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OPTIMIZATION OF OPERATING CONDITIONS IN OXIDATION OF DIBENZOTHIOPHENE IN THE LIGHT HYDROCARBON MODEL

Article Highlights

- The oxidation of DBT in a light hydrocarbon model was examined by response surface methodology
- The considerable interactive effects of process variables were investigated and optimized
- The global reactions mechanism and the effects of process variables on them were discussed
- The optimum value of H₂O₂ oxidant was obtained near the stoichiometric amount

Abstract

In this research, the effects of process variables on the efficiency and mechanism of dibenzothiophene oxidation in formic acid/H₂O₂ system for deep desulfurization of a light hydrocarbon model were systematically studied by statistical modelling and optimization using response surface methodology and implementing the central composite design. A quadratic regression model was developed to predict the yield of sulfur oxidation as the model response. The model indicated that temperature was the most significant effective factor and suggested an important interaction between temperature and H₂O₂/sulfur ratio; at temperatures above 56 °C, more excess oxidant was necessary because of instability of active peroxy intermediates and loss of H₂O₂ due to thermal decomposition. In contrast, the water hindrance effect of H₂O₂ aqueous solution in desulfurization progress was more significant at temperatures below 56 °C. In the optimization process, minimizing H₂O₂/sulfur ratio and catalyst consumption for maximum yield of desulfurization was economically considerable. The optimal condition was obtained at temperature of 57 °C, H₂O₂/sulfur mole ratio of 2.5 and catalyst dosage of 0.82 mL in 50 mL solution of DBT in n-hexane leading to a maximum oxidation yield of 95% after 1 h reaction. Good agreement between predicted and experimental results (less than 4% error) was found.

Keywords: oxidative desulfurization, response surface methodology, central composite design, dibenzothiophene, light hydrocarbon.

Deep desulfurization of fuels to obtain a product with less than 10 ppm sulfur has become an important research subject worldwide [1]. The conventional hydrodesulfurization process (HDS) is highly efficient in removal of thiols, sulfides and disulfides from fuel but less effective for eliminating dibenzothiophene

(DBT) and its derivatives, due to the steric hindrance of these compounds on the catalyst surface [2]. Therefore, elimination of these compounds by HDS requires severe operating conditions, including high H₂ pressure and temperature as well as larger reactors and high active catalysts. From the economical point of view, catalytic oxidative desulfurization (ODS) is one of the most promising alternative processes for obtaining ultra-low sulfur fuel. This process can potentially be used after HDS for deep desulfurization of fuel. In this process the organosulfur compounds are oxidized to their corresponding polar sulfones and then removed by solvent

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extraction or solid adsorption. The main advantage of ODS is the removal of refractory organosulfur compounds such as DBT and its derivatives under atmospheric pressure and mild temperature (below 80 °C), without the use of expensive hydrogen.

Various oxidant agents including hydrogen peroxide [3,4], oxygen [5] and tertbutyl hydroperoxide [6,7] have been used in the previous studies. However, hydrogen peroxide has been reported as the more promising oxidant due to the high selectivity, safety, environmental friendliness and process economics. To enhance the oxidation activity of the oxidizing reagent, several homogeneous and heterogeneous catalysts including organic acids [3,4,8], polyoxometalates [2,9], Ti-containing zeolites [10], mesoporous molecular sieves [10-13] or metal oxide supported on alumina or silica [14-18] are evaluated in different ODS systems. Some extractive solvents such as acetonitrile [15,19], DMF [4,20], methanol [4,19] and DMSO [21] have been used for subsequent removal of the polar sulfones which were produced during ODS reactions in different systems. Recently, some ionic liquids (ILs) such as Brønsted acidic ILs such as [Hnmp]BF₄ [22] and [(CH₂)₂COOHmim][HSO₄] [23], Lewis acidic ILs such as [C₄mim]Cl/MCl₂ (M = Zn, Fe, Cu, Mg, Sn or Co) [24] and [C_n³MPy] FeCl₄ (n = 4, 6 or 8) [25], acetic acid-based ILs [26] have also been used as both extractant solvent and catalyst providing a new efficient option for ODS process. In addition, the previous research studies have investigated the effect of various operational variables to enhance the yield of desulfurization using classical methodology (varying a single variable while keeping all other variables fixed), with no consideration of the possible interactions between variables. In this regard, no systematic optimization has been performed and the reported results are questionable. For industrial application, selection of the cost effective ODS process with maximum yield of sulfur elimination is highly preferred. Response surface methodology (RSM) is a suitable statistical technique for systematic experimental design and modelling in order to investigate the effects and interactions of experimental variables and also to find the optimal process conditions, with a limited number of experiments [27]. The main purpose of this paper is to apply response surface methodology as a novel approach for examination of the interactive effects of ODS process variables including temperature, H₂O₂/sulfur ratio and catalyst dosage on the mechanism and the yield of DBT oxidation when hydrogen peroxide is used as oxidant and formic acid as catalyst. Furthermore, this paper presents the optimal oper-

