

Oxidative Desulfurization of Sour Gas Condensate and Optimization of Parameters with Response Surface Methodology

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Abstract

Reducing environmental pollution via elimination of sulfur compounds from gas condensate was the aim of this research. Whereby oxidative desulfurization from gas condensate with 3200 ppm initial sulfur was accomplished by hydrogen peroxide (30% wt) as oxidant and formic acid as catalyst. The sulfones after generation in the oxidation step were extracted through a method of liquid-liquid extraction by acetone as a polar solvent. The effects of variables: coefficient of oxidant to sulfur molar ratio (O/S), temperature (T), and coefficient of catalyst to oxidant molar ratio (C/O) were investigated. The experiments were designed with response surface methodology based on central composite design (CCD). The results of experiments demonstrated that none of these variables (O/S, T, and C/O) have any interaction, and among these variables, O/S plays a significant role with the most influence on desulfurization and C/O and T are of the second and third primary of importance, respectively. In addition, 86% desulfurization was obtained in the optimum conditions.

Keywords: Oxidative desulfurization (ODS); Gas condensate; Hydrogen peroxide; Formic acid; CCD.

Introduction

One of the crucial issues in these days is environmental pollution and the importance of environmental preservation is evident for everyone. A major portion of contaminants is devoted to transition fuels, which the reason is the existence of some harmful ingredients like sulfur and its derivations in these fuels. Combustion fuels such as gasoline and diesel cause generation and emission of sulfur oxides. Whereby numerous consequences will be created, for instance: air

pollution and acid rains, demolition of buildings, poisoning of lakes and distraction of forests in the effect of acid rains. In addition, deactivation of catalysts used in oil refining and petrochemical industry, corrosion of tanks and reactors, etc., all are damages of sulfur compounds in crude oil and its products [1, 2]. Therefore, in different parts of the world, including USA, Europe, Japan, and China, the laws were laid down for allowed limited sulfur in transformation fuels [3].

Various processes are used for desulfurization that

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Table 1. Oxidation potential of some of the common oxidant's in ODS process [22, 25]

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

some of the most important of them are Hydrodesulfurization (HDS), Extraction, Adsorption desulfurization, Biodesulfurization, and Oxidative Desulfurization (ODS) [3-5]. HDS is the most common process in desulfurization which is highly effective for eliminating sulfur components like thiols, sulfides, and disulfides, but this method requires more difficult operating conditions for thiophene and thiophene derivatives because of a structure with double bond [3, 6]. The minimum reactivity is related to dibenzothiophene with methyl groups in 4 and 6 positions. These two are tough sulfur compounds which make deep hydrodesulfurization too hard [7].

ODS process as a main alternative desulfurization method is done in lower temperature and pressure in comparison to HDS and has the ability of oxidation and separation of tough sulfur compounds such as thiophenic compounds and its derivatives that HDS eliminates them slightly [8]. This process includes two parts: converting sulfur to sulfone by oxidation and separation of produced sulfones. In oxidation step, which is mostly done with catalyst, sulfur compounds are oxidized and are converted to sulfones and in next step, these sulfones are separated from fuel by liquid-liquid extraction with a polar solvent because of the increase of their polarity [8]. Other methods such as adsorption and thermal decomposition can be used in sulfone separation from fuel [3, 9].

In the previous researches, different oxidants and catalysts have been used in ODS process [9, 10]. According to the phase of oxidant (liquid or gaseous), reactional systems can be divided into two groups. In the first group with gaseous oxidant, the following researches can be considered; molecular oxygen-FePC(NO₂)₄ [11], air-MoO₃/SiO₂ [12], molecular oxygen-cobalt(ii) acetate-aldehyde [13], air-Tert Butyl hydroperoxide-aldehyde [14], ozone-TiO₂-MCM-41 [15], and ozone-Co₃O₄-Al₂O₃ [16]. For the reactional systems with liquid phase, some of the common oxidants and catalysts are: hydrogen peroxide-MoO₃-WO₃/Al₂O₃ [1], hydrogen peroxide-acetic acid [17], hydrogen peroxide-Polyoxometalate [18], hydrogen peroxide-Na₂WO₄/ZSM5 [19], hydrogen peroxide-tungstate catalyst [20], Tert Butyl hydroperoxide-Fe-MoO₃/Al₂O₃ [21] and Tert Butyl hydroperoxide-

Mo/Siral1 [10]. In addition, in some researches, more than one type of oxidant was used in ODS which the usage of hydrogen peroxide with ozone by Zhao et al. [22] and by Behin et al. [23] are examples of that.

