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# Experimental Design of Oxidative Desulfurization of Kerosene Through Response Surface Methodology (RSM)

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## Keywords:

Analysis of Variance (ANOVA); Composite Nanocatalyst; Experimental Design; Oxidative Desulfurization.

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**Abstract:** Sulfur compound content in fuels is one of the most undesirable pollutions regarding standard environmental regulations that demand to reduce sulfur concentration limit to 5-10% in fuels. Hence, kerosene's oxidative desulfurization (ODS) as a model fuel (sulfur content 1158ppm) with air as an oxidant is studied. The goal of the study is to use two different synthesized nanosilica-supported catalysts, CuO/SiO<sub>2</sub> (CAT-1) and CuO/TiO<sub>2</sub>-SiO<sub>2</sub> (CAT-2), for the ODS of kerosene. Thirty-two experimental runs were designed via Central Composite Design (CCD) to select the experiments that will be utilized most efficiently. The analysis of variance (ANOVA) was used for statistical analysis to determine the models' significance. The Response surface methodology (RSM) was used to determine the optimum conditions and parameters significantly affecting the response. Temperature and time are two variables studied due to their impact on oxidative desulfurization. The actual results of sulfur conversion in kerosene from lab experiments were 87% with a sulfur content of 153.3ppm and 99.22% with a sulfur content of 8.9ppm by CAT-1 and CAT-2, respectively, at conditions of 140°C and 100min. The predicted results from experimental design were 86.66% and 99.8% by CAT-1 and CAT-2 at conditions of 140°C and 100min, showing errors less than 3.1% and 1.2% for CAT-1 and CAT-2, respectively, from ANOVA. The optimal parameters of ODS were determined through the sulfur conversion maximization by numerical optimization via ANOVA. The results showed that the maximum conversion by CAT-1 was 99.5% at 140 min and 180°C, and by CAT-2 was 99.7% at 100.1 min and 140.1°C. Also, the rate data were fitted with an empirical kinetic model. The results showed that CAT-1 and CAT-2 activation energies were  $E_a = 28.2$  kJ/mol and  $E_a = 38.7$  kJ/mol, respectively.

## التصميم التجريبي لازالة الكبريت باكسدة الكيروسين من خلال منهجية سطح الاستجابة (RSM)

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### الخلاصة

تمت دراسة إزالة الكبريت المؤكسدة (ODS) من الكيروسين كوقود نموذجي مع الهواء كمؤكسد باستخدام محفزين مختلفين مدعومين بالنانو سيليكيا، وهما CuO / SiO<sub>2</sub> (CAT-1) و CuO / TiO<sub>2</sub>-SiO<sub>2</sub> (CAT-2)، والتي وُجد أنها تعطي 87% و 99.22% تحويل كبريت في الكيروسين على التوالي. كانت مادة الكيروسين موضوع تحقيق تجريبي في هذه الدراسة. درجة الحرارة والوقت هما متغيران تم دراستهما فيما يتعلق بتأثيرهما على إزالة الكبريت. تم تطبيق منهجية سطح الاستجابة أو RSM لهذا الغرض. بناءً على التصميم المركب المركزي (CCD)، تم اختيار وقت ودرجة الحرارة لتحسين التحويل. أظهرت النتائج أن الحد الأقصى للتحويل الذي تنبأ به CAT-1 كان 99.5% عند 140 دقيقة و 140.1 درجة مئوية وبواسطة CAT-2 كان 99.7% عند 100.1 دقيقة و 140.1 درجة مئوية. لوحظ أن التحويل الأقصى المتوقع بواسطة CAT-1 كان 99.5% عند 140 دقيقة (وقت) و 180 (درجة حرارة) وبواسطة CAT-2 كان 99.7% عند 100.1 دقيقة (وقت) و 140.1 (درجة حرارة). تم تزويد بيانات المعدل بنموذج حركي تجريبي. تم تحديد طاقة التنشيط لـ CAT-1 و CAT-2 لتكون  $E_a = 28.2 \text{ kJ/mol}$  و  $E_a = 38.7 \text{ kJ/mol}$ ، على التوالي. الكلمات الدالة: تحليل التباين (ANOVA)، محفز النانو المركب، تصميم تجريبي، نزع الكبريت التأكسدي.

### 1. INTRODUCTION

Kerosene, diesel, and gasoline are common fuels essential for technological growth in industry and transportation applications. Sulfur content in kerosene can reach 2000 ppm [1], which is mainly composed of dibenzothiophene (BDT), benzothiophene (BT), and their alkylated derivatives. Sox gas is produced during the combustion process of sulfur [2], and it reacts with atmospheric water vapor to produce acid rain, which harms ecosystems, forests, and buildings [3]. As a result, immediate action is required to mitigate the negative effects of sulfur emissions. For that, strict environmental requirements are used worldwide to limit the kerosene sulfur content and other fuels to less than or equal to 10 ppm [4]. Desulfurization refers to the process of removing sulfur compounds from fuel. In industrial applications, Hydrodesulfurization (HDS) is the most commonly used desulfurization process for fuel oil [5]; however, it has numerous drawbacks, such as high energy needs and high running expenses due to difficult process conditions of high temperatures (300-400 °C) and pressures (3-6MPa) and poor reactivity of aromatic sulfur compounds [4]. Therefore, research in the alternative HDS method has been studied to address these limitations. The oxidative desulfurization (ODS) process is a new technology that uses ambient pressure and temperature conditions that solve HDS concerns [6]. The ODS requires a two-step procedure to transform sulfur compounds into their sulfone equivalent. In the first step, the ODS reaction oxidizes sulfur to sulfones (1-oxides) and sulfoxides (1,1-dioxide) [7]. The second step is a phase separation by solvent extraction to remove sulfur compound oxidants from the oxidized product sample [8]. Using an efficient catalyst for ODS is essential. Many types of composite catalysts and different

