown in Table 4. Acetone purchased from Merck Company was used as an extraction solvent in the extraction step. Potassium Iodide¹ purchased from KANTO CHEMICAL CO. was applied with sodium thiosulfate² 0.1 M for Iodometric titration.

2. Analysis

The total sulfur levels of all samples such as feed and final products were measured by Analytik Jena EA 5000 instrument according to the ASTM D5453 standard.

The gas chromatography analysis of feed revealed that a significant part of sulfur components belonged to the thiophene (T), Benzothiophene (BT), Dibenzothiophene (DBT), Dimethyl disulfide (DMDS), and Mercaptans. The product was identified using a gas chromatograph (Varian model CP 3800) equipped with the sulfur chemiluminescence detector³ and CP-Sil column (30 m×0.32 mm i.d.), operated with He carrier gas. The program of temperature was from 32 to 220 °C with a rate of 5 °C min⁻¹.

3. Apparatus and Oxidative Desulfurization Method

For the reaction of ozone with sulfur compound and converting sulfur to sulfone, first, based on Eq. (1), ozone was formed from oxygen in the ozone generator [30,31]. The generated ozone was sensitive against temperature and collision with other components where increase in these two factors can result in decomposition of ozone to oxygen (Eq. (2)) [24,32]. Then, after the generation of ozone, according to Eq. (3), each mole of sulfur compound would react with two-moles ozone where sulfone is produced [7,24].



Fig. 1 illustrates the experimental apparatus for the ODS process.

¹KI

² $\text{Na}_2\text{S}_2\text{O}_3$

³GC-SCD

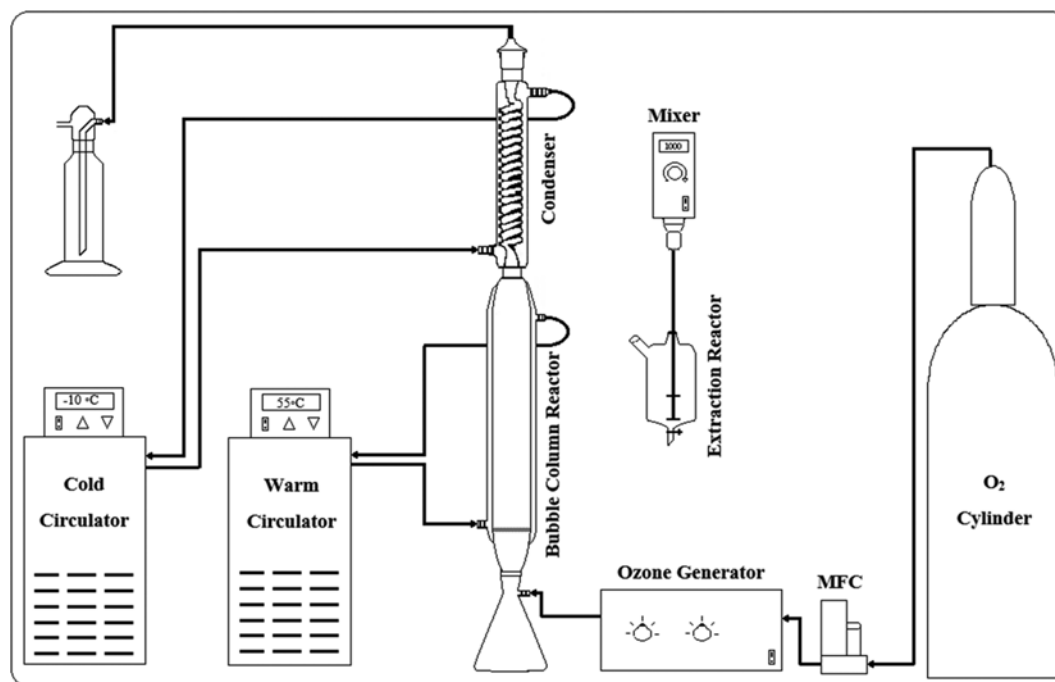


Fig. 1. the schematic of the experimental apparatus for the ODS process.