During the oxidation, the polarity of sulfur is raised by converting to sulfone. Thereby the created sulfones will have more polarity than hydrocarbon bulk. In the following, these sulfones can be extracted by a solvent or a mixture of solvents, and then the solvent is recovered by distillation. Some of the useful solvents in ODS are Acetone, Methanol, Acetonitrile, Ionic Liquid, N-Methyl-pyrrolidone (NMP) and Dimethylformamide (DMF) [8, 24].

In this study, in order to desulfurization from Sour gas condensate with 3200 ppm sulfur compound, hydrogen peroxide, formic acid, and acetone were applied as an oxidant, catalyst and polar solvent, respectively. Possessing more active oxygen, high oxidation potential (Table 1), being clean in terms of reaction (water production as a byproduct), having safety in storage and in the oxidation reaction, etc., are the rational reasons for opting hydrogen peroxide as the oxidant [1,26,27,28]. Formic acid and acetone were chosen based on the previous researches which had an appropriate function [17]. The investigation of gas condensate as real fuel was done seldom in literature, and this study with CCD method provides valuable information for ODS.

Materials and Methods

Materials

Sour gas condensate was provided from gas refinery of Iran South Pars. Hydrogen peroxide (30%wt), formic acid and acetone purchased from Merck Company were used as oxidant agent, catalyst and the extraction solvent, respectively.

Analysis

The sulfur content of feed and product were measured by Analytik Jena EA 5000 equipment that follows ASTM D5453 standard.

Oxidative desulfurization method

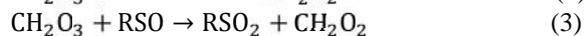
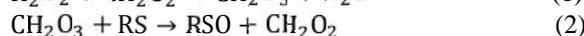
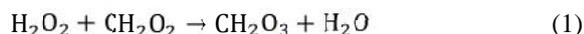
For the reaction of hydrogen peroxide with sulfur compound and converting sulfur to sulfone, for one-

mole sulfur, two-moles hydrogen peroxide is required. Also, for each mole hydrogen peroxide, one-mole formic acid is needed [8, 29]. Mechanism of reaction is according to the following [3, 29]:

- At first in the reaction between hydrogen peroxide and formic acid, peroxy acid and water (byproduct) are produced (Eq.1)

- Then in the reaction of peroxy acid and sulfur compounds, sulfoxide is produced and peroxy acid is returned to formic acid (Eq.2)

- Finally, sulfoxide is converted to the sulfone by another peroxy acid molecule (Eq.3)



For experimenting, after weighing and pouring the feed in a glass reactor, oxidant and catalyst were determined. In the following, formic acid was introduced into the reactor. Then with adding hydrogen peroxide to the feed, the stirring started, and the reaction was begun. The temperature of reaction was provided using a warm bath. A -15 °C condenser was joined to the reactor for condensing and returning light component vapored. After elapsing reaction time by turning off the stirrer, the reactants became two phases. After organic phase separation (gas condensate containing sulfone), extraction with acetone was done. To complete sulfone extraction from the feed, two times extraction was done and in any step, volume ratio of solvent to feed was 2:1. Eventually, for separation of remaining acetone from the feed, water wash was done.

Experimental design

Response Surface Methodology, which was introduced by Box and Wilson for the first time, is a statistical and mathematical collection used for development, improvement, and optimization of processes that the desired response is influenced by some variables. The aim of this methodology is describing the correlation between response and independent variables by mathematical model and response optimization. This method specifies the impact of independent variables on process individually or in the combination of other variables [30, 31]. In this research for the design of experiments, Central Composite Design (CCD) method was used. Effective variables after the selection were normalized and each of the coded variables is in range of -1 to +1 and Factorial Points with -1 and +1, Central Point with 0 and Axial Points with + and - are identified. Statistical software makes optimal layouts according to

the special criteria which the user considers. After scheme selection, model correlation and its coefficients are estimated. In Response Surface Methodology, the used model generally is a second order equation as follows [31, 32].

$$Y_m = \mu + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \epsilon \quad (4)$$

Where, Y_m , x_i , k , and ϵ represent predicted response, independent variables, the number of independent variables and residual value, respectively [31].