supports could be synthesized [9]. The clear advantage of composite catalysts is their high surface area, active surfaces to oxidize the sulfur compounds, and easy separation from the subsequent oxidized oil. Nanosilica has been used as support for the most nano-catalysts [10]. CuO nanoparticles create distinct optical, semiconductor, magnetic, and electrical capabilities among metals utilized in ODS. CuO is recognized as a safe, low-cost, and readily accessible material [11]. As an active metal, it is loaded on certain supports using a wet impregnation approach to produce catalysts with greater optical adsorbents, particularly with SiO<sub>2</sub> supports [12] and more stable catalysts [13]. SiO<sub>2</sub>-TiO<sub>2</sub>-based catalysts are promising techniques to maintain optimal adherence and activity for ODS processes. Silica combined with TiO<sub>2</sub> is considered an appropriate support for the Cu oxides to generate a highly effective catalyst [14]. As a result, the catalyst system becomes more cost-effective significantly for the ODS process. As an oxidant, the composite catalyst combines with air to form an intermediate product better at oxidizing sulfur compounds found in fuel oils [15]. Moreover, experimental design and optimization of the CuO/SiO<sub>2</sub> and CuO/TiO<sub>2</sub>-SiO<sub>2</sub> catalysts in the ODS system have yet to be conducted. The response surface methodology (RSM) combines statistical and mathematical methods to set experimental models [16] through two steps function estimation and the experimental design. The number of previous works studied using RSM to minimize the experimental data to achieve the best operating conditions for desired response in the ODS process field of different transportation fuels and other fields. For example, Ghahremani, Nasri, and Eikani [17] studied the optimization and statistical analysis of ODS of Iranian heavy crude oil by performing ultrasonic waves, using

acetic acid as a catalyst, PTA as a phase transfer agent, and  $H_2O_2$  as oxidant. The applied parameters were temperature at 60–80 °C, power at 10–15W/ml, catalyst (4.8–19.2wt%), and PTA (0–1wt%) with constant time at 10min through 27 experiments. The Box Behnken Design (BBD) showed a good agreement between the experimental and model results with a regression coefficient of 0.9. The optimization results showed a temperature of 72.47 °C, power of 14.63 W/ml, PTA of 0.79 wt%, catalyst of 4.84 wt%, and desulfurization of 45.10 wt%. Zaid et al. [18] reviewed many studies about using RSM for different chemical processing optimization. According to the recent studies they reviewed, RSM effectively optimized biodiesel in fats and oils made from various feedstocks. The Response Surface Methodology is the most cost-effective methodology for optimizing environmentally friendly and sustainable methodologies for multiple experimental procedures. Owolabi et al. [19] utilized central composite design (CCD) to plan twenty experiments and adopted RSM to evaluate the effect, interplay, and interaction of various process factors on the biodiesel output utilizing methanol and castor oil as feedstocks in the presence of bovine bones as a bio-catalyst. The model was subjected to ANOVA tests to determine the process variables' relative importance. At 60°C, 120 min, a molar to oil ratio of 6:1, a catalyst concentration of 10% w, and a stirring velocity of 900 rpm, an optimal yield of 95.12% was attained. This study's underlying innovation focuses on synthesizing and integrating experimental design and numerical optimization of nanosilica composite catalysts in the ODS method application. Also, it fills a research gap in the literature by using only one sort of nanosilica support. The design of experiments (DOE) approach was used to select the experiments that would be utilized most efficiently [20]. In this study, two new synthetic composite catalysts of  $CuO/SiO_2$  and  $CuO/TiO_2-SiO_2$  were used in the ODS process of a kerosene sample under reaction conditions (temperature and time). In investigating the sulfur removal in the ODS process, the examined parameters included temperature and time and analyzing the built model.

## 2. MATERIALS AND METHODOLOGY

### 2.1. Materials

Copper nitrate tri-hydrate solid, extra pure, and sodium silicate solid were attained from Sober Life company-Sigma Aldrich. Titanium isopropoxide (TTIP) (97% purity) was purchased as a liquid from Razan Company-Sigma Aldrich. Absolute ethanol (97% purity) and Sulfuric acid (98% purity) were obtained from Lab City Company-Sigma Aldrich. The

kerosene sample (1158ppm) was acquired from North Refineries Company-Iraq. The air as an oxidant has been supplied through a compressor.

### 2.2. Preparation of Nanosilica-Supported Catalysts

#### 2.2.1. Preparation of Nanosilica Support

Sol-gel technique was used to prepare nanosilica support for two types of catalysts [21]. To prepare the sodium silicate solution, 40g of sodium silicate was dissolved in 100 mL of distilled water and mixed for two hours above a heating magnetic stirrer at room temperature. After that, drops of sulfuric acid (98%) were added to the solution with stirring until pH decreased to 2, and a gel state was noticed. The gel aged for 24 hours at room temperature. Then filtered using Whatman No.41 filter paper and washed many rounds with vacuum pump assistance to save time till the gel pH was 7. Finally, the pure gel was dried in an oven at 110°C and 24h, then calcined at 500°C for one hour in a muffle furnace to get 6g of nanosilica powder.

#### 2.2.2. Preparation of $CuO/SiO_2$ and $CuO/TiO_2-SiO_2$ Catalysts

Two types of catalysts, i.e., 15% $CuO$ / 85%  $SiO_2$  (CAT-1) and 15% $CuO$ / 10% $TiO_2$ -75% $SiO_2$  (CAT-2), were synthesized utilizing the wet impregnation method [22]. For 3g of CAT-1, firstly, Cu metal solution was prepared by dissolving 1.4g of copper nitrate in 56 mL of distilled water and mixing for 30min using an ultrasonic mixer. Then it was loaded over 2.55g of nanosilica support with continuous mixing via a magnetic stirrer for one hour. As the gel was noticed, the solution was dried in an oven at 110 °C and 12 hours, then calcination in a furnace at 500°C for three hours. CAT-2 was prepared with two steps. In the first step, TTIP was loaded over nanosilica support. Hence, 15g of nanosilica was dissolved in 70 mL of ethanol. Then a solution of 0.7mL HCl, 20mL ethanol, and 3mL of  $H_2O$  was prepared and added to the dissolved nanosilica over a magnetic stirrer for one hour until gel was attained. Then another solution of 11.9mL TTIP and 40mL ethanol was added to the prepared gel drop by drop and stirred for two hours. After aging the gel for 24h, it was dried at 100 °C and 24h, then calcined at 500 °C and three hours [23]. In the second step, the copper metal was loaded over the prepared composite  $TiO_2-SiO_2$ . Hence, 11.5g of copper nitrate was dissolved in 100 mL of distilled water. Then the entire solution was loaded over the composite drop by drop with continuous stirring for two hours. The solution was left to precipitate overnight. At last, the precipitate was dried at 100°C and 24h, then calcined at 500°C and two hours to get 10g of catalyst.