For the experiment, the required mass flow of oxygen was adjusted by MFC⁴. Then, gas condensate was poured into the bubble column reactor. Some part of pure oxygen was converted to ozone while passing through ozone generator, where this gas was injected to the bubble column reactor equipped to a sparger causing an acceptable distribution of ozone in the gas condensate. The reaction was initiated concurrent with turning on the ozone generator. Warm bath supplied the reaction temperature. Also, a condenser overhead of the reactor prevented vaporization of the feed. The temperature variation for one experiment was measured by a thermometer with an accuracy of tenths of centigrade, which was negligible (less than 1 °C). The output gas was evaluated to determine any unreacted ozone after the reactor. Following the oxidation step, the generated sulfones were extracted by acetone in a glass reactor equipped with a mixer via liquid-liquid extraction. Finally, water wash was done on feed for eliminating the acetone remained in the gas condensate.

4. Determining Ozone Concentration

For understanding the amount of ozone consumed in the reaction, the concentration of produced ozone was a vital parameter. Thus, it was determined via Iodometric titration. In this method, first, ozone reacted with potassium iodide in the acidic condition, which produced iodine [33]. Then, the produced iodine was titrated with sodium thiosulfate 0.1 M [34]. Finally, with back-calculation, ozone concentration was determined. The following equations indicate the mechanism of reactions.



⁴Mass Flow Controller

5. Experimental Design

For examining parameters and the interactions between them, central composite design (CCD) from response surface methodology was used. In this method, independent variables are coded at five levels: -1 and +1 coded levels represent factorial points; the central point is represented by 0; finally, $+\alpha$ and $-\alpha$ are known as axial points. The mathematical model in the response surface methodology generally is a second-order equation as follows [35,36].

$$Y_m = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon \quad (6)$$

where, Y_m represents the predicted response (sulfur removal, %). X_i and X_j denote independent variables. β_0 , β_i , β_{ii} and β_{ij} refer to coefficients of the intercept, linear, square, and interaction effects, respectively. Also, k is the number of independent variables, and ε represents the residual value [35].

According to the literature review, the superficial gas velocity of ozone in gas condensate (v) in terms of centimeters per second, temperature (T) in Celsius, and oxidant-to-sulfur molar ratio (O/S) can be considered as three possible effective variables for the oxidative desulfurization of gas condensate with ozone [21,24,37,38].

The advantage of this study over the past literature is the use of the oxidant-to-sulfur molar ratio parameter instead of the time of reaction for exploring the effective parameters. Previous studies, such as Ma et al., introduced the time of reaction as an effective variable, i.e., ozone was being injected to the reactor during that presented time. This directly influences the oxidant-to-sulfur molar ratio, and according to the ozone generator apparatus variety with different yields, the concept of oxidant-to-sulfur molar ratio is more logical and clearer than the time of reaction. Although at different superficial gas velocities of ozone for adjusting the value of O/S, the time of ozone injection was changed, the oxidant-to-sulfur molar

Table 5. The level of variables in CCD

Parameters	Low axial ($-\alpha$)	Low factorial (-1)	Center point (0)	High factorial ($+1$)	High axial ($+\alpha$)
X_1 , v	0.67	0.77	0.99	1.21	1.31
X_2 , T	33.8	40	55	70	76.2
X_3 , O/S	2.88	3.5	5	6.5	7.12

Table 6. Results of experiments

Test number	Coded value of variables			Actual value of variables			Desulfurization (%)
	X_1	X_2	X_3	X_1	X_2	X_3	
1	-1	+1	-1	0.77	70	3.5	88
2	-1	-1	-1	0.77	40	3.5	90
3	-1.41	0	0	0.68	55	5	93
4	0	+1.41	0	0.99	76.21	5	93
5	+1.41	0	0	1.31	55	5	93
6	+1	+1	+1	1.21	70	6.5	95
7	0	0	0	0.99	55	5	91
8	+1	-1	-1	1.21	40	3.5	83
9	0	0	0	0.99	55	5	92
10	0	-1.41	0	0.99	33.8	5	92
11	-1	+1	+1	0.77	70	6.5	94
12	0	0	0	0.99	55	5	92
13	0	0	0	0.99	55	5	92
14	0	0	+1.41	0.99	55	7.12	94
15	0	0	-1.41	0.99	55	2.88	81
16	+1	+1	-1	1.21	70	3.5	83
17	+1	-1	+1	1.21	40	6.5	94
18	-1	-1	+1	0.77	40	6.5	93

ratio was introduced as an effective variable in this study [24].