Due to the literature review, effective variables in this system are oxidant to sulfur molar ratio (O/S), catalyst to oxidant molar ratio (C/O) and temperature (T) according to Celsius [3,17,33].

Base on the oxidation of sulfur with hydrogen peroxide reaction equation, for oxidizing each mole of a sulfur component to the corresponding sulfone, two-moles of hydrogen peroxide are required (Eqs 1, 2 and 3). But oxidant consumption raises because of other components in the real fuel (such as nitrogen, aromatics etc.) and oxidant is in competitive reactions for oxidizing of the sulfur component or other non-sulfur components [7, 8, 34]. That's why this parameter was investigated in the range of 1 to 3 times the stoichiometric coefficient [17].

In the reaction between formic acid and hydrogen peroxide (Eq. 1), for each mole of hydrogen peroxide, one-mole formic acid is required. This acidic catalyst in reaction with oxidant gets one oxygen atom and changes to peroxy acid. Then generated peroxy acid in the reaction with a sulfur component losses its oxygen atom and with converting sulfur to the sulfoxide, returns to the initial catalyst (Eq 2 and 3). Amounts in the range of 0.5 to 2 times the stoichiometry coefficient were used in these experiments [3, 17]. In this system, another effective parameter was the temperature which its effects in the range of 40 °C to 70 °C was investigated. The upper line of this limitation was selected based on light components evaporation in feed and hydrogen peroxide decomposition [3, 17, 28]. All the experiments were done in 45 minutes. This time was selected as the best time according to the initial tests and the presented results by Ghaedian et al. [17].

The number of experiments can be calculated according to Eq. (5):

$$N = 2^k + 2k + C_p \quad (5)$$

Where k is the number of independent variables, and C_p is the number of repetitions in central point [30]. Design of experiment was done by Design Expert7 software and 2^2 was chosen 1.41. Table 2 represent

² Orthogonal Quadratic

Table 2. The level of variables in CCD

Parameters	Low axial (-)	Low factorial (-1)	Center point (0)	High factorial (+1)	High axial (+)
X ₁ , O/S	0.58	1	2	3	3.41
X ₂ , T	33.8	40	55	70	76.2
X ₃ , C/O	0.19	0.5	1.25	2	2.31

different levels of operational variables.

The number of independent variables and repetitions in central point were 3 and 4, respectively. Therefore, the number of experiments became 18 (Eq 5).

Results and Discussion

Table 3. presents the results of experiments, and in this table X₁, X₂, and X₃ are coefficient of oxidant to sulfur molar ratio, temperature, and coefficient of catalyst to oxidant molar ratio.

For presenting a statistical model based on experimental results (Table 3) and Analysis of variance, due to the three reasons, the use of transformation functions are needed:

- Stabilizing of response Variance
- Getting close the response distribution to the normal distribution
- Improving the fitting experimental data [32]

For these reasons, power function with lambda 1.79 (that it was the best lambda in Box-Cox Curve Figure 1) was selected for response transforming. Figure 2 is Studentized Residuals vs. Normal Probability, and Figure 3 is Studentized Residuals vs. Predicted. Table 4 shows the effect of power transformation function on some important parameters.

Figure 2, which is a Normal plot of Residuals, must be liner. This figure has been converted from S shape (2-B) to normal liner state (2-A) by the use of power transformation function [32]. In general, Figure 3, which is Studentized Residuals vs. Predicted, must be in funnel [32] that the use of power transformation function has helped it to be in this shape (3-A in comparison whit 3-B). According to Table 4, amounts of R², R_{adj}², and R_{pred}² rose because of power transformation function and also the parameter of Lack of Fit significantly increased.

Based on the experimental results (Table 3), a quadratic model was presented for predicting Y response (%Desulfurization) according to operating variables. After removing some of the inefficient variables with a backward method, the modified statistical model and the modified analysis of variance table were obtained like following.

$$Y^{1.79} = 2679.94 + 569.34X_1 + 236.13X_2 + 321.01X_3 - 156.53X_2X_3 - 392.95X_1^2 - 85.18X_2^2 - 210.99X_3^2 \quad (6)$$

Analysis of variance (ANOVA) for the above statistical model is in Table 5 which confirms the statistical model with high signification.