### 2.3. Oxidative Desulfurization

#### Experiment Runs

The ODS desulfurization process was done in a lab-scale batch reactor system. A three-neck flask (250mL) was used to run ODS reactions of feed inside. One neck was connected with an air compressor to supply air reaching the bottom of the flask through a tube at an airflow rate of 4-5 L/min and at atmospheric pressure. The second neck was connected with a condenser to prevent kerosene's evaporation and allow air to exit the reactor. The third neck was used for the thermometer to insert the amount of catalyst for each run and withdraw the product after the run. The three-neck flask was fixed on a heating mantle to heat the reactor with magnetic stirring of reactants during the run. The batch reactor system is presented in Fig. 1. The process was conducted at reaction conditions, i.e., temperature 353, 373, 393, and 413 K and time 40, 60, 80, and 100 min). For each run, 50 mL of kerosene was added to the three-neck flask; once it reached the desired temperature, 0.5 g of synthesized catalysts were added, i.e., CAT-1= 15% CuO/ 85% SiO<sub>2</sub> and CAT-2 =15% CuO/ 10%TiO<sub>2</sub>- 75% SiO<sub>2</sub>, and the time was recorded. Once the time was over for each run, the system turned off, and the desulfurized kerosene was kept in a container to test the sulfur content.



**Fig.1** ODS Process of Oxidative Desulfurization of Kerosene via Batch Reactor. The sulfur conversion after the ODS process is calculated according to Eq. (1) [24]:

$$X_{sulfur} = 1 - \frac{C_{sulfur_{in}}}{C_{sulfur_{out}}} \quad (1)$$

where:

$X_{sulfur}$ : is the sulfur conversion.

$C_{sulfur}$ : is the sulfur concentration after the run

$C_{sulfur0}$ : is the initial sulfur concentration.

### 2.4. Experimental Design and Analysis of Variance (ANOVA)

An experimental design is a series of runs in which the input parameters of a particular configuration are modified to determine the output response's behavior. Experiments are used to test the performance of systems and processes in any domain [25]. In this study, the ideal parameters for the ODS process may be achieved through Central Composite Design (CCD) under consideration of Response surface methodology (RSM). RSM combines statistical and mathematical methods to set experimental models [16]. The RSM's benefit over the conventional full-factorial trial design is its economic viability while still considering interaction variables [26]. Also, the RSM aims to reduce the associated numerical noise of conventional ones by allowing for the application of a derivative-based algorithm [27]. Experimental data are fitted to two main equation models used in the RSM for ODS regarding coded values [28]. The first-degree equation is:

$$Y_i = b_o + \sum b_i x_i + \varepsilon \quad (2)$$

and the second-degree equation is:

$$Y_i = b_o + \sum b_i x_i + \sum b_{ii} x_i^2 + \sum b_{ij} x_i x_j + \varepsilon \quad (3)$$

where Y is the response;  $x_i$  and  $x_j$  are the variables;  $b_o$  is the constant coefficient;  $b_i$ ,  $b_j$ , and  $b_{ij}$  are the interaction coefficients of linear, quadratic, and second-order terms, respectively, and  $\varepsilon$  is the modeling error. The experimental design goal is to determine which parameters have the most significant effect on the response, to verify where to set the effective, controllable parameters so that the response is close to the preferred optimal value, resulting in low variability in the response, and to minimize the effect of uncontrollable parameters. The Experimental design tool (Design Expert 13) is used for RSM regression analysis. Design-Expert is used to carry out the design of experiments (DOE). It provides optimization, adaptable parameter design, combination designs, and mixture designs. Analysis of variance (ANOVA) is used to determine the statistical significance of various components. The effects of each component on the desired results are shown graphically, and variations in the data are shown graphically [29]. It is critical to analyze the model after it has been built. Models are evaluated using two methods: residual plots and lack of fit. Residual plots are several sorts of residual plots that are developed to ensure that there are no error-related patterns. The lack of fit is investigated using ANOVA data [27]. The variance can be analyzed in detail using a so-called analysis of variance (ANOVA) table. An ANOVA table can be used to: (i) determine whether a model is significant; for this purpose, it needs to perform

both regression plots and residual plots, (ii) check on its lack of fit, which is examined by comparing Fobs to the F-value, and (iii) analyze the model via R<sup>2</sup> values, the greater the value of R<sup>2</sup>, the better the model's ability to describe experimental data.

**3. RESULTS AND DISCUSSION**

**3.1. Experimental Results of ODS**

Table 1 shows all ODS runs result. According to the results, maximum sulfur conversion was 99.2% and 87% by CAT-1 and CAT-2, respectively, at 140°C.

**Table 1** The Results of ODS Experimental Runs.

Run	Reaction conditions		Final Sulfur content (%) (ΔS)		Conversion%	
	Temperature (K)	Time (min)	CAT-1	CAT-2	CAT-1	CAT-2
1	353	40	0.060	0.0492	0.48	0.57
2		60	0.054	0.0426	0.54	0.63
3		80	0.050	0.0364	0.57	0.69
4		100	0.044	0.0320	0.62	0.72
5	373	40	0.046	0.0345	0.61	0.70
6		60	0.042	0.0301	0.64	0.74
7		80	0.037	0.0271	0.68	0.77
8		100	0.032	0.0216	0.73	0.81
9	393	40	0.036	0.0275	0.69	0.76
10		60	0.032	0.0232	0.73	0.80
11		80	0.028	0.0191	0.76	0.83
12		100	0.022	0.0133	0.81	0.89
13	413	40	0.028	0.0116	0.75	0.90
14		60	0.024	0.0091	0.80	0.92
15		80	0.020	0.0046	0.83	0.96
16		100	0.015	0.0009	0.87	0.99

**3.2. Experimental Design and Statistical Analysis of Variance (ANOVA)**

An analysis of variance (ANOVA) was carried out based on the parametric response of sulfur oxidation to validate the relevance of the single and interaction parameters besides the oxidation in the response. Additionally, the ANOVA findings may be used to detect the need for more optimization studies using response surface methods. The data obtained from the analysis of variance through 2k factorial runs of ODS using CAT-1 and CAT-2 through the Design Expert software (v.13) is shown in Table 2. The model F-value of 1914.68 for CAT-1 indicates that the model is significant. The high F-value caused by noise rarely happened, with a 0.01% probability. The model terms are considered significant when the P-value is less than 0.05. In this instance, key model terms were A, B, AB, and A<sup>2</sup>. The model terms are insignificant if the value is higher than 0.1. However, this shows that the quadratic model is adequate for optimizing sulfur oxidants in kerosene. The model F-value of 324.35

