

# Alumina supported polymolybdate catalysts utilizing *tert*-butyl hydroperoxide oxidant for desulfurization of Malaysian diesel fuel

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**Abstract**—The performance of oxidative desulfurization (ODS) of commercial diesel by alumina supported polymolybdate based catalyst system was studied using *tert*-butyl hydroperoxide (TBHP) as an oxidizing agent. From catalytic testing, MoO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> calcined at 500 °C was the most potential catalyst which gave the highest sulfur removal under mild condition. The sulfur content in commercial diesel was successfully reduced from 440 ppmw to 105 ppmw followed by solvent extraction. Response surface methodology involving Box-Behnken was employed to evaluate and optimize MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> preparation parameters (calcination temperatures, molybdenum loading precursor and catalyst loading), and their optimum values were found to be 510 °C, 0.98 g and 11.18 g/L of calcination temperature, molybdenum loading precursor and catalyst loading, respectively. Based on results, the reaction mechanism for oxidation of sulfur compounds to the corresponding sulfones occur in the presence of MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was proposed.

**Keywords:** Polymolybdates Catalyst, Oxidative Desulfurization, Commercial Diesel, Box Behnken Design, *Tert*-butyl Hydroperoxide

## INTRODUCTION

Diesel is extensively used as a fuel in highway transportation vehicles. Nevertheless, it suffers from associated particulate, NO<sub>x</sub> and SO<sub>x</sub> emissions that are harmful to human health and a major cause of acid rain. In many countries around the world, environmental regulations have been introduced to reduce the sulfur content of diesel fuel and other transportation fuels to ultra-low levels (10-15 ppmw) [1]. Hydrodesulfurization (HDS) is the conventional method for lowering sulfur levels in diesel oil, but this technology requires severe conditions and is expensive. Consequently, some progressive desulfurization technologies have been developed. Among these alternative processes, the oxidative desulfurization (ODS) combined with extraction is considered to be one of the promising processes [2,3]. Common available oxidative desulfurization (ODS) methods are now facing the problem of reducing sulfur content in diesel fuel to concentration nearly to 50 ppmw. The use of catalysts is vital in the oxidative desulfurization reaction. Various studies on catalytic oxidation systems have been reported such as *tert*-BuOCl/Mo-Al<sub>2</sub>O<sub>3</sub> [4], *tert*-BuOOH/Mo-Al<sub>2</sub>O<sub>3</sub> [5], and H<sub>2</sub>O<sub>2</sub>/Mo/Al<sub>2</sub>O<sub>3</sub> [6]. *Tert*-butyl hydroperoxide (TBHP) is the most widely used in the oxidation process, but requires an efficient catalyst. Recently [7] reported that MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was an active catalyst for the oxidation of dibenzothiophenic compounds. The development of alumina supported catalysts containing molybdenum and their evaluation in the oxidative desulfurization process of diesel fuel has been widely investigated. However, molybdenum containing phosphorus have not been widely used for its ability as a based catalyst

for the oxidative desulfurization. Therefore, it is interesting to explore the behavior of polymolybdate based catalysts in the ODS reaction of commercial diesel under mild condition in this paper. The potential catalyst was used to investigate the activity of the catalyst. Design of experiments (DOE) is a statistical method used for process characterization, modeling, and optimization. Implementation of DOE allows us to see how parameters interact and how the whole system functions. With DOE, empirical mathematical models are obtained, which enables us to predict responses for all possible inlet factor combinations. With these models it is possible to optimize critical factors and identify the best combination of value [8]. Box-Behnken design (BBD) is the most frequently employed and offers some advantages, requiring few experimental points and high efficiency [9]. A Box-Behnken design was applied to determine the optimum sulfur removal, and also to explain the relationships between sulfur removal and three parameters, calcinations temperature, molybdenum loading precursor, and catalyst loading. Finally, a mechanism of the process, combining metal - catalyzed oxidation was proposed.

## EXPERIMENTAL METHOD AND MATERIAL

### 1. Materials and Methods

All solvents and reactants were purchased and used without further purification of phosphomolybdic acid hydrate (Across Organic),  $\lambda$ -Al<sub>2</sub>O<sub>3</sub> beads 3-5 mm diameter (Sigma-Aldrich), *tert*-butyl hydroperoxide 70 wt% in water (Acros Organic), dimethylformamide (DMF) (MERCK) were used. The fuel tested was a commercial Petronas diesel fuel from Malaysia with 440 ppmw of sulfur content. Dibenzothiophenes in *n*-Octane (100 ppmw) was used as model diesel.