In the bubble column reactor, the superficial gas velocity of ozone is an effective parameter, which is a simple expression of the volumetric flow rate per cross-sectional area of column [39]. The volumetric flow rate for gas within the range of 350-550 ml/min was chosen according to the literature review [7,24]. Temperature as the second independent variable was investigated from 40 °C to 70 °C, which this limit was chosen based on preliminary experiments and the same research findings [7,21]. For the last parameter, the oxidant-to-sulfur molar ratio (O/S), the lower and upper limits were 3.5 and 6.5, respectively. The concept of this variable depends on gas injection time, i.e., O/S will reach its values when the time of reaction is terminated. Many pre-tests were done to narrow the range of parameters for finding their best limit.

The number of experiments was calculated via Eq. (7):

$$N=2^k+2k+C_p \quad (7)$$

where, k represents the number of independent variables, and C_p is the number of repetitions in the central point [40]. Design-Expert software (Version7.0.0) was used for design of experiment, mathematical modeling, and optimization by CCD. Table 5 reports the operational variables at 5 levels (α^5 was chosen 1.41).

In this design, C_p was 4, and the number of independent variables was 3. Hence, the number of experiments became 18 (Eq. (7)).

RESULTS AND DISCUSSION

The results of oxidation desulfurization of gas condensate with ozone designed by CCD method are reported in Table 6, where X_1 , X_2 , and X_3 denote superficial gas velocity of ozone, reaction temperature, and oxidant-to-sulfur molar ratio, respectively. The repetition of the central point for four times, which resulted in the same desulfurization, indicates that the experiments were done meticulously. Thus, the difference among the ODS yields is significantly important and cannot to be attributed to the experimental errors.

According to the experimental results of Table 6, a quadratic model was presented, predicting Y response (%Desulfurization) based on operational variables. Some of the operational variables proved inefficient based on analysis of variance (ANOVA) and were removed by the backward method in CCD to enhance the regression quality of the mathematical model. P-value is an indication of the significance for model terms. A P-value of less than 0.05 indicates that the model term is significant, and values greater than 0.1 show insignificant term. The modified statistical model and modified analysis of variance table resulted in the following. Eqs.

⁵Orthogonal Quadratic

Table 7. Analysis of variance of the predicted model for the responses

Source		Sum of squares	Degree of freedom	Mean square	F value	P value
Model		287.94	4	71.99	80.19	<0.0001
Linear	X_1	8.33	1	8.33	9.28	0.0094
	X_2	-	-	-	-	-
	X_3	211.55	1	211.55	235.66	<0.0001
	X_1X_2	-	-	-	-	-
Interaction	X_1X_3	24.50	1	24.50	27.29	0.0002
	X_2X_3	-	-	-	-	-
	X_1^2	-	-	-	-	-
	X_2^2	-	-	-	-	-
Quadratic	X_3^2	43.56	1	43.56	48.52	<0.0001
Residual		11.67	13	0.90	-	-
Lack of fit		10.92	10	1.09	4.37	0.1258
Pure error		0.75	3	0.25	-	-
Total		299.61	17	-	-	-

(8) and (9) introduce relations in terms of coded and actual factors, respectively.

$$Y = 92.28 - 0.83X_1 + 4.20X_3 + 1.75X_1X_3 - 2.33X_3^2 \quad (8)$$

$$Y = 82.35609 - 30.19071(V) + 7.91952\left(\frac{O}{S}\right) + 5.28337(V)\left(\frac{O}{S}\right) - 1.03704\left(\frac{O}{S}\right)^2 \quad (9)$$

In the coded factors equation, the factors are coded as the codes of +1 and -1 for the high levels and the low levels, respectively. This useful equation can identify the impact of the factor relative to another factor through comparing the factor coefficients. In the form of actual factors for mathematical modeling, the levels of each factor are defined in the original units.

Analysis of variance for this statistical model is shown in Table 7. This analysis with F-value=80.19 and P-value<0.0001 confirms the statistical model with a high significance.