**Table 2** Analysis of Variance (ANOVA) 2k Factorial Design of ODS for CAT-1 and CAT-2

Source	Sum of Squares*		Degree of freedom		Mean Square		F-value		p-value		Remark
	CAT-1	CAT-2	CAT-1	CAT-2	CAT-1	CAT-2	CAT-1	CAT-2	CAT-1	CAT-2	
<b>Model</b>	0.182	0.208	5	9	0.036	0.023	1914.7	324.3	< 0.0001	< 0.0001	significant
<b>A-A</b>	0.148	0.005	1	1	0.148	0.005	7764.7	67.6	< 0.0001	0.0002	
<b>B-B</b>	0.032	0.002	1	1	0.032	0.002	1687.7	26.3	< 0.0001	0.0022	
<b>AB</b>	0.0002	0.001	1	1	0.0002	0.0006	8.10	8.96	0.0174	0.0242	
<b>A<sup>2</sup></b>	0.0021	0.0005	1	1	0.0021	0.0005	112.3	6.5	< 0.0001	0.0434	
<b>B<sup>2</sup></b>	9.000E-06	0.0000	1	1	9.000E-06	0.0000	0.47	0.21	0.5074	0.6646	
<b>A<sup>2</sup>B</b>		0.0000		1		0.0000		0.481		0.5139	
<b>AB<sup>2</sup></b>		0.0001		1		0.0001		1.5		0.2617	
<b>A<sup>3</sup></b>		0.0017		1		0.0017		24.2		0.0026	
<b>B<sup>3</sup></b>		3.042E-06		1		3.042E-06		0.043		0.8433	
<b>Residual</b>	0.0002	0.0004	10	6	0.0000	0.0001					
<b>Cor Total</b>	0.1825	0.2088	15	15							

indicated that the model was significant. In this term, important model terms were A, B, AB<sup>2</sup>, and A<sup>3</sup>.

**3.2.1. Fit Statistic Analysis of Variance**

The model's R<sup>2</sup> correlation and p-value for lack of fit were used to confirm the model's fitness. Table 3 shows the statistical analysis findings for both catalysts, which revealed that the predicted R<sup>2</sup> and adjusted R<sup>2</sup> were reasonably in agreement with the difference between them was less than 0.2 for both catalysts. Adequacy of precision (Adeq precision) also has to do with the signal-to-noise ratio, which correctly reflects the signal's sufficiency. This may measure the contrast of the expected sulfur oxidation based on the error in the experimental run [26]. A ratio of at least 4 indicated a suitable signal; in this case, the observed adequate ratio was 141.5. The design space may be explored using this model. Thus, the sulfur oxidation reaction in the ODS process may be accurately predicted by the developed quadratic model equation based on the variable's temperature and time with just a little related error. Based on the accuracy, treatments were compared using the coefficient of variation (C.V.%). When the coefficient was low, the experiments were quite accurate. In ODS experiments, the resultant C.V.% of 0.63 based on the sulfur oxidation displayed remarkable consistency.

**Table 3** Analysis of Variance (ANOVA) Statistics for Response Surface Quadratic Model of CAT-1 and Cubic Model for CAT-2

	CAT-1	CAT-2
Std. Dev.	0.004	0.008
Mean	0.69	0.79
C.V. %	0.63	1.06
R <sup>2</sup>	0.999	0.998
Adjusted R <sup>2</sup>	0.998	0.995
Predicted R <sup>2</sup>	0.99	0.977
Adeq Precision	141.5	62.7

The independent variables and sulfur conversion percentage in kerosene from experimental and predicted responses of 16 runs for each CAT-1 and CAT-2 type are depicted in Table 4, which shows that the error between actual and predicted data was less than 3.1% and 1.2% for CAT-1 and CAT-2, respectively. Also, the Std Error of Design was the same for CAT-1 and CAT-2 AS was shown by 3D plot using ANOVA in Fig. 2.

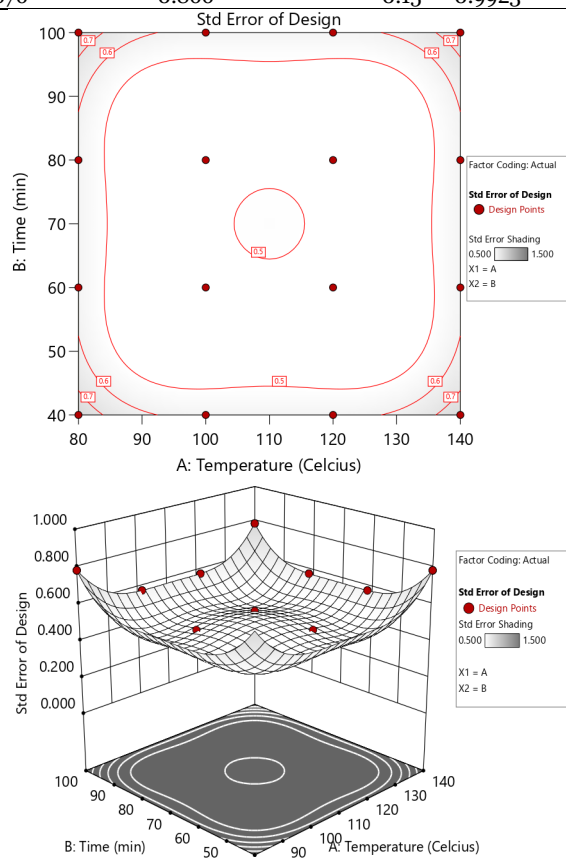
**3.2.2. Diagnostics for ODS Model**

Figs. (3, 4) show diagnostics for the ODS model for each CAT-1 and CAT-2, respectively. Fig. (a) shows the experimental runs versus residual values plot. The results presented no signs of patterns from points because of the scattered points. Fig. (b) displayed the normal distribution plot. The results illustrated the findings and established if the residual points adhered to a normal distribution. A model transformation is required if a pattern, such as the S-shape pattern, is seen in the plot. In this instance, the plot demonstrated that the dots are dispersed and devoid of any particular pattern. The data points are also close to the