Table 3. 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	0	+1.41	0	2	76.21	1.25	85
2	-1.41	0	0	0.59	55	1.25	46
3	0	0	0	2	55	1.25	81
4	0	-1.41	0	2	33.8	1.25	71
5	-1	+1	-1	1	70	0.5	61
6	+1	-1	+1	3	40	2	82
7	-1	-1	-1	1	40	0.5	40
8	+1	-1	-1	3	40	0.5	70
9	0	0	0	2	55	1.25	84
10	0	0	-1.41	2	55	0.19	62
11	-1	+1	+1	1	70	2	66
12	+1.41	0	0	3.41	55	1.25	83
13	-1	-1	+1	1	40	2	66
14	0	0	+1.41	2	55	2.31	84
15	+1	+1	-1	3	70	0.5	82
16	+1	+1	+1	3	70	2	86
17	0	0	0	2	55	1.25	83
18	0	0	0	2	55	1.25	83

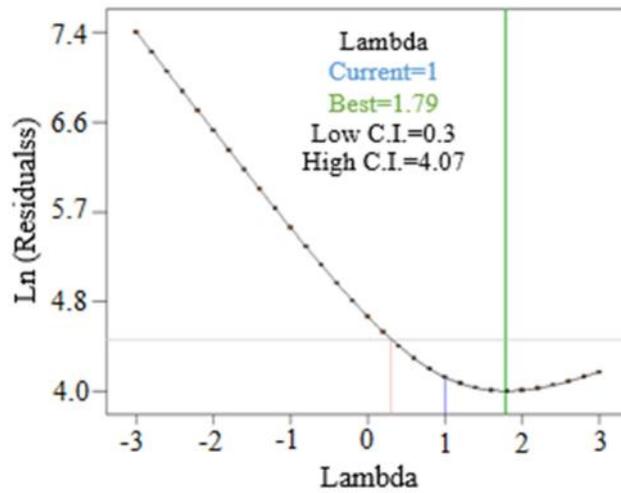


Figure 1. Box-Cox Plot for Power Transforms

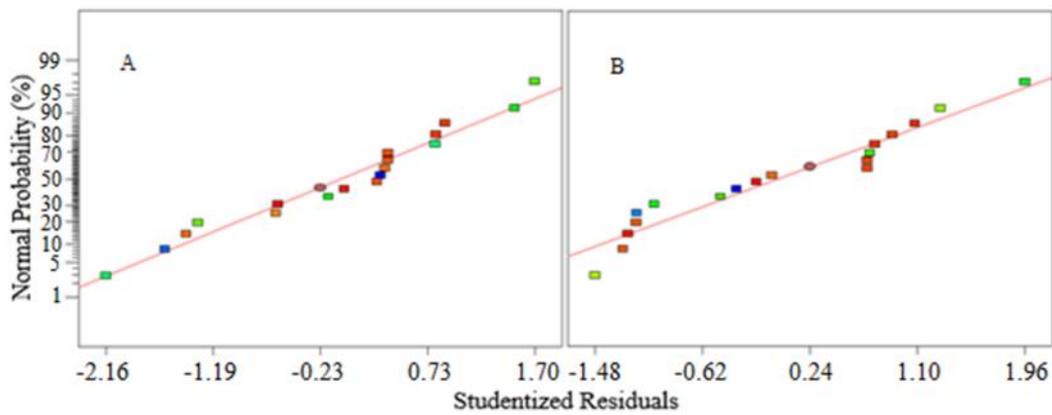


Figure 2. Normal Probability Vs Studentized Residuals, with power transformation function (A) and without this function (B)