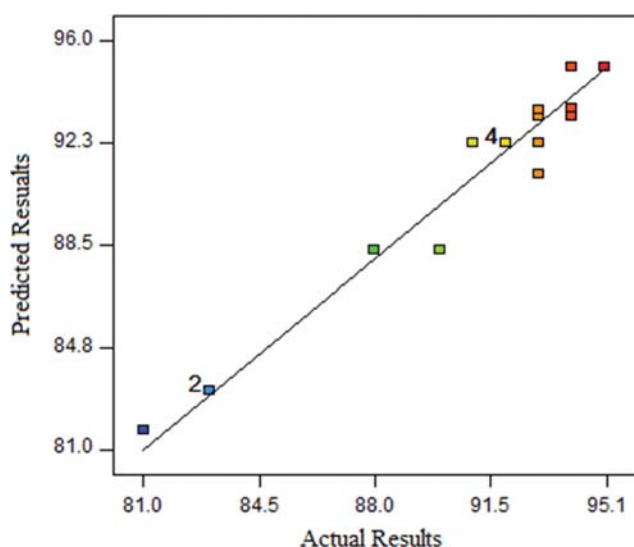


Fig. 2. Predicted results vs. Actual results for desulfurization.

Verification curve (Fig. 2) verifies the statistical model. In this figure, which is a comparison between the amount of experimental desulfurization and its predicted amount in the statistical model, if the points are along the 45 degrees line (diagonal line), the prediction is closer to experimental findings. Hence, Fig. 2 confirms plausible experimental results fitting [36].

The lack of fit test is used for comparing the residual errors and pure errors. The P-value greater than 0.05 for this parameter is a sign of significance for the mathematical model.

R^2 coefficient is a measure for the extent of variation around the mean from the model. This coefficient, which is calculated by Eq. (10), is used to evaluate the accuracy of the mathematical model.

$$R^2 = 1 - \frac{SS_{residual}}{SS_{model} + SS_{residual}} \quad (10)$$

$R^2_{adjusted}$ is a measure for the variation around the mean from the experiment. This value is adjusted to the number of terms of the mathematical model. The Eq. (11) calculates the $R^2_{adjusted}$.

$$R^2_{adj} = 1 - \frac{SS_{residual}/DF_{residual}}{SS_{model} + SS_{residual}/DF_{model} + DF_{residual}} \quad (11)$$

In Eqs. (10) and (11), SS is the sum of squares and DF is the degree of freedom.

In addition, $R^2_{predicted}$ shows the ability of the model for predicting responses in the new condition. For the appropriate model, this parameter should be within 0.2 of $R^2_{adjusted}$.

Highly significant model, non-significance of lack of fit, $R^2 = 0.9610$, $R^2_{adj} = 0.9491$, and $R^2_{pred} = 0.9194$ on the one hand and verification curve with acceptable fitting, on the other, confirm the statistical model represented by CCD method.

1. Effect of the Superficial Gas Velocity of Ozone on Desulfurization

The superficial gas velocity of ozone is one of the effective variables on desulfurization. The results of examining this parameter are illustrated in Fig. 3. It shows that an increase in this variable has an inverse influence on desulfurization. Desulfurization from 93.1% at $V = 0.77$ (cm/s) declined to 91.4% at $V = 1.21$ (cm/s) while

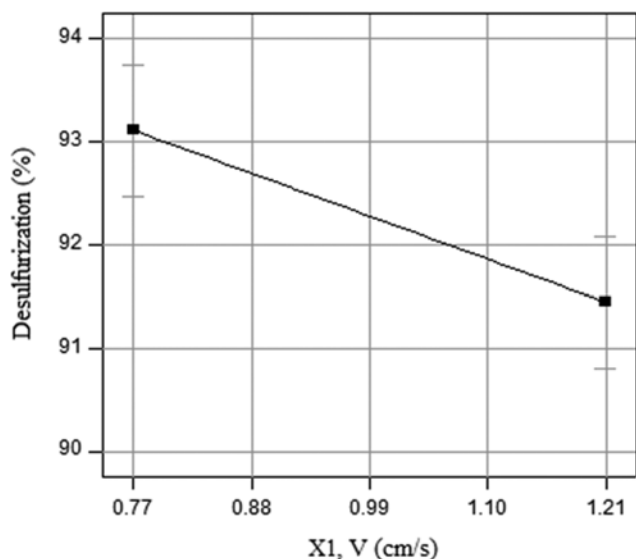


Fig. 3. Effect of the superficial gas velocity of ozone on desulfurization.

the oxidant-to-sulfur molar ratio and reaction temperature were in their central points. This inverse impact within this range has been reported by Ma et al. and Ban et al. [24,28]. Ozone is an unstable molecule, and collision with other components (O_2 or impurity) can lead to decomposition of this molecule according to Eq. (2); thus, the concentration of O_3 in the reaction diminishes, thereby reducing desulfurization [24,28].