### 2. Preparation of Catalyst

Molybdenum oxide catalyst was prepared by incipient wetness

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impregnation method supported on  $\text{Al}_2\text{O}_3$  (Sigma-Aldrich, specific surface area  $292.07 \text{ m}^2/\text{g}$  and 3-5 mm diameter). The precursor salt of phosphomolybdic acid hydrate (Across Organic) was dissolved in deionized water, aged at  $80^\circ\text{C}$  for 24 hours and calcined in air at  $500^\circ\text{C}$  for 5 hours. The potential catalyst was further calcined at various temperatures. Catalysts were characterized by X-ray diffraction (XRD) using a Bruker Advance D8 with Siemens 5000 Diffractometer and  $\text{Cu K}\alpha$  radiation. FESEM analysis was by a Philips XL 40 microscope with energy of 15.9 kV and bombarded with electron gun with tungsten filament under 25 kV resolutions to get the required magnification image.

### 3. Catalytic Oxidative Desulfurization

All the extractive desulfurization experiments were in a 10 mL flask. The calculated volume of DMF and commercial diesel was mixed together at a ratio of diesel/solvent=1. The extraction was at different extraction temperature from  $30^\circ\text{C}$  to  $60^\circ\text{C}$  and extraction time from 10 min to 60 min. The mixture was left for 2 h for phase separation between solvent and diesel. All ODS reactions were conducted in a 100 mL round-bottom flask, equipped with a magnetic stirrer and fitted with condenser. In a typical run, the oil bath was first heated and stabilized at a constant temperature ( $45^\circ\text{C}$ ). Then, commercial diesel (10 mL) was poured into the flask, followed by the addition of oxidant and catalyst. The mixture was refluxed for 30 minutes under vigorous stirring at atmospheric pressure. The oxidized diesel was extracted with dimethylformamide, DMF at ratio diesel/solvent=1.0. The extraction process was vigorously stirred for 30 minutes followed by phase separation between diesel and solvent. The treated diesel was analyzed by gas-chromatography (Agilent 6890N GC) equipped with FPD detector. Dibenzothiophene (DBT) was used as the model compound to study the ODS mechanism of commercial diesel using tert-butyl hydroperoxide, TBHP. The oxidation steps were performed as previously described for the ODS procedure. Samples were drawn from the flask at regular intervals for analysis. The GC-FPD was used to identify the oxidation products.

**Table 1. The amount and levels (coded and uncoded) of the independent variables in experimental design**

Independent variables	Range and level		
	-1	0	1
Calcination temperature $^\circ\text{C}$ , $X_1$	400	500	600
Molybdenum loading precursor g, $X_2$	1	2	3
Catalyst loading, g/L, $X_3$	9	12	18

### 4. Experimental Design

The sulfur removal in ODS was optimized by response surface methodology using Box-Behnken design (BBD) with three effective variables: calcination temperature,  $X_1$  ( $400$ – $600^\circ\text{C}$ ), molybdenum precursor loading,  $X_2$  (1–3 g), catalyst loading,  $X_3$  (9–18 g/L). The statistical software Design Expert 7.0 was used for the analysis. Three independent variables with their levels are presented in Table 1. The following quadratic equation was used for the optimization process:

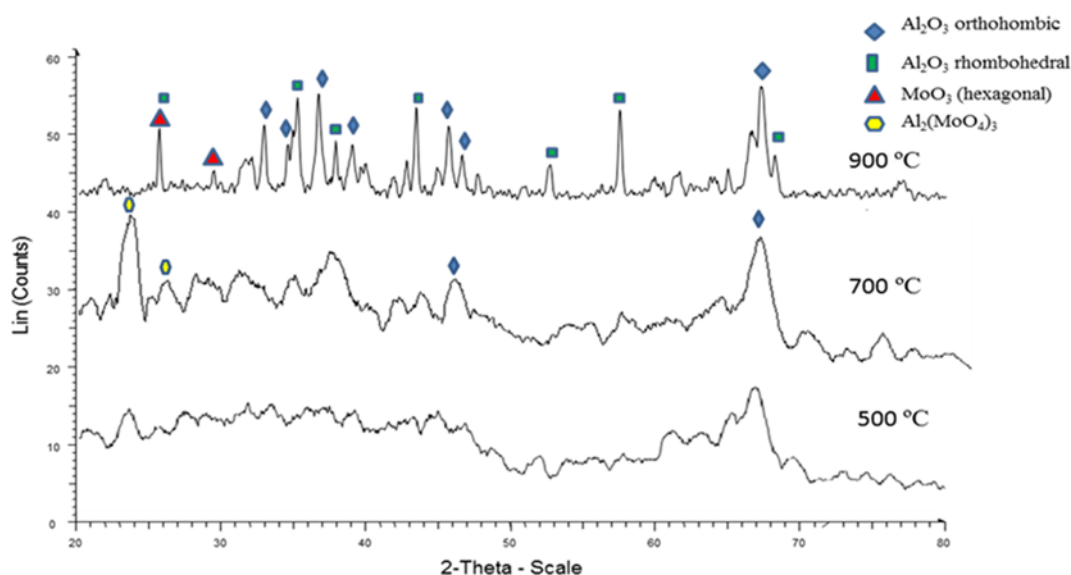
$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (1)$$