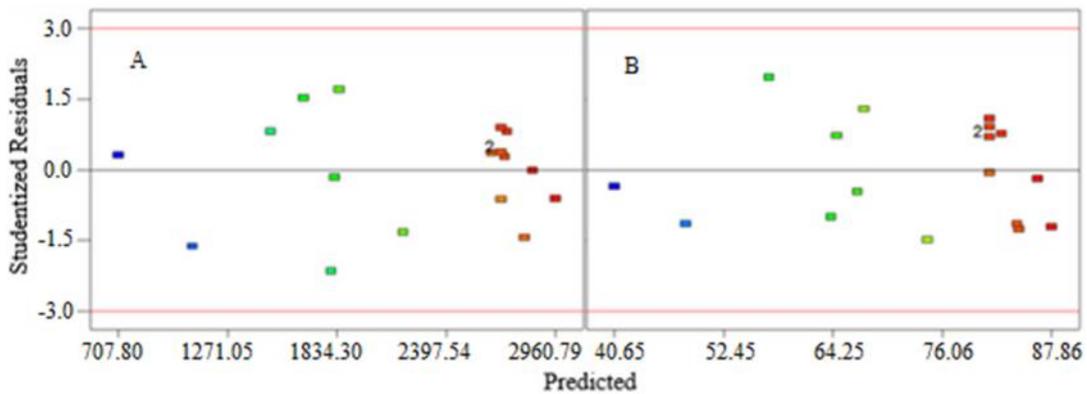


Figure 3. Studentized Residuals Vs Predicted, with power transformation function (A) and without this function (B)

Verification Curve is used for confirming the statistical model (Fig. 4). This figure compares the amount of experimental desulfurization with the predicted desulfurization in the statistical model. If the points are randomly scattered along the 45 degrees line, the prediction is closer to experimental results. Groups

of points above or under the line show areas of over or under prediction [32]. Figure 4 indicates an acceptable fitting of experimental results.

According to Table 5, highly significant of the represented model, not significant of lack of fit, $R_2 = 0.9762$, $R_{adj}^2 = 0.9595$, $R_{pred}^2 = 0.9048$ and verification

Table 4. Effect of power transformation function on R^2 , R_{adj}^2 , R_{pred}^2 and Lack of Fit

	Without transformation function	With transformation function
R^2	0.9748	0.9781
R_{adj}^2	0.9572	0.9627
R_{pred}^2	0.6045	0.9121
Lack Of Fit	0.0689	0.1368

Table 5. Analysis of variance of predicted model for the responses

Source		Sum of Squares	Degree of Freedom	Mean Square	F Value	P Value
Model		7.641×10^6	7	1.092×10^6	63.77	<0.0001
Linear	X_1	3.89×10^6	1	3.89×10^6	227.24	<0.0001
	X_2	6.691×10^5	1	6.691×10^5	39.09	<0.0001
	X_3	1.237×10^6	1	1.237×10^6	72.24	<0.0001
Interaction	X_1X_2	-	-	-	-	-
	X_1X_3	-	-	-	-	-
	X_2X_3	1.96×10^5	1	1.96×10^5	11.45	0.0070
Quadratic	X_1^2	1.235×10^6	1	1.235×10^6	72.16	<0.0001
	X_2^2	58039.05	1	58039.05	3.39	0.0954
	X_3^2	3.561×10^5	1	3.561×10^5	20.80	0.0010
Residual		1.712×10^5	10	17117.94	-	-
Lack of Fit		1.55×10^5	7	22139.88	4.10	0.1368
Pure Error		16200.24	3	5400.08	-	-
Total		7.812×10^6	17	-	-	-

curve, they all confirm the represented model.

Effect of the coefficient of oxidant to sulfur molar ratio

Figure 5 indicates the result of coefficient of O/S molar ratio on desulfurization in the range of 1 to 3 while C/O = 1.25 and T = 55 C. This figure shows that desulfurization was 64.2% at the beginning of the range and with the increase of O/S molar ratio, the desulfurization raised. After reaching to the maximum of desulfurization (85.7%) in O/S = 2.71, with the raising in O/S molar ratio by O/S=3, desulfurization decreased nominally and approached to 85.2%. This

variable in the high concentration has a lower impact on desulfurization, like the results presented by Li et al. [26]. The reason for this event is that H_2O_2 in the high concentration is between two competitive reactions; sulfur oxidation and decomposition of oxidant. Therefore some of H_2O_2 is decomposed and does not participate in oxidation reaction [26]. On the other hand, at higher concentrations, the concentration of water will increase, and this phenomenon leads to the decline of desulfurization [27].