2. Effect of Reaction Temperature on Desulfurization

In this study, reaction temperature was investigated as an effective parameter on desulfurization [21]. Fig. 4 shows the influence of this variable on desulfurization from $T=40^\circ\text{C}$ by $T=70^\circ\text{C}$ with $O/S=5$ and $V=0.99\text{ cm/s}$. During this range, with temperature rise, desulfurization is constant without any significant change. This result is confirmed by Ban et al. where the rise of temperature from

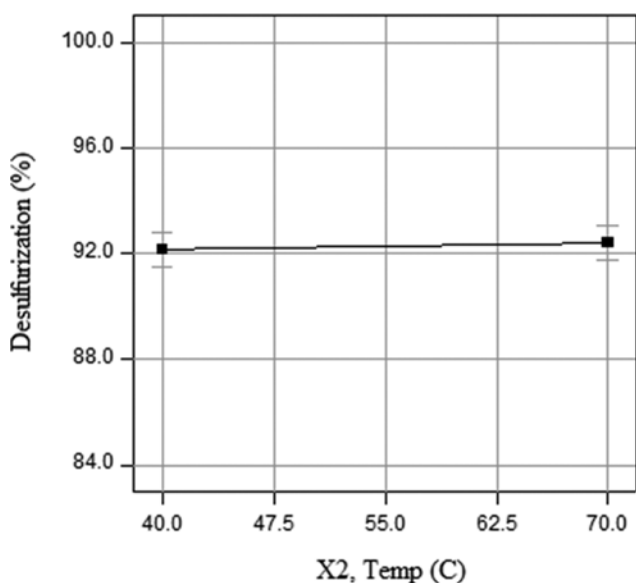


Fig. 4. Effect of reaction temperature on desulfurization.

25°C to 60°C did not influence the desulfurization [28].

The reason for this ineffectiveness is the dual effect of reaction temperature on desulfurization. Although the rise of temperature leads to enhancement of desulfurization through escalating the rate of oxidation reaction, the increase of temperature contributes to the decomposition of ozone whereby the concentration of ozone in the reaction drops and subsequently desulfurization declines [21,26]. Thus, within the range of 40°C by 70°C , the total impact of reaction temperature on desulfurization is approximately zero.

Although Zhang et al. used ozone in the non-catalytic ODS, their experiments were performed at a constant temperature, and the influence of this parameter was not evaluated. Accordingly, the findings of the present research are valuable in the ODS process [23].

3. Effect of Coefficient of Oxidant-to-sulfur Molar Ratio on Desulfurization

The oxidant-to-sulfur molar ratio was another operational variable in this system. As oxidant was in the gas phase and was injected permanently into the reaction media during the time of reaction, at the starting time of reaction this ratio was zero. Through time and with injection of oxidant to reaction, this ratio increased and at the end reaction, the oxidant-to-sulfur molar ratio reached a favorable amount. Based on the mentioned reaction mechanism (Eq. (3)), for each mole of the sulfur compound, two-moles ozone are required [7,24].

Fig. 5 indicates the impact of the oxidant-to-sulfur molar ratio on desulfurization from 3.5 to 6.5. In this figure, two other variables are in the central point ($T=55^\circ\text{C}$ and $V=0.99\text{ cm/s}$). According to Fig. 5, desulfurization from 86% in $O/S=3.5$ increased by 94% in $O/S=6.5$. The slope of this curve continuously decreased with the rise of O/S and from $O/S=6$ to $O/S=6.5$, it is approximately zero. The oxidation of non-sulfur components in the feed led to a climb in oxidant consumption more than the stoichiometric ratio, which was 2 [7,18]. This parameter had the greatest influence on the response in comparison with the other parameters,

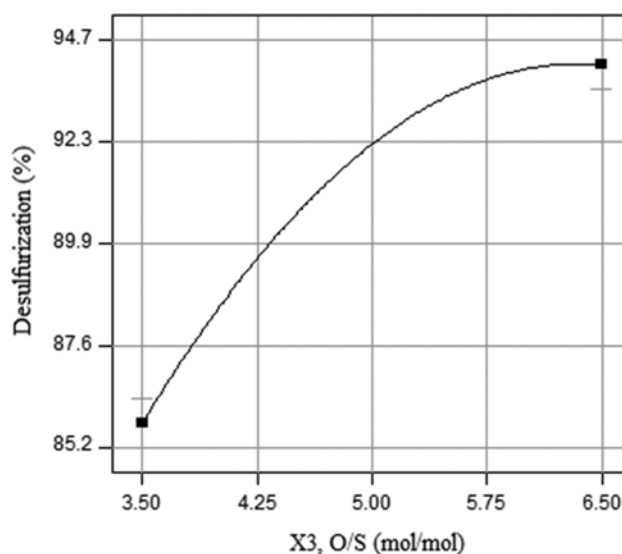


Fig. 5. Effect of coefficient of oxidant-to-sulfur molar ratio on desulfurization.