where  $Y$  is the response,  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$  are coefficients of the intercept, linear, square and interaction effects, respectively.

## RESULTS AND DISCUSSION

### 1. Catalyst Characterization

The XRD patterns of the  $\text{MoO}_3/\text{Al}_2\text{O}_3$  revealed that catalysts calcined at  $500^\circ\text{C}$  and  $700^\circ\text{C}$  were highly amorphous. The reflections due to the spinel compound of  $\text{Al}_2(\text{MoO}_4)_3$  can be seen at  $2\theta=26.24$  ( $I_{58}$ ) and  $23.47^\circ$  ( $I_{100}$ ). This showed that the presence of  $\text{MoO}_3$  phase formed a solid state reaction with  $\text{Al}_2\text{O}_3$  to produce well crystallized  $\text{Al}_2(\text{MoO}_4)_3$ . According to Ibrahim et al. [10], when calcination temperature was increased from  $500^\circ\text{C}$  to  $700^\circ\text{C}$ ,  $\text{Al}_2(\text{MoO}_4)_3$  was produced on  $\text{Al}_2\text{O}_3$ . The increase of calcination temperature to  $900^\circ\text{C}$



**Fig. 1. XRD diffractogram patterns of (a)  $\text{MoO}_3/\text{Al}_2\text{O}_3$  calcined at (a)  $500^\circ\text{C}$ , (b)  $700^\circ\text{C}$  and (c)  $900^\circ\text{C}$ .**

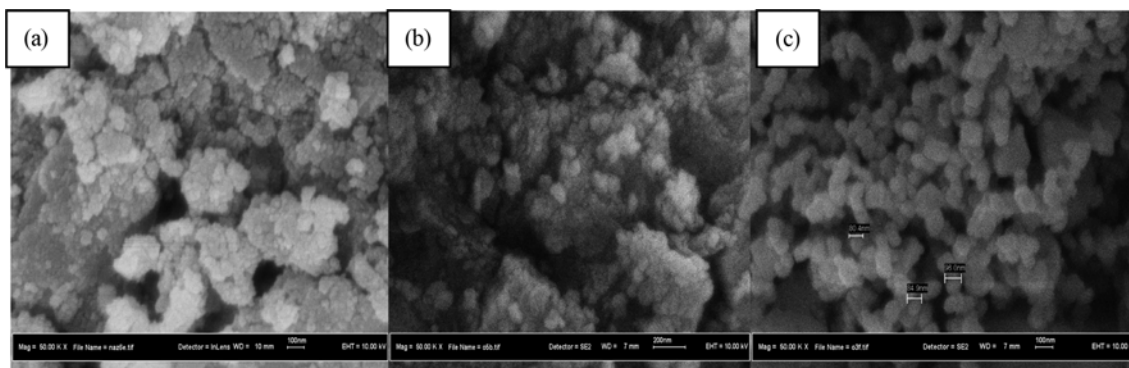


Fig. 2. FESEM micrographs of Mo/Al<sub>2</sub>O<sub>3</sub> calcined at (a) 500 °C, (b) 700 °C, (c) 900 °C with magnification; 50000× and scale bar; 1 μm.