Effect of temperature

The temperature is the other effective variable in

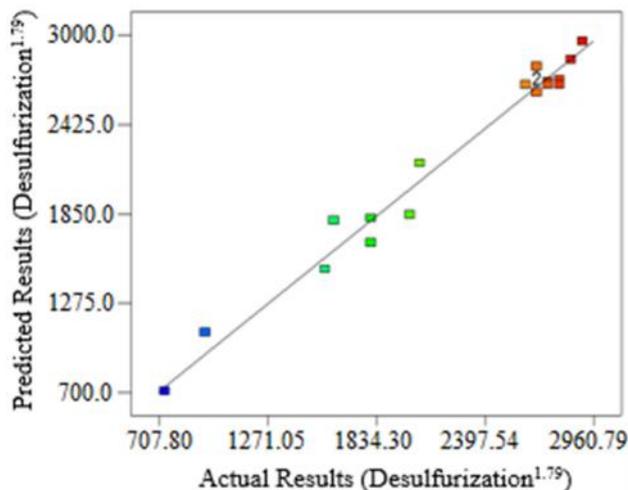


Figure 4. Predicted results Vs Actual results for desulfurization (to the power of 1.79)

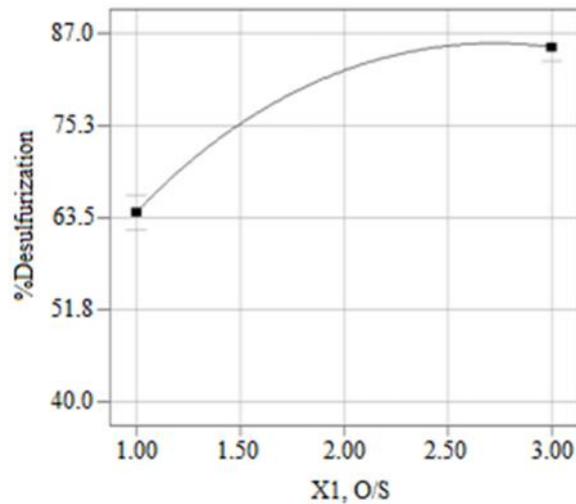


Figure 5. Effect of coefficient of oxidant to sulfur molar ratio on desulfurization

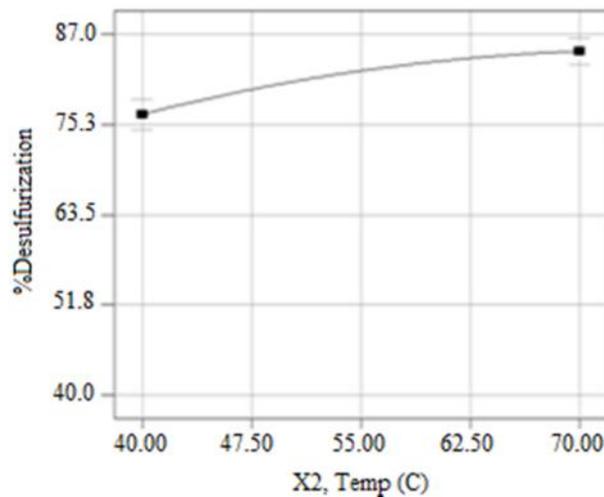


Figure 6. Effect of temperature on desulfurization

ODS and its influence is shown in Figure 6. Two other variables in this figure are at the central levels ($O/S=2$ and $C/O=1.25$). In $T=40$ C desulfurization was 76.6% and raised to 84.8% in $T=70$ C. The rise of 8% in desulfurization from the beginning by the end of the investigated temperature, shows this parameter has the lowest impact on desulfurization in comparison to effects of molar ratios of O/S and C/O . This factor plays a positive role in the enhancement of the rate of oxidation reaction and these results are confirmed by consequences of Imtiaz's et al. [1, 29, 35].

As it is shown in Figure 6, the slope of the desulfurization curve is decreased by the rise of temperature and goes toward zero. This reduction is because of hydrogen peroxide decomposition with the rise of temperature which occurs in reaction media. The rate of hydrogen peroxide decomposition climbs after

50 C [28]. For preventing the increase in hydrogen peroxide consumption in reaction, doing the reaction must be avoided in the temperatures over 50 C [28].