Table 8. Unreacted ozone in the reactor outlet

Operational variables			Excess ozone (%wt ⁶)
V (cm/s)	Temperature (°C)	Molar ratio O/S	
0.77	40	3.5	0.2
0.99	55	5.5	0.1
1.31	55	5.5	0
0.99	40	5.5	1.02
0.99	70	5.5	0

and this superiority was predictable based on the high coefficient of variable X_3 in Eq. (8).

For examining the unreacted ozone in the reactor outlet, the concentration of ozone was measured in the outlet of the reactor. This measurement was via Iodometric titration, with its results for some experiments presented in Table 8. These results suggest that unreacted ozone in the outlet is negligible and all of this oxidant was used for the oxidation.

The use of oxidant more than stoichiometric ratio and lack of unreacted ozone in the outlet of the reactor denote that some part of oxidant was consumed for the oxidation of non-sulfur components in the gas condensate as verified by the study of Sundararaman et al. [18,41].

4. Interaction of the Superficial Gas Velocity of Ozone and Coefficient of Oxidant-to-sulfur Molar Ratio on Desulfurization

Regarding the interaction between parameters, Li et al. reported the interaction of catalysis parameters and reaction temperature in the oxidative desulfurization reaction with oxygen [42]. Likewise, the interaction of reaction temperature with the oxidant-to-sulfur molar ratio was noted by Dizaji et al. in the oxidative desulfurization of model oil (DBT, 1-BT, 4,6-DMDBT) with hydrogen peroxide and graphene oxide-based phosphomolybdic acid catalyst [43].

Fig. 6 illustrates the 2D and 3D figures for the interaction of superficial gas velocity of ozone (X_1) and coefficient of oxidant-to-

sulfur molar ratio (X_3) on desulfurization. In these figures, the temperature is in the central point ($T=55^\circ\text{C}$). According to these figures, when X_3 is low, the rise of X_1 leads to decline in desulfurization. This reverse result of X_1 on desulfurization will remained at $X_3=5.7$. After this value for X_3 , growth of X_1 contributes to small enhancement in desulfurization. As X_1 has a negative and positive influence on desulfurization when X_3 is low and high, respectively, the interaction of these two parameters on desulfurization can be concluded. The increase in superficial gas velocity of ozone, on the one hand, escalates decomposition of ozone and thus reduces desulfurization [24]. On the other hand, the rise of the superficial gas velocity of ozone with the increase of turbulence improves the distribution of gas in the liquid, causing enhancement of mass transfer coefficient and desulfurization [28,44]. Fig. 6 indicates that at low oxidant-to-sulfur molar ratios, the rise of superficial gas velocity of ozone, decomposes some part of ozone, and the remaining ozone, which has not been decomposed, oxidizes at higher rate. However, since this value of oxidant is inadequate, thus the negative effect of superficial gas velocity of ozone outweighs its positive impact on desulfurization. In the condition when the oxidant-to-sulfur molar ratio is high, growth of superficial gas velocity of ozone decomposes the same amount of ozone in comparison with when O/S is low. As a result, in this state, ozone which has not been decomposed is greater than the previous state and oxidizes with a higher rate. Thus, the positive influence of the superficial gas velocity of ozone is dominant. Likewise, Fig. 7 shows this interaction.

Although the interaction of parameters in the ODS with different oxidants, as mentioned above, was evaluated in the literature, the interaction of variables in the ODS with ozone has never been reported by references who used ozone like 21, 24, 26, 28, and 45. Therefore, the statistical investigation of experiments which revealed the interaction of parameters adds to the importance of this study.