led to apparent crystalline hexagonal phase MoO<sub>3</sub> catalyst with new peaks obtained at  $2\theta$  value = 25.529° ( $I_{100}$ ) and 29.315° ( $I_{40}$ ). At 900 °C, the phase is dominated by the alumina support, assigned as corundum rhombohedral Al<sub>2</sub>O<sub>3</sub> that occurred at  $2\theta$  = 35.102 ( $I_{999}$ ), 43.315 ( $I_{976}$ ), 57.412 ( $I_{944}$ ), 25.529 ( $I_{638}$ ), 68.122 ( $I_{551}$ ), 52.572 ( $I_{485}$ ), 37.758 ( $I_{469}$ ); meanwhile orthorhombic Al<sub>2</sub>O<sub>3</sub> showed at  $2\theta$  = 67.151 ( $I_{100}$ ), 45.575 ( $I_{80}$ ), 36.57 ( $I_{80}$ ), 34.443 ( $I_{80}$ ), 46.479 ( $I_{50}$ ), 38.887 ( $I_{50}$ ), 32.791 ( $I_{50}$ ). Fig. 2 shows the FESEM micrographs of MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 500 °C, 700 °C and 900 °C with 50,000 times magnification. As can be seen from the micrographs, the increasing of calcination showed the formation of aggregated and agglomerated undefined shapes on the surface of the catalyst (Fig. 2(c)). The catalyst showed rough surface morphology with an inhomogeneous undefined shape and in a mixture of larger and smaller particle sizes. In this research, the particle size of fresh MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is categorized at the nano (<100 nm) level, which varies from 26 to 96 nm. The smaller particle size plays an important role in exhibiting higher catalytic activity. This results in good agreement with XRD intensity as the larger the particle size, the higher the crystallinity.

## 2. Effect of Extraction Time

Extraction, a well-known process in petroleum industry, can be used to extract sulfur compounds. The efficiency of desulfurization is not only due to the oxidation process, but also contributed by solvent extraction. In this present work, DMF was selected as potential solvent. As a preliminary step, commercial diesel without oxidation reaction was treated with DMF extraction step. The influence of time is necessary to extract organosulfur compounds in diesel. To determine the time needed to reach maximum extraction efficiency, the experiments were carried out at different periods of time, ranging from 15 min to 60 min. The effect of extraction time was adapted in the commercial diesel, and the results are shown in Fig. 3. Initially, the desulfurization rate increased parallel to the increase in extraction time. When the extraction time was moved up to 35 min, the results shown were not obviously different from that at 30 min, indicating that the extraction processes reached equilibrium. The desulfurization efficiency in commercial diesel started to decrease till 55.5% beyond the extraction duration of 35 min. This is because an excess time of extraction contributed to a re-extraction effect; where the extracted sulfur was transferred back from the solvent into the diesel phase.

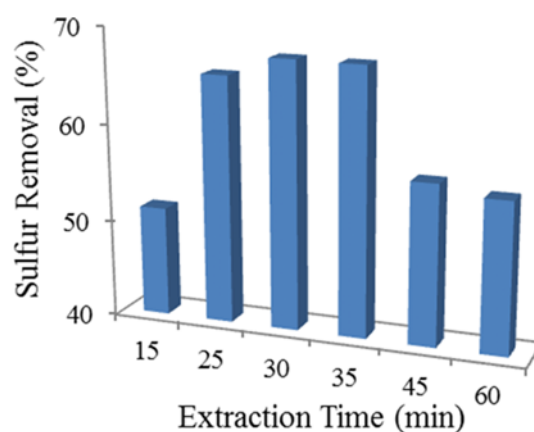


Fig. 3. Effect of extraction time on the EDS reaction in commercial diesel. Extraction conditions: T=30 °C, DMF/diesel ratio=1.0, stirring speed=1,000 rpm and no. of extraction stage=1.

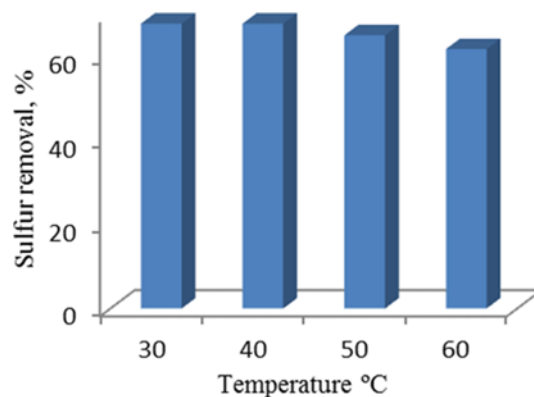


Fig. 4. Effect of extraction temperature on the extractive desulfurization of commercial diesel. Extraction conditions: DMF/diesel ratio=1.0, t=30 min, stirring speed=1,000 rpm and no. of extraction stage=1.