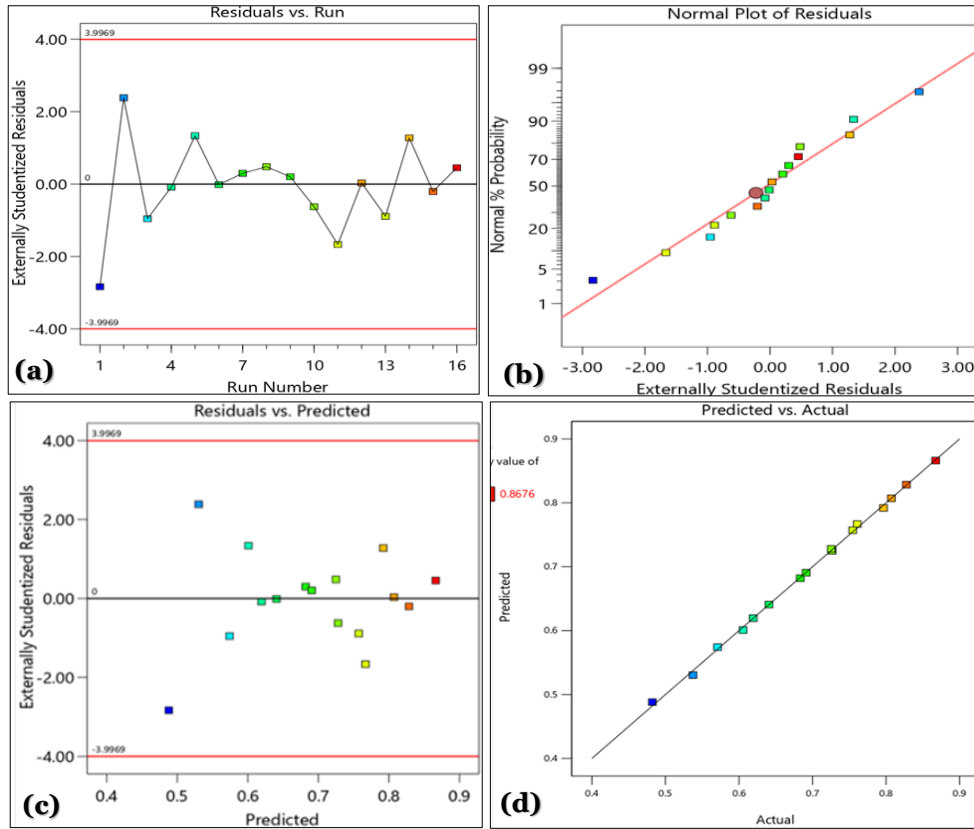
normal line, establishing a good model fit. Also, Fig. (c) shows the residuals compared to the expected response values. This result is used to confirm the requirement for further model modification. In this example, a pattern was not noticed for the points in this point. As a result, no transformation is necessary. Fig. (d) shows the performance of catalysts for ODS of kerosene by plotting exact predicted values from the model and actual values from the runs. The points are found to be close to the line. This indicates that predicted and actual sulfur oxidation in kerosene was in a high agreement and effective procedure as it indicated the fit model's quality.

**Table 4** Observed Responses from the ODS Process using CAT-1 and CAT-2

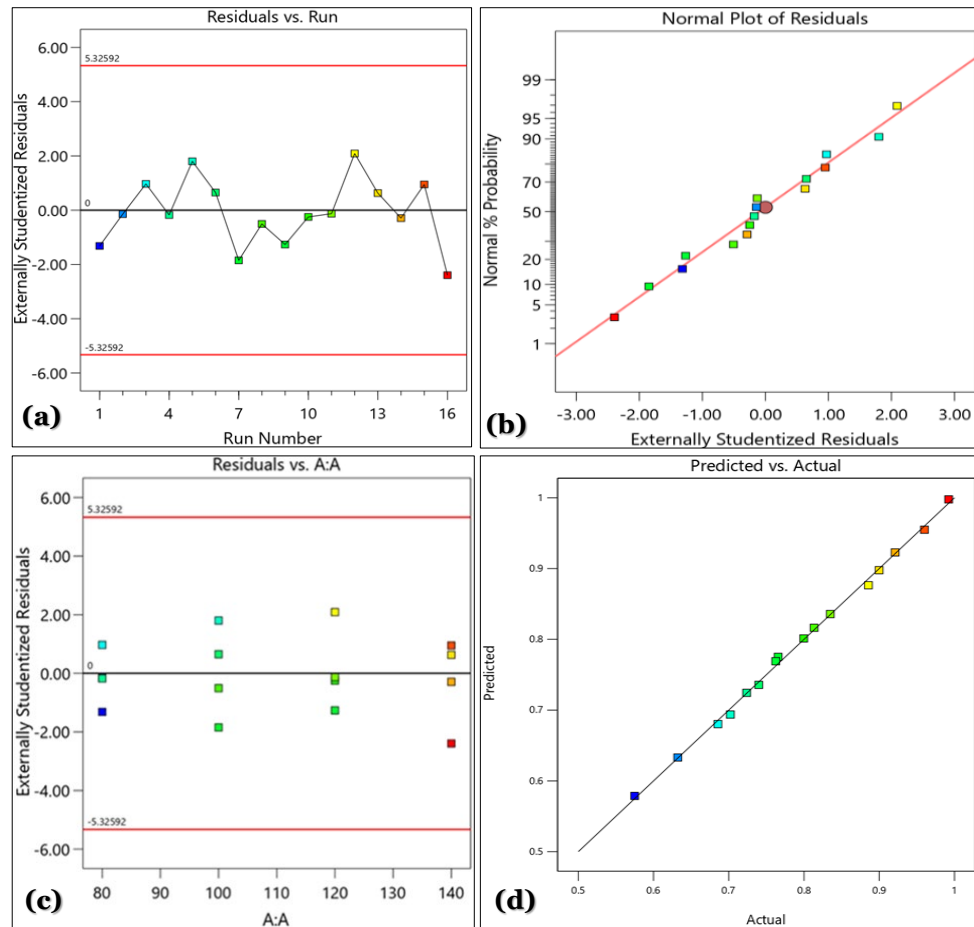
Run	Temp. (°C)	Time (min)	CAT-1			CAT-2		
			Actual Conversion (%)	Predicted Conversion (%)	Error (%)	Actual Conversion (%)	Predicted Conversion (%)	Error (%)
1	80	40	0.482	0.488	1.202	0.575	0.578	0.540
2	80	60	0.537	0.530	1.377	0.632	0.633	0.126
3	80	80	0.571	0.574	0.560	0.686	0.680	0.817
4	80	100	0.61930	0.60000	3.117	0.72380	0.72440	0.083
5	100	40	0.6193	0.620	0.032	0.702	0.694	1.196
6	100	60	0.6407	0.6407	0.000	0.7399	0.736	0.582
7	100	80	0.6833	0.682	0.178	0.7656	0.775	1.253
8	100	100	0.7267	0.725	0.25	0.8134	0.816	0.356
9	120	40	0.691	0.691	0.12	0.763	0.769	0.852
10	120	60	0.7255	0.728	0.33	0.7996	0.801	0.200
11	120	80	0.7609	0.767	0.78	0.8349	0.836	0.096
12	120	100	0.8073	0.807	0.01	0.8856	0.876	1.029
13	140	40	0.7548	0.7572	0.32	0.8998	0.898	0.234
14	140	60	0.797	0.792	0.57	0.921	0.923	0.185
15	140	80	0.8277	0.828	0.08	0.960	0.955	0.552
16	140	100	0.8676	0.866	0.15	0.9923	0.998	0.555