5. Optimization of Parameters

For finding the operating conditions contributing to the maximum desulfurization, the optimization of variables was via Design-

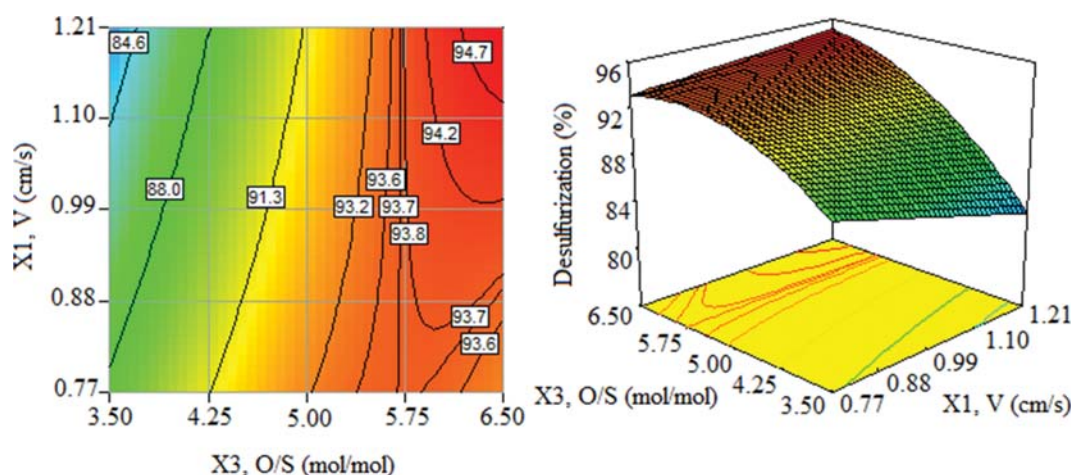


Fig. 6. Combined effects of superficial gas velocity and coefficient of oxidant to sulfur molar ratio on desulfurization.

⁶Mass fraction of unreacted ozone in the reactor outlet to total injected ozone into the reactor.

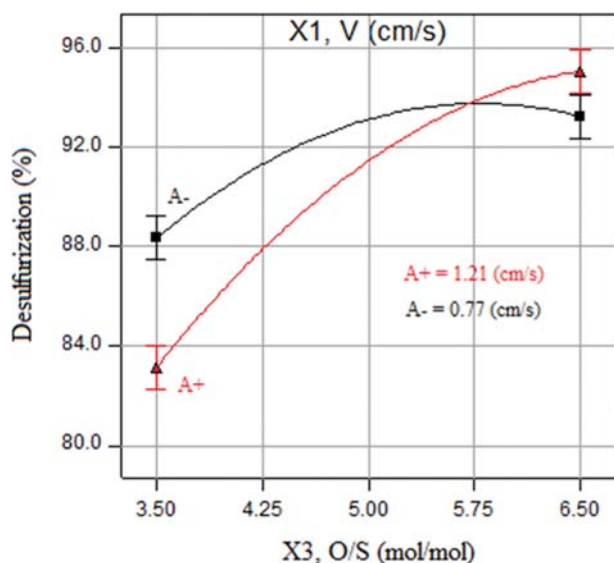


Fig. 7. Interaction of superficial gas velocity of ozone and coefficient of oxidant-to-sulfur molar ratio on desulfurization.

Expert software. In the optimization process, the effective variables were in their range, and the response (desulfurization) was set to reach the maximum. Under the optimum conditions, the desirability value, which is from zero to one, should be set to one. The optimized parameters are reported in Table 9. As shown, the desulfurization under the optimum conditions for parameters with the desirability of 1 was predicted to be 95%.

The 95% confidence interval was presented for this response (from 93.82% by 96.19% desulfurization). After the oxidation, 95.8% desulfurization was obtained (reduction of the sulfur component in gas condensate from 3,700 ppm to 155 ppm) which was in the 95% confidence interval and verified the statistical model represented by CCD method.

Note that the temperature, which is not in the mathematical model, could not influence the response. Indeed, there is no opti-

imum value for temperature in this research. In the optimization of the parameter by Design-Expert® software, this software offered some experiments with the desirability value of one, with the temperature varying from 40 to 70 °C with no effect on response. Thus, the optimized experiment was done in the mentioned conditions.

The GC-SCD demonstrated (figures not shown) that DBT was the most refractory component in the oxidation with ozone as verified by Ma et al. and Wang et al. [21,24]. The selectivity of sulfur removal followed the order of mercaptans>BT>DMDS>T>DBT.

6. The Great Advantages: Sediment of Sulfones

In all tests and during the oxidation reaction, brown substances formed over time and adhered to reactor wall like flocculation. The majority of that substances deposited in the bottom of the reactor due to more density than gas condensate. Fig. 8 shows gas condensate at the beginning and at end of oxidation, in which brown substances are visible.