Effect of the coefficient of catalyst to oxidant molar ratio

According to the analysis of variance (Table 5), the latest effective variable is the coefficient of molar C/O ratio. Figure 7 indicates the growth of desulfurization with C/O raising (two other variables are in central level $O/S=2$ and $T=55$ C). Although the increase of C/O has a positive influence on the desulfurization, C/O raising is accompanied by figure's slope reduction and this slope has become zero from $C/O=1.75$ to $C/O=2$. This is an indication of the ineffectiveness of C/O raise after 1.25 on desulfurization. This amount is more than the stoichiometric ratio for the reaction of formic acid with

hydrogen peroxide and is justifiable based on the being an incomplete reaction. Another reason for oxidant and catalyst consumption more than their stoichiometric coefficient is that some of the oxidant and catalyst are used for oxidation of non-sulfur component in feed [7, 8, 34].

Interaction of coefficient of catalyst to oxidant molar ratio and temperature on desulfurization

According to the analysis of variance for variables interaction (O/S-C/O, O/S-T, and C/O-T), just C/O-T affects desulfurization; therefore just this interaction was investigated.

Figure 8 shows the simultaneous effects of temperature and coefficient of catalyst to oxidant molar ratio on desulfurization in the form of contour and 3-D figures. In these figures, oxidant to sulfur molar ratio is at the central level (O/S=2). Based on the contour figure, when X₂ is low, the growth of X₃ in the range of

0.5 to 2 continually increases the desulfurization by about 17%. In the amounts more than 47.5 for X₂ and while X₂ is constant, the rise of X₃ has a dual effect on the response. At the first X₃ raises desulfurization and then decreases it. But this reduction is insignificant. Consequently, because in all constant amounts for each variable, the rise of other variable grows desulfurization, these two variables in the mentioned ranges don't have interaction with each other. Likewise, Figure 9 confirms the lack of interaction in these two variables, because of failure in collide of two lines with each other.

Also based on Figure 8, in 40 C, raising C/O ratio has a significant effect on desulfurization but in 70 C with increasing C/O ratio, desulfurization is increased by lower intensity. With the growth of temperature, hydrogen peroxide decomposition increases and as a result, the oxidant concentration decreases in reaction media and peroxy acid generation declines [36]. Also

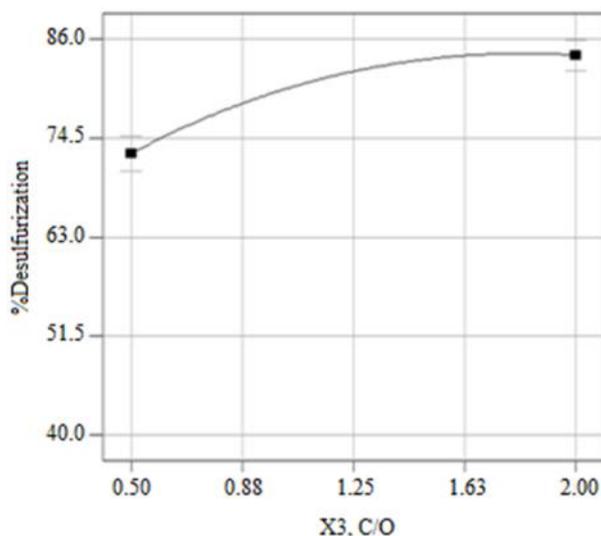


Figure 7. Effect of coefficient of catalyst to oxidant molar ratio on desulfurization