**Fig. 2** Std and 3D Error Plot of the Design for Catalysts.



**Fig. 3** Diagnostic Plots of (a) Residual vs. the Run, (b) Normal Plot of Residuals, and (c) Residuals vs. Predicted (d) Predicted vs. Actual for CAT-1.



**Fig. 4** Diagnostic Plots of (a) Residual vs. the Run, (b) Normal Plot of Residuals, (c) Residuals vs. predicted, and (d) Predicted vs. Actual for CAT-2.



### 3.2.3. The Effect of ODS Variables on Oxidative Desulfurization

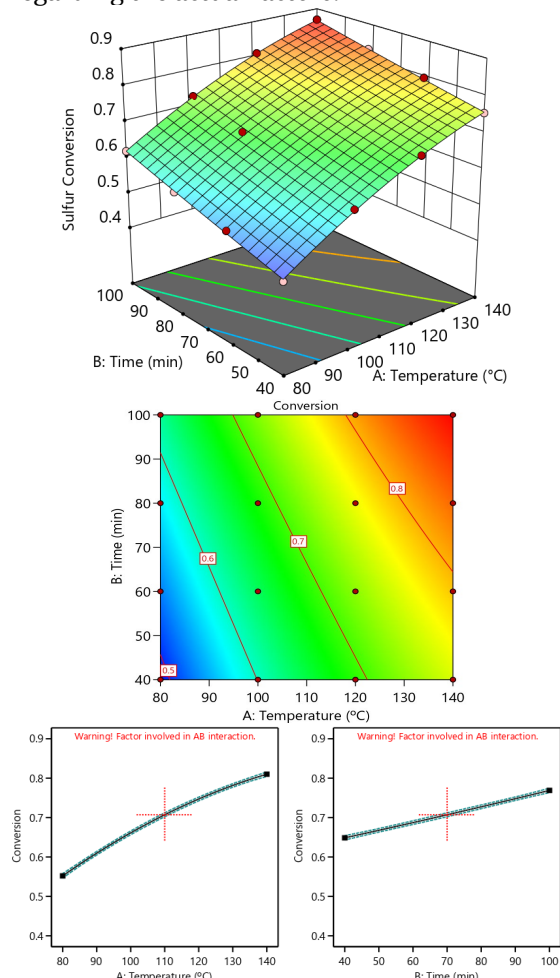
The model graphs were created after the diagnostic plots were analyzed. These graphs are useful for showing how each parameter affects the percent of sulfur removal by oxidation and showing the parameters' interactions. To anticipate the reaction at specific amounts of each variable, the quadratic equation, i.e., as suggested from ANOVA, for CAT-1 is used:

$$R_1 = -0.29 + 0.0111 A + 0.0024 B - 6.21 \times 10^{-6} A * B - 2.9 \times 10^{-5} A^2 + 1.87 \times 10^{-6} B^2 \quad (4)$$

where A is the temperature (°C), B is time (min), and R1 is conversion (%). In this case, each variable's level must be stated in its original units. The Cubic equation, i.e., as suggested by ANOVA, for CAT-2 is as follows:

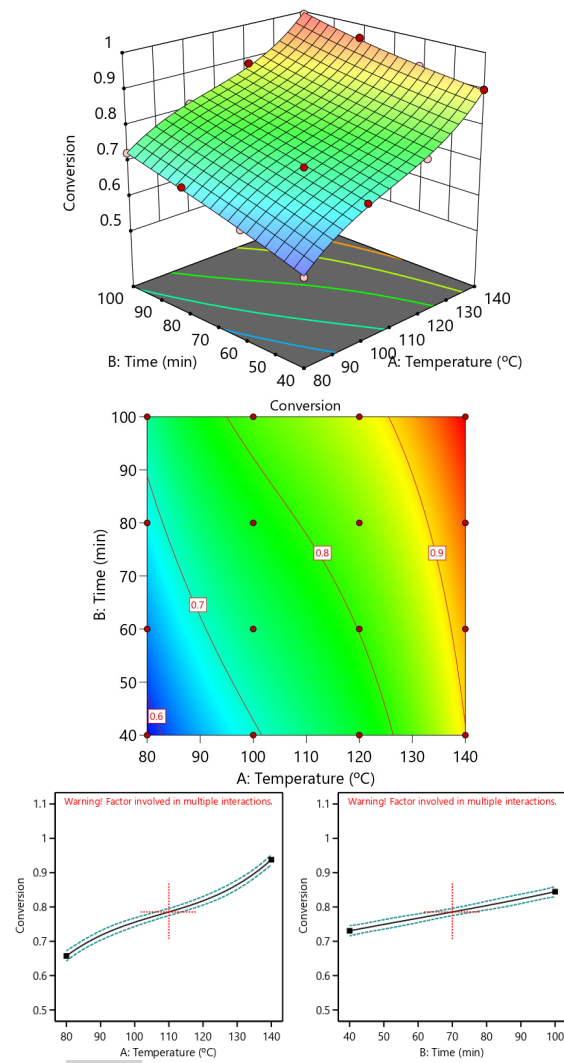
$$R_1 = -2.5 + 0.075 A + 0.0106 B - 9.0 \times 10^{-6} A * B - 6.4 \times 10^{-4} A^2 + 4.7 \times 10^{-6} B^2 + 1.64 \times 10^{-7} A^2 * B + 2.92 \times 10^{-7} A * B^2 + 1.94 \times 10^{-6} A^3 + 8.125 \times 10^{-8} B^3 \quad (5)$$

It is possible to predict the reaction for a certain amount of each element using both equations regarding the actual factors.