## 3. Effect of Extraction Temperature

Fig. 4 illustrates the extraction performance of commercial diesel at various temperatures (30, 40, 50 and 60 °C). As can be seen, optimum yield of sulfur removal was at the lowest/ambient temperature (30 °C) due to the lower mutual solubility of the DMF and

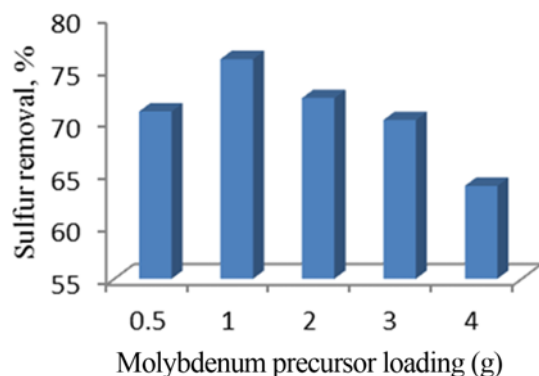


Fig. 5. Effect of molybdenum precursor loading of  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst on the ODS reaction in commercial diesel. Calcination temperature:  $500^\circ\text{C}$ , catalyst/oil ratio:  $12\text{ g/L}^{-1}$ . Catalytic oxidation=O:S molar ratio=3:1, solvent=DMF, commercial diesel/solvent ratio=1, oxidation  $T=45^\circ\text{C}$ , oxidation time=30 min.

diesel. As reported by Wan Mokhtar et al. [11], the extraction process was exothermic at a higher temperature and was ruled by van't Hoff law. In other words, sulfur-extraction is insensitive to the temperature and has little influence on desulfurization. Therefore, from this investigation, 30 min and  $30^\circ\text{C}$  were taken as the extraction time and temperature in the further experiments.

#### 4. Effect of Molybdenum Precursor Loading

EDS process is still not enough to meet the need of ultra deep desulfurization in the absence of a catalyst. Therefore, alumina supported polymolybdate oxide based catalysts were prepared to be used in oxidation reaction to optimize the desulfurization degree. Fig. 5 represents the effect of molybdenum loading on the sulfur removal. The highest percentage of sulfur removal was observed in the system catalyzed by  $\text{MoO}_3/\text{Al}_2\text{O}_3$  with 1g of phosphomolybdic acid precursor, where the removal of sulfur was 76%. The performance of sulfur removal was lowered with increasing of molybdenum loading. This is probably because increasing Mo loading produces more polymerization of Mo, leading to decrease of the catalyst activity especially in ODS as discussed by Akbari et al. [12].

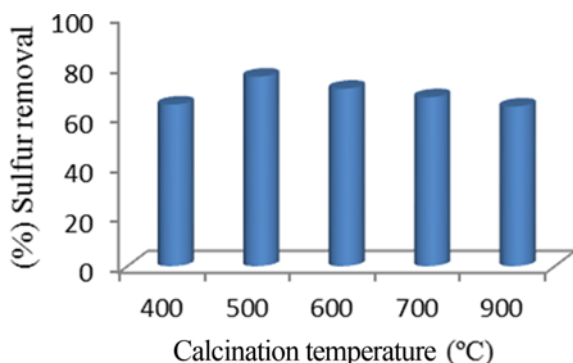


Fig. 6. Effect of calcination temperature on  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst in the ODS reaction of commercial diesel. Mo precursor loading: 1 g, catalyst/oil ratio:  $12\text{ g/L}^{-1}$ . Catalytic oxidation=O:S molar ratio=3:1, solvent=DMF, commercial diesel/solvent ratio=1, oxidation  $T=45^\circ\text{C}$ , oxidation time=30 min.

Besides, the decrease in the activity of the catalyst at highest loading of Mo may be attributed due to the aggregation of Mo particles on  $\text{Al}_2\text{O}_3$  support. In this study, 1 g molybdenum precursor loading gave the best result for sulfur removal.