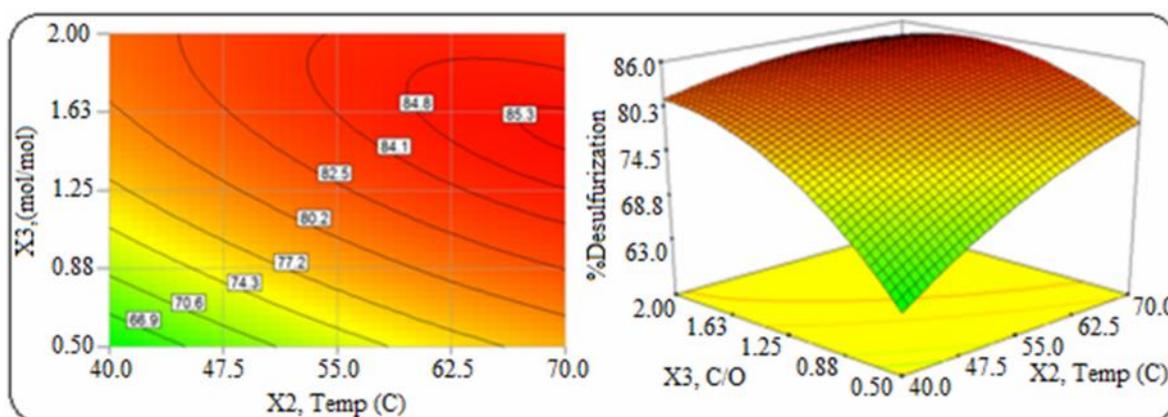


Figure 8. Combined effects of temperature and coefficient of catalyst to oxidant molar ratio on desulfurization

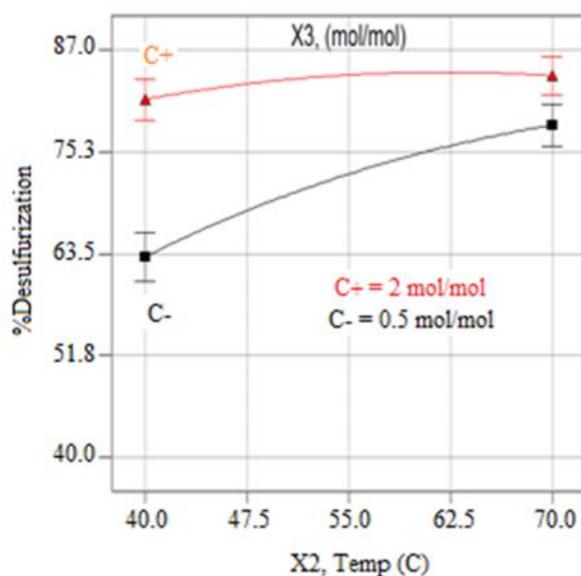


Figure 9. Interaction of coefficient of catalyst to oxidant molar ratio and temperature on desulfurization

generated peroxy acid is unstable in high temperature, and decomposition of some of the peroxy acids in 70 C contributes to decreasing the impact of C/O ratio raising on desulfurization [28].

Optimization of parameters

The optimization of parameters was done with the aim of maximum desulfurization. The optimized conditions are represented in Table 6.

To validation of predicted response by the statistical model, 95% confident interval was presented for this response, which the lower limit of this range is 84.72% and the upper limit is 89.06% desulfurization. After experimenting in the optimized conditions, 86% desulfurization was obtained (reduction of the sulfur component in gas condensate from 3200 ppm to 450 ppm) which is in the 95% confident interval.

In addition, after the oxidation and separation of the organic phase and aqueous phase, the sulfur of the oxidized feed (without any extraction with solvent) was measured and observed that 672 ppm sulfur component exists in the product after oxidation and before extraction. The comparison of this amount with the final sample which after oxidation and extraction, its desulfurization was 86%, indicates 79% of desulfurization is related to oxidation and separation of the organic and the aqueous phase and 7% remaining desulfurization is sulfone extraction with the solvent. As it is mentioned in literature [3], the oxidation reaction is

done in the aqueous phase and interface of organic and aqueous phase [29].

Therefore, the generated sulfones are at the interface that during the separation of two phases in this experiment, 79% of generated sulfones were separated from gas condensate along with the aqueous phase.

Conclusions

In this study, oxidative desulfurization of gas condensate was done with hydrogen peroxide (30%wt) as an oxidant and formic acid as a catalyst and the following results were obtained:

1. Effective variables in this system were oxidant to sulfur molar ratio, temperature and catalyst to oxidant molar ratio which the maximum desulfurization (86%) was obtained in O/S=2.65, T=50 C, and C/O=1.87.

2. Statistical design of experiments was done by CCD method and analysis of results showed there is no significant interaction between operational variables. Although based on the Table 5 temperature and coefficient of catalyst to oxidant molar ratio have interaction, this interaction is negligible and can be ignored. Therefore the lack of interaction in this system is valid.

3. In this study, 86% desulfurization was achieved, which 79% of this desulfurization could be done just with the oxidation step and without extraction by the solvent.

Table 6. Optimized conditions for desulfurization

Molar ratio O/S	Temperature (C)	Molar ratio C/O	Desulfurization (%)	desirability
2.65	50	1.87	87	1

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