ational conditions for maximum efficiency of DBT oxidation for deep oxidative desulfurization of light hydrocarbon model *via* development a quadratic statistical model.

EXPERIMENTAL

Materials

All chemical materials used in this study were purchased from Merck chemical company and were used without further purification. The solution of dibenzothiophene (DBT) in *n*-hexane with 500 ppm concentration of sulfur was used as the light hydrocarbon model. Hydrogen peroxide (aqueous solution, 30 wt.%) was used as the oxidation reagent and formic acid (HCOOH, purity > 99%) as the catalyst.

Experiment method

Oxidation of DBT was carried out using H₂O₂ and formic acid catalyst in a 100 mL glass batch reactor equipped with a condenser, thermometer, magnetic stirrer and a water bath for temperature control. In a typical run, 50 mL of solution of DBT in *n*-hexane with 500 ppm sulfur concentration was added to the reactor at atmospheric pressure. The reactor was heated up to a specified temperature. Then the desired amount of H₂O₂ and formic acid catalyst were added and the solution was vigorously stirred (800 rpm) to minimize the resistance to mass transfer. The effect of three control factors including constant reaction temperature, initial molar ratio of H₂O₂ to total initial amount of sulfur, and catalyst dosage were investigated. Upon completion of the reaction (after 1 h), the oil phase was taken for analysis of DBT oxidation. The samples were analyzed by a 3420A gas chromatograph using a flame ionization detector (GC-FID). A DB-5 capillary column (32 m length and 0.25 mm inner diameter) was used for the separation. Nitrogen was used as a carrier gas at a flow rate of 5 mL/min. The column temperature program used was: 100 °C for 3 min, heating rate of 6 °C/min up to 280 °C and maintaining for 10 min. The injector and detector temperatures were set at 280 and 300 °C, respectively.

Experimental design

Central composite design (CCD) which is the most popular response surface method (RSM) was selected for design of the experiments. All factors are studied in five levels (- α , -1, 0, +1 and + α) and the significance of the results is tested. Equation (1) is applied to transform a real value of each variable (X_i) to a dimensionless coded value (x_i) for statistical calculations [27]:

$$x_i = (X_i - X_0) / \delta X \quad (1)$$

where X_0 is the real value in the central point and δX is the distance between the real value in the central point and real value in the superior or inferior level of the variable [27]. In this study, the reaction temperature (X_1), initial H_2O_2 /sulfur mole ratio (X_2) and catalyst dosage (X_3) are chosen as three independent control variables. Levels of these variables and the central composite design including four replicate at the central point (eighteen oxidation experiments) are shown in Tables 1 and 2, respectively. In the designed experiments, the effect of temperature variation is investigated from ambient to below n-hexane boiling point (67 °C) in order to avoid solvent evaporation. Also, the variation effect of H_2O_2 /sulfur ratio is studied using excess amount of oxidant (H_2O_2 /sulfur ratio > 2) to ensure the presence of available oxidant for DBT oxidation. High and low axial levels of catalyst dosage were specified by range finding experiments.

The response is the yield of desulfurization in the oxidation reaction as the dependent variable which is calculated from:

$$Y = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where C_0 and C_t are initial and final sulfur concentration (ppm) in the oil phase of the reaction mixture, which was determined by GC-FID analysis.