#### 5. Effect of Calcination Temperature on $\text{MoO}_3/\text{Al}_2\text{O}_3$

The  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts calcined at five different temperatures show significantly different catalytic activity. Fig. 6 demonstrates that the desulfurization activity increased initially up to  $500^\circ\text{C}$  and then decreased with increasing of calcination temperature. The  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst activity can be arranged in the order of  $900^\circ\text{C}<400^\circ\text{C}<700^\circ\text{C}<600^\circ\text{C}<500^\circ\text{C}$ . Here, the  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst calcined at  $500^\circ\text{C}$  showed the optimum calcination temperature with 76% of sulfur removal. It is suggested that the mild calcination temperature assures that the surface metal oxide is fully oxidized and dispersed and that the formation of solid solutions or compounds is avoided [13]. Furthermore, an increase of calcination temperature led to decrease of specific area of the solids and, hence, reduced the catalytic activity. This is probably due to metal particles sintering, which limits its diffusion by reducing the pore size [14].

#### 6. Effect of the Catalyst/oil Ratio on the Desulfurization Rate

Fig. 7 demonstrates the relationship between the amount of  $\text{MoO}_3/\text{Al}_2\text{O}_3$  and sulfur removal in ODS experiment. The results show that the catalyst loading of  $12\text{ g/L}^{-1}$  performed the optimum sulfur removal, which was 76% as compared to other catalyst loading. Beyond this value catalyst particles started to reunite, which decreased the contact area between catalysts and the oil phase, hence, decrease the percentage of sulfur removal [15].

#### 7. Optimization by Box-Behnken Design

In the Box-Behnken design, 15-experimental observations were taken at random orders for the optimization of sulfur removal in the ODS process. Table 2 presents the data resulting from the experiments, which involved their actual values and the corresponding responses (predicted values). Three variables were selected: calcination temperature ( $X_1$ ), molybdenum loading precursor ( $X_2$ ), and catalyst loading ( $X_3$ ), and the experimental results were analyzed through RSM to obtain an empirical model for the best response. The final quadratic equation was obtained to explain the mathematical relationship between the independent parameters and the

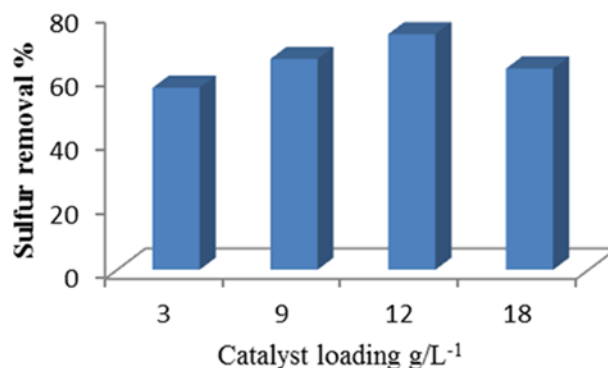


Fig. 7. Effect of loading of alumina supported  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst calcined at  $500^\circ\text{C}$  on ODS reaction of commercial diesel. Mo precursor loading: 1 g. Catalytic oxidation=O:S molar ratio=3:1, solvent=DMF, commercial diesel/solvent ratio=1, oxidation  $T=45^\circ\text{C}$ , oxidation time=30 min.

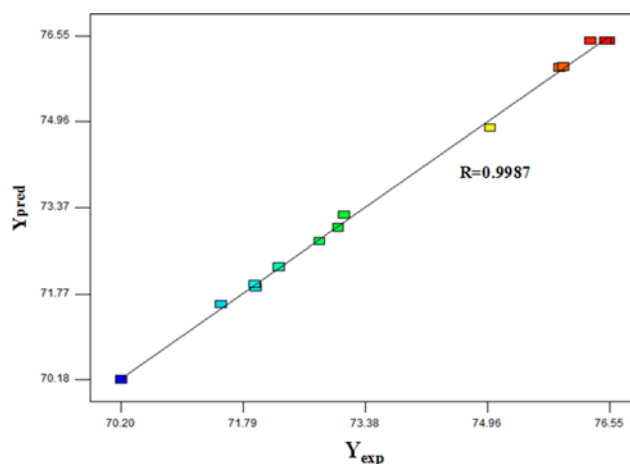
**Table 2. Box-Behnken design matrix**

Observation	Actual values			Sulfur removal		
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Y <sub>exp</sub>	Y <sub>pred</sub>	Residual
1	500	3	18	70.20	70.18	0.015
2	500	1.25	12	76.55	76.45	0.100
3	400	3	12	72.78	72.74	0.044
4	500	2	18	72.25	72.27	-0.021
5	500	3	9	70.20	70.18	0.018
6	600	1.25	18	75.95	75.97	-0.024
7	600	2	12	75	74.84	0.16
8	400	1.25	18	73.02	72.99	0.030
9	500	2	9	71.94	71.95	-0.013
10	400	2	12	73.10	73.22	-0.12
11	600	3	12	71.50	71.58	-0.077
12	400	1.25	9	71.95	71.90	0.051
13	500	1.25	12	76.50	76.45	0.050
14	600	1.25	9	75.90	75.96	-0.057
15	500	1.25	12	76.30	76.45	-0.15