**Fig. 5** Contour and 3D Surface Plot of Temperature and Time Versus Sulfur Conversion for ODS by CAT-1 and Effect of the Interaction of Each Variable.

Figs. (5, 6) display the conversion of sulfur response surface graphs in the 3-D response surface plot. The maximum conversion observed was > 87% at 140 min for CAT-1 and 99.2% at 140 min and 140°C. Regarding the interaction plots for CAT-1 and CAT-2, the results showed that temperature and time conditions positively increased the sulfur conversion in kerosene during the ODS. As was confirmed through ANOVA results, both factors remarked with a p-value less than 0.05. The obtained trend could be attributed to increasing time during ODS, resulting in higher interaction between reactants and sulfur compounds to be oxide. As well as the reaction rate and activation energy are functions of reaction temperature; hence, once the oxidation reaction began, the rate of molecule adsorption and dispersion increased, resulting in increasing the sulfur conversion. In addition, it was observed from the one-factor interaction plot that temperature influenced sulfur conversion more than time for both CAT-1 and CAT-2.

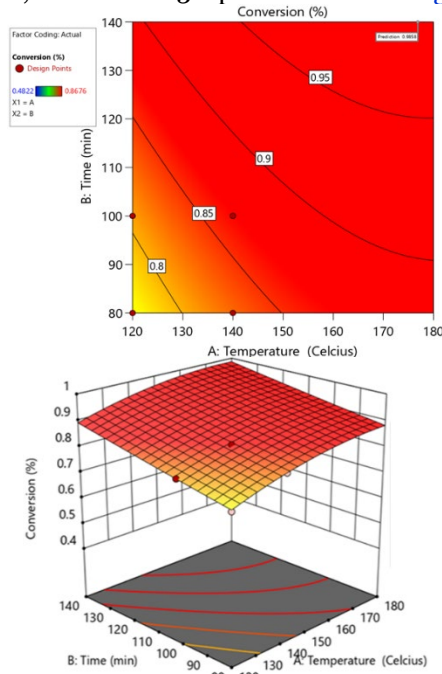


**Fig. 6** Contour and 3D Surface Plot of Temperature and Time Versus Sulfur Conversion for ODS by CAT-2 and Effect of the Interaction of Each Variable.



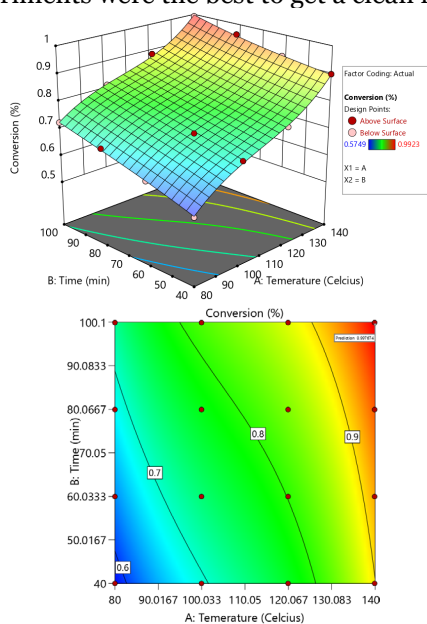
### 3.2.4 Numerical Optimization of ODS Process for CAT-1 and CAT-2

The sulfur oxidation was maximized using numerical optimization through using Design Expert program, and the results were used to calculate the ODS system's ideal parameters. After tests under reaction conditions, the best parametric conditions of 140 min and 180°C resulted in predicted oxidation of 98.5% for CAT-1, as the RSM 3D plot is shown in Fig.7.



**Fig.7** 3D-Plot of Numerical Optimization of CAT-1.

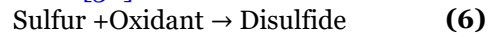
For CAT-2, the best parameter conditions were 100.1 min and 140.1°C to get the highest sulfur conversion, i.e., 99.7%, as the RSM 3D plot shown in Fig. 8. This result confirmed that the parameters used for this catalyst in the experiments were the best to get a clean fuel.



**Fig. 8** 3D Plot of Numerical Optimization of CAT-2.

### 3.3. Kinetic Model of Oxidative Desulfurization (ODS) Process

The sulfur removal kinetic model via oxidation was studied in a batch reactor system with different reaction conditions. The three-phase heterogeneous chemical reaction involved reactant sulfur in the organic phase, oxidant air in the aqueous phase, and solid phase of nanosilica-supported catalysts, i.e., CuO/SiO<sub>2</sub> and CuO/TiO<sub>2</sub>-SiO<sub>2</sub>. The reaction may be written as [30]:



Due to its simplicity, an empirical kinetic model was used to estimate the reaction rate without mass transfer. The chemical reaction may be considered by assuming the n<sup>th</sup>-order kinetics based on the first-order reaction rate as [31-33]:

$$-r_A = -\frac{dc_s}{dt} = k(C_s)^n(C_{O_2})^m \quad (8)$$

The term depending on O<sub>2</sub> concentration was ignored because too much air was taken in, i.e., higher oxygen content, ignoring the concentration shift of O<sub>2</sub> to sulfur concentration. The air was taken in excess amount, i.e., excess oxygen content, neglecting the concentration change of O<sub>2</sub> to sulfur concentration; thus, the term dependent on O<sub>2</sub> concentration was neglected. The reaction rate may be expressed as:

$$-r_A = -\frac{dc_s}{dt} = k(C_s)^n \quad (9)$$

where

$$k = (C_{O_2})^m \quad (10)$$

where *k* is the apparent rate constant. Eq. (12) was integrated with limit t = 0, C<sub>s</sub> = C<sub>o</sub> and t = t, C<sub>s</sub> = C<sub>t</sub>, and the following equation is obtained for the first-order reactions, i.e., n = 1:

$$-r_A = -\int_{C_{S_0}}^{C_S} \frac{dC_A}{dt} = \int_{C_{S_0}}^{C_S} k(C_S)^n \quad (11)$$

$$-\ln\left(\frac{C_S}{C_{S_0}}\right) = k.t \quad (12)$$

$$-k.t = \ln\left(\frac{C_{S_0}}{C_S}\right) \quad (13)$$

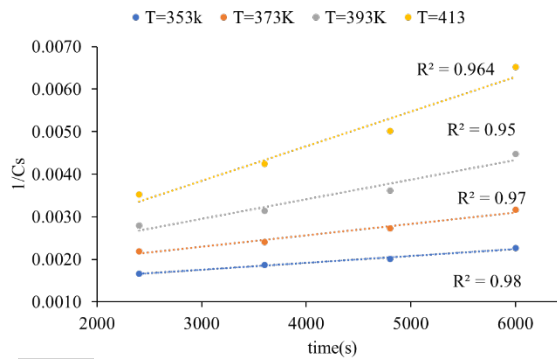
The second-order reaction rate equation could be used to determine the most accurate data about kinetics by comparing it with first-order reaction rate equation results using the following equation:

$$-\frac{dC_S}{dt} = k.(C_S)^2 \quad (14)$$

$$\frac{1}{C_S} - \frac{1}{C_{S_0}} = k.t \quad (15)$$

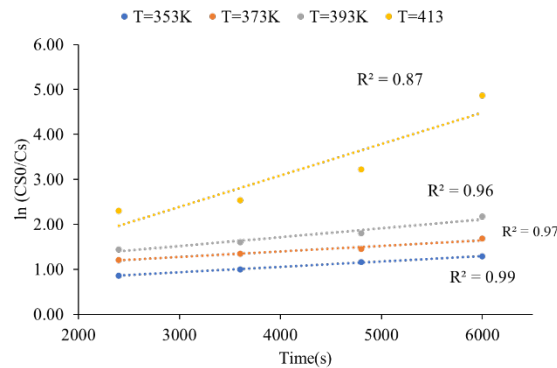
The (*k*) values were predicted through linear regression of plot  $\ln\left(\frac{C_{S_0}}{C_S}\right)$  versus time for the first-order reaction and plot of 1/C<sub>s</sub> versus time for the second-order reaction. After applying both first and second-order reactions for CAT-

1 and CAT-2, the most fitted data was selected for both catalysts. For CAT-1, the data were more fit and accurate by the second-order reaction. Fig. 9 shows the plot of  $1/C_s$  for CAT-1.



**Fig. 9**  $1/C_s$  Plot of the Second Order Reaction Versus Time at Different Temperatures for CAT-1.

For CAT-2, the data were more fit and accurate by the first-order reaction. Fig. 10 shows the plot of  $\ln\left(\frac{C_{S_0}}{C_s}\right)$  for CAT-2.



**Fig. 10**  $\ln\left(\frac{C_{S_0}}{C_s}\right)$  Plot of the First Order Reaction Versus Time at Different Temperatures for CAT-2.

The kinetic data fit well with the pseudo-first and order -order kinetic rate to the previous studies on the catalytic oxidation of sulfur compounds of fuel oils [28]. The kinetic results found for the model parameters for each catalyst type are stated in Table 5.

**Table 5** Kinetic Model Parameters Found using the First-Order Reaction Rate for CAT-2 and the Second-Order Reaction Rate for CAT-2.

Parameters	Predicted Vales		Unit
	CAT-1	CAT-2	
n	2	1	-
Correlation factor 1	0.9886	0.993	-
Correlation factor 2	0.9777	0.990	-
Correlation factor 3	0.9547	0.979	-
Correlation factor 4	0.964	0.87	-
$K_1$	0.0000002	0.0001	$s^{-1}$
$K_2$	0.0000003	0.0001	$s^{-1}$
$K_3$	0.0000005	0.0002	$s^{-1}$
$K_4$	0.0000008	0.0007	$s^{-1}$

### 3.4. Activation Energy for Oxidative Desulfurization Process

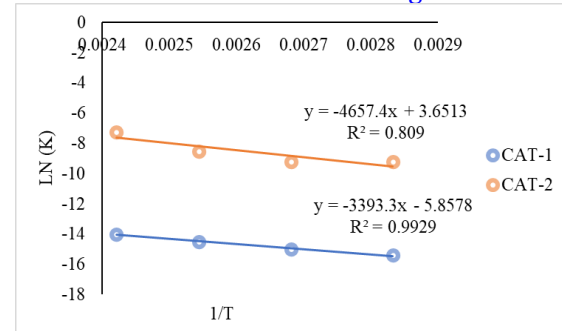
Activation energy could be found according to the Arrhenius equation. That was obtained through the plot of  $\ln\left(\frac{C_{S_0}}{C_s}\right)$  versus time and  $1/C_s$

versus time, which are linear plots depending on the Arrhenius equation, as shown in Eqs. (16, 17):

$$K_{in} = K_0 e^{\left(-\frac{EA}{RT}\right)} \quad (16)$$

$$\ln(K_{in}) = \ln K_0 - \frac{EA}{RT} \quad (17)$$

The rate constant (k) values were calculated from the plots of  $\ln\left(\frac{C_{S_0}}{C_s}\right)$  and  $1/C_s$  versus time; then, after getting the plot of  $\ln(k)$  versus  $1/T$ , its slope value is equal to  $(EA/R)$ . Other values will be inserted into Eq. 17 to get the exact amount of activation energy in the kJ/mol unit. The results of the Arrhenius equation plot for CAT-1 and CAT-2 are shown in Fig. 11.



**Fig. 11** Arrhenius Equation Plot for CAT-1 and CAT-2.

The activation energy mathematical results were  $E_a = 28.2116$  kJ/mol for CAT-1 and for CAT-2  $E_a = 38.721$  kJ/mol. The value of  $E_a$  depends on the catalyst type. The metal oxide CAT-1 needs less energy to start a chemical reaction than CAT-2, a composite.

## 4. CONCLUSIONS

This study found that the sulfur concentrations in kerosene could be effectively removed using synthesized nanosilica catalysts via the ODS approach. In the experimental runs, the sulfur compounds were successfully removed by CAT-1 and CAT-2 by 87% and 99.2%, respectively. The 2k factorial-design-based parametric response showed a significant model in the ODS process through CCD. The kinetic parameters were estimated by linear regression based on experimental findings. The optimized parameters for ODS were 140 min (time) and  $180^\circ\text{C}$  (temperature), resulting in the predicted sulfur conversion of 98.5% and 100.7% by CAT-1 and CAT-2, respectively. The first-order reaction rate approach showed more accurate data about CAT-2, and the second-order reactions showed more accurate data about CAT-1 for experimental data. Empirical kinetics from analysis of variance (ANOVA) showed a high accuracy regarding the error between the experimental and predicted data, as the P-values were less than 0.0500. Accordingly, the MAOD method may remove sulfur compounds while maintaining kerosene's essential qualities. It can be recommended for further research ideas that

the CAT-1 type improved more by producing the same catalyst with a different range of composite support TiO<sub>2</sub>-SiO<sub>2</sub> to give a higher conversion range.

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