For statistical modeling, as well as description and optimization of the response, a quadratic model was chosen and fitted to the results according to [27]:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where Y , k , β_0 , x_i and ε represent the predicted response, number of variables, constant term, independent variables, and residual associated to the experiments, respectively; β_i , β_{ii} and β_{ij} represent linear, quadratic and interaction coefficients, respectively [27].

RESULTS AND DISCUSSION

Evaluation of the developed model

The results of desulfurization at experimental conditions were listed in Table 2. The yield of desul-

Table 1. The levels of variables in CCD

Variable	Low axial ($\alpha = -1.68$)	Low factorial (-1)	Center (0)	High factorial (+1)	High axial ($\alpha = +1.68$)
X_1 : Temperature (°C)	25	33.1	45	56.9	65
X_2 : H_2O_2 /sulfur mole ratio	2.5	4.43	7.25	10.07	12
X_3 : catalyst dosage (mL)	0.1	0.28	0.55	0.82	1

Table 2. Experimental plan and results of DBT oxidation

Run	Coded value of variables			Actual value of response
	Temperature (x_1)	H_2O_2 /sulfur (x_2)	Catalyst dosage (x_3)	Desulfurization yield, %
1	-1	-1	-1	33.1
2	+1	-1	-1	78.8
3	-1	+1	-1	15.0
4	+1	+1	-1	81.0
5	-1	-1	+1	62.6
6	+1	-1	+1	96.8
7	-1	+1	+1	45.8
8	+1	+1	+1	95.3
9	-1.68	0	0	34.4
10	+1.68	0	0	96.3
11	0	-1.68	0	72.4
12	0	+1.68	0	59.1
13	0	0	-1.68	22.0
14	0	0	+1.68	84.1
15	0	0	0	69.2
16	0	0	0	64.5
17	0	0	0	66.6
18	0	0	0	71.0

furization was varied from 15 to 96.8%. Design Expert (DX 7) was employed for determination of the response model coefficients and the statistical analysis of the results. The predicted quadratic model was obtained as follows:

$$Y = +67.70 + 21.93X_1 - 4.14X_2 + 14.43X_3 + 4.45X_1X_2 - 3.50X_1X_3 - 0.30X_2X_3 - 0.32X_1^2 - 0.18X_2^2 - 4.67X_3^2 \quad (4)$$

where X_1 , X_2 and X_3 represent the temperature, H_2O_2 /sulfur ratio and catalyst dosage, respectively. All the variables are in terms of coded values. The presented results of analysis of variance (ANOVA) in Table 3 indicate that the developed quadratic model is significant for prediction of yield of desulfurization under the studied experimental domain. The P -value (< 0.05) shows that the fitted model is significant by 95% confidence.

The comparison of the predicted and actual values of the sulfur elimination yield is presented in Figure 1. The high value of correlation coefficient ($R^2 = 0.97$) indicates that the proposed mathematical model is well fitted to the experimental data.

Consideration of main variables effects

According to the previous studies and our experimental results, the reversible reaction of formic acid with H_2O_2 produces peroxyformic acid (Scheme 1a) as a high active oxidant which can efficiently oxidize DBT to respective sulfoxide (DBTO) and then to respective sulfone (DBTO₂), as shown in Scheme 1b and c, respectively. Filippis *et al.* [28] conducted a kinetic and mechanism study on the peroxyformic acid formation in H_2O_2 /formic acid system at temperatures ranging 30–60 °C, which is very close to our present experimental conditions. No hydrogen bonded dimer pairs were postulated and observed by Filippis *et al.* in their proposed reaction kinetics and mechanism at the investigated conditions. Therefore, the global reaction mechanism in Scheme 1 for H_2O_2 /formic acid ODS system is different from that proposed by Heimlich and Wallace [29] based on dimeric oxidizing agent for ODS of white oil solutions in a H_2O_2 /acetic acid system at 50–100 °C. No DBTO was observed by GC-FID analysis of the oxidized DBT in n-hexane solution that confirmed a rapid oxidation of DBTO to DBTO₂. Moreover, thermal decomposition of H_2O_2 can occur at our experimental condition