These brown substances were easily dissolved after the end of oxidation in acetone and this solubility in a polar solvent fortified the possibility of sulfone. For this reason, analysis of total sulfur measurement for these substances was done. In one of the ODS experiments with 3,700 ppm sulfur in feed, sampling was done with three samples in three different stages of desulfurization. Sample 1 was the final product after oxidation and extraction process with acetone with the sulfur in this sample being 155 ppm (95.8% desulfurization). Sample 2 was gas condensate after oxidation and without any solvent extraction, which contained 580 ppm sulfur components (84.3% desulfurization). These two outcomes demonstrated that 84.3% out of 95.8% desulfurization was done in the extraction stage. Sample 3 was the brown substances deposited in the bottom of the reactor; after measurement of its total sulfur, it was found that this sample contained 3.73%wt sulfur components. As these substances were easily dissolved in acetone, sulfonic essence of these substances can be inferred with this result confirmed by the findings of Wang et al. [21].

Table 9. Optimized conditions for desulfurization

V (cm/s)	Temperature (°C)	Molar ratio O/S	Predicted desulfurization (%)	Desirability
1.21	50.5	6.48	95	1

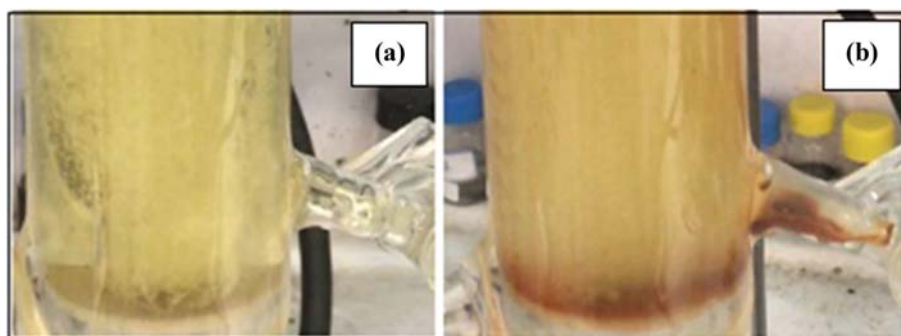


Fig. 8. Gas condensate in oxidation with ozone, (a) the beginning of the reaction (b) the end of the reaction.

CONCLUSIONS

Non-catalytic oxidative desulfurization of gas condensate with 3,700 ppm sulfur components was done in two steps, where ozone was the oxidant in the oxidation process, and acetone was a polar solvent of the extraction step. The impact of three parameters of V (cm/s), T ($^{\circ}\text{C}$), and O/S was evaluated. To investigate the effect of V , T , and O/S on the desulfurization of the gas condensate, CCD was applied through Design-Expert® software. In addition, a mathematical model was developed and validation of the model proved its accuracy. In the optimized conditions ($V=1.21$ cm/s, $T=50.5$ $^{\circ}\text{C}$, and $O/S=6.48$), the developed model predicted that 95% desulfurization would result. At the same time, the verification experiment led to 95.8% desulfurization, which confirmed that that the mathematical model agreed with the results of experiments. The results revealed that the reaction temperature did not influence desulfurization. While the increase in temperature enhances the rate of oxidation reaction, this growth leads to the decomposition of ozone, and hence, temperature becomes a neutral parameter. It was proved that V and O/S parameters had an interaction. Further, 84.3% desulfurization occurred under the conditions which only oxidation reaction was done, and this amount of reduction in the sulfur components occurred with the sedimentation of sulfones. The GC-SCD analysis showed that DBT was the toughest component in the oxidation with ozone and the selectivity of sulfur removal followed the order of mercaptans>BT>DMDS>T>DBT. The remarkable advantages of this study are:

1. The use of oxidant-to-sulfur molar ratio parameter instead of the time of reaction for investigation of effective parameters.
2. The interaction was demonstrated with statistical investigation, while previous studies of ODS with ozone were done via the classic method and the interaction of variables has never been reported by them.
3. The enhancement of desulfurization with ozone and without the catalyst in comparison with the literature.

ACKNOWLEDGEMENT

Financial support from Research Institute of Petroleum Industry is acknowledged.

COMPETING INTERESTS

The authors declare that they have no competing interest.

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