Table 3. ANOVA results of the response model

Item	Degree of freedom	Sum of squares	Mean square	F value	$P > F$
Model	9	10190.6	1132.3	27.8	< 0.0001
Residual	8	326.2	40.8	-	-
Total	17	10516.8	-	-	-

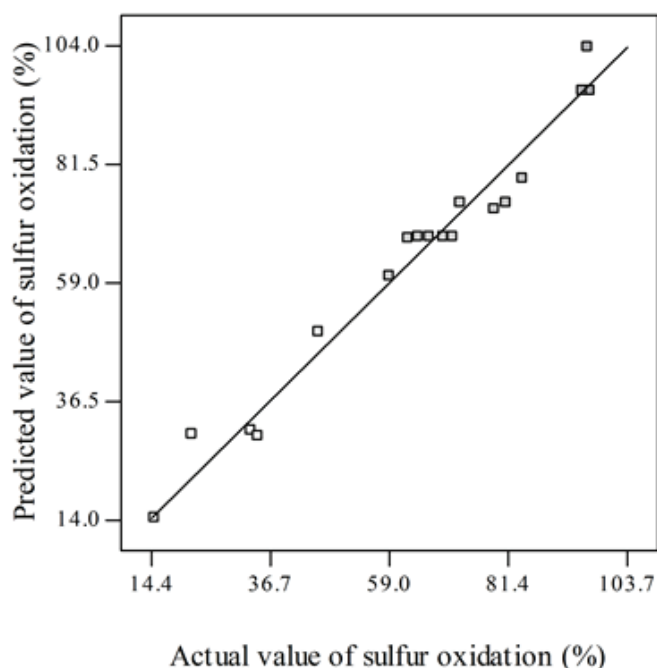


Figure 1. Predicted vs. actual values of the response ($R^2 = 0.97$).

To display and compare the combined effects of two variables, three-dimensional response surface and the corresponding contour plots obtained from the fitted model are shown in Figure 3a-c. Each of these plots shows the effect of variation of two inde-

pendent variables in the studied experimental range on the response, while the third variable is fixed at its central level.

Figure 3a illustrates that both temperature and catalyst amount have positive significant effects on

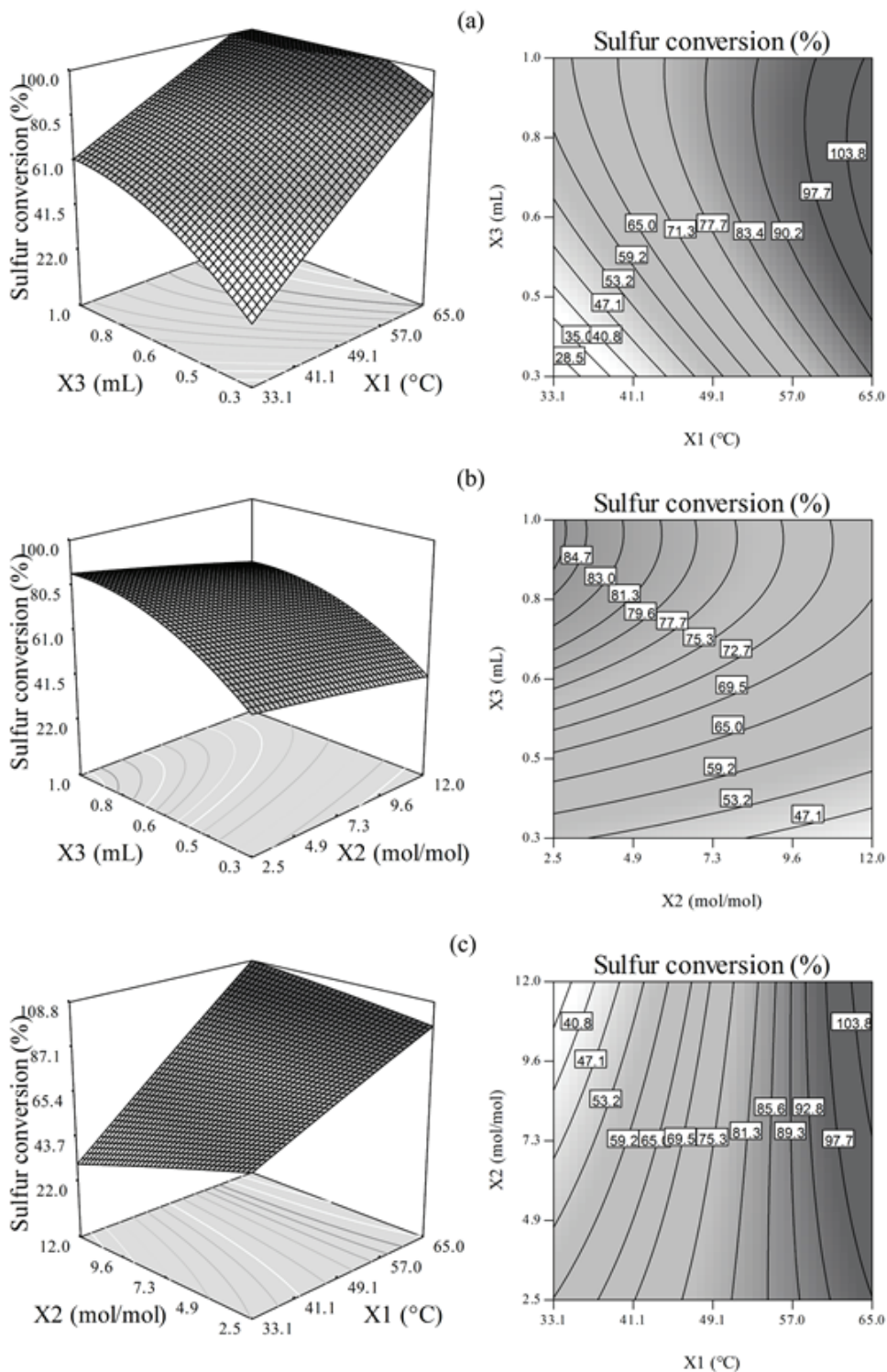


Figure 3. Response surface and contour plots of variables effects.

the response, but the influence of temperature is slightly more pronounced. Figure 3b indicates that at central level of temperature (45 °C), the increase of excess H₂O₂/sulfur ratio does not enhance the yield of DBT oxidation with hydrogen peroxide and formic acid mixture as the oxidizing system, because of the steric hindrance of water which has been in attendance of H₂O₂ aqueous solution. Thus, as shown in Figure 3b, the effect of formic acid is much stronger than H₂O₂ for improvement the formation of peroxyformic acid (Scheme 1a), and then the oxidation of DBT (Scheme 1b and c). The combined effect of temperature and H₂O₂/sulfur ratio shown in Figure 3c, illustrates that except at high temperatures (above 56 °C), the higher yields of sulfur elimination are located at lower H₂O₂/sulfur ratios near the stoichiometric value of 2. In addition, Figure 3c can confirm the interaction between temperature and H₂O₂/sulfur ratio, previously shown in Figure 2. As a result, the water hindrance of excess H₂O₂ aqueous solution in desulfurization progress is in contrast with the effect of excess reactant for the further formation of unstable active intermediates at high temperatures and reparation of H₂O₂ concentration declined due to the thermal decomposition. Hence, the control and optimization of these operational variables should be very important for the maximum yield of sulfur elimination in this system.

Determination of the optimal conditions by proposed model

The purpose of response surface optimization in this research is to find the optimal process conditions for maximum yield of sulfur elimination. Moreover, minimizing H₂O₂/sulfur ratio and catalyst consumption are the other two principal targets for the industrial interests. Table 4 shows the results of three optimal cases obtained by the regression model based on the aforementioned targets. In the first case, the objective is only the maximization of sulfur elimination yield. This has been achieved as 96% when the temperature is 57 °C, H₂O₂/sulfur molar ratio is 7.3 and catalyst dosage is 0.81 mL. The objective in second case is maximizing the yield of sulfur elimination and

minimizing H₂O₂/sulfur ratio together. Here the model suggests that temperature of 57 °C, H₂O₂/sulfur molar ratio of 2.5 and catalyst dosage of 0.82 mL are the optimal conditions predicting a yield of 95% for desulfurization process. This means that for 1% growth in process yield from 95 to 96%, H₂O₂/sulfur ratio is to be increased from 2.5 to 7.3 which does not seem economical. The third case deals with the most general situation when the objective is maximizing yield of sulfur elimination along with minimization of H₂O₂/sulfur ratio and catalyst consumption. In this case the model reveals that the temperature of 57 °C, H₂O₂/sulfur ratio of 2.5 and catalyst dosage of 0.4 mL are the optimal conditions leading to maximum yield of 80% for sulfur elimination.

Validation of the model

The desulfurization process was carried out under predicted optimal conditions to validate the statistical model and optimization. The obtained experimental results are presented in the last column of Table 4. Comparison between predicted and actual values of maximum desulfurization yields indicates a good agreement (less than 4% error).

CONCLUSION

Efficient oxidation of DBT with H₂O₂ and formic acid catalyst was modelled and optimized by central composite design. The results indicated that temperature was the most effective variable on the oxidation mechanism. At high temperatures, thermal decomposition of H₂O₂ and instability of peroxyformic acid intermediates led to increase oxidant usage for DBT oxidation. The maximum yield of desulfurization and the use of minimum amount of oxidant and catalyst were the main targets for optimization. The results showed that after 1 hour, the maximum yield of desulfurization (95%) is achieved at temperature of 57 °C, minimum H₂O₂/sulfur ratio of 2.5, while catalyst (formic acid) dosage was 0.82 mL in 50 mL of model hydrocarbon. The actual optimum result obtained from experiment (93%) was in good concurrence with the predicted result.

Table 4. Optimum process conditions and desulfurization results

Case	Target	X ₁ / °C	X ₂	X ₃ / mL	Predicted desulfurization yield, %	Actual desulfurization yield, %
1 Desulfurization yield	Maximize	57	7.3	0.81	96	97
2 Desulfurization yield	Maximize	57	2.5	0.82	95	93
H ₂ O ₂ /sulfur ratio	Minimize					
3 Desulfurization yield	Maximize	57	2.5	0.40	80	83
H ₂ O ₂ /sulfur ratio	Minimize					
Catalyst dosage	Minimize					

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NAUČNI RAD

OPTIMIZACIJA OPERATIVNIH USLOVA OKSIDACIJE DIBENZITIOFENA U MODELU LAKOG UGLJOVODONIKA

U ovom radu je proučavan uticaj promenljivih parametara na efikasnost i mehanizam oksidacije dibenzotiofena u sistemu mravlja kiselina/H₂O₂ u procesu duboke desulfurizacije modela lakog ugljovodonika statističkim modelovanjem i optimizacijom pomoću metode odzivne površine i centralnog kompozitnog plana. Razvijen je kvadratni regresioni model radi predviđanja prinosa oksidacije sumpora kao odgovor primenjenog modela. Na osnovu modela je zaključeno da je temperatura najznačajniji faktor i da je interakcija između temperature i odnosa H₂O₂/sumpor veoma važna; na temperaturama iznad 56 °C, neophodan je višak oksidanta zbog nestabilnosti aktivnih perokso intermedijera i gubitka H₂O₂ usled termičkog razlaganja. Nasuprot tome, uticaj sternih smetnji vode u vodenom peroksidnom rastvoru u procesu desulfurizacije je značajniji na temperaturama manjim od 56 °C. U procesu optimizacije, minimiziranje odnosa H₂O₂/sumpor i potrošnje katalizatora pri maksimalnom prinosu desulfurizacije je od ekonomskog značaja. Maksimalni prinos oksidacije od 95% ostvaren je nakon 1 h pri sledećim optimalnim uslovima: temperatura 57 °C, molski odnos H₂O₂/sumpor 2,5 i količina katalizatora 0,82 ml u 50 mL rastvora DBT u n-heksanu. Postignuto je dobro slaganje između predviđenih i eksperimentalnih rezultata, sa greškom manjom od 4%.

Ključne reči: oksidativna desulfurizacije, metoda odzivne površine; centralni kompozitni plan; dibenzotiofen; laki ugljovodonik.