dependent responses (Y) and is presented below:

$$Y = 76.81 + 1.76 X_1 - 2.63 X_2 + 0.28 X_3 - 1.04 X_1 X_2 - 0.27 X_1 X_3 - 0.12 X_2 X_3 - 0.18 X_1^2 + 0.35 X_2^2 - 2.43 X_3^2 \quad (2)$$

The results of analysis of variance presented in Table 3 show the successful fitting of the experimental data to the quadratic model. The degree of freedom value (*F*-test) for the model was found to be 442.33, which implied that the model was significant, and only a 0.01% chance that such a large *F*-value could occur due to noise. A low *p*-value (*p*<0.05) indicates that the model was statistically significant for sulfur removal. Therefore, obtained model ensures an accurate representation of the experimental data. A very high *R*<sup>2</sup> (*R*-Sq) value of 0.9987 indicated that the predicted quadratic model was reasonably well fitted with the data. The predicted *R*<sup>2</sup>

**Fig. 8. Comparison between experiment and predicted Y.**

(Pred *R*-Sq) value of 0.9724 is in line with the adjusted *R*<sup>2</sup> (Adj *R*-Sq) value of 0.9965. The comparison between experimental and predicted values of Y is shown graphically with a 45°-line in Fig. 8.

The importance of each of three independent factors (calcination temperature, molybdenum loading precursor and catalyst loading) on sulfur removal was determined by illustrating the response surfaces as three-dimensional (3D) plots. In Fig. 9(a), the catalyst loading was kept constant at 13.50 g/L, while the molybdenum loading precursor and calcination temperature were kept constant at 1.35 g and 500 °C in Fig. 9(b) and (c), respectively. From Fig. 9(a), the sulfur removal increased as the calcination temperature was increased. The highest sulfur removal (>76%) occurred when molybdenum loading precursor and calcination temperature were kept at about 1.25–1.44 g and 500–600 °C, respectively. Different calcination temperature results in different oxidation states of MoO<sub>3</sub>, so the calcination temperature affects the catalyst activity. Fig. 9(b) represents the effect of catalyst loading and calcination temperature

**Table 3. Analysis of variance (ANOVA) for conversion**

Source	DF <sup>b</sup>	SS <sup>b</sup>	MS <sup>b</sup>	F <sup>b</sup>	P <sup>b</sup>	CE
Model <sup>a</sup>	9	73.12	8.12	442.33	<0.0001	
Calcination temperature, X <sub>1</sub>	1	14.08	14.08	766.51	<0.0001	1.76
Molybdenum loading precursor, X <sub>2</sub>	1	6.33	6.33	344.49	<0.0001	-2.63
Catalyst loading, X <sub>3</sub>	1	0.35	0.35	19.16	0.0072	0.28
X <sub>1</sub> X <sub>2</sub>	1	7.63	7.63	415.50	<0.0001	-1.04
X <sub>1</sub> X <sub>3</sub>	1	0.29	0.29	15.91	0.0104	-0.27
X <sub>2</sub> X <sub>3</sub>	1	0.10	0.10	5.65	0.0634	-0.12
X <sub>1</sub> <sup>2</sup>	1	0.12	0.12	6.38	0.0528	-0.18
X <sub>2</sub> <sup>2</sup>	1	0.65	0.65	35.49	0.0019	0.35
X <sub>3</sub> <sup>2</sup>	1	16.32	16.32	888.67	<0.0001	-2.43
Residual	5	0.092	0.018			
Lack of fit	3	0.057	0.019	1.08	0.5131	
Pure error	2	0.035	0.018			
Total	14	73.22				

<sup>a</sup>*R*-Sq=99.87%, *R*-Sq (adj)=99.65%, *R*-Sq (pred)=97.24%

<sup>b</sup>DF: degree of freedom of different source, SS: sum of square, MS: mean of square, F: degree of freedom, P: probability, CE: coefficient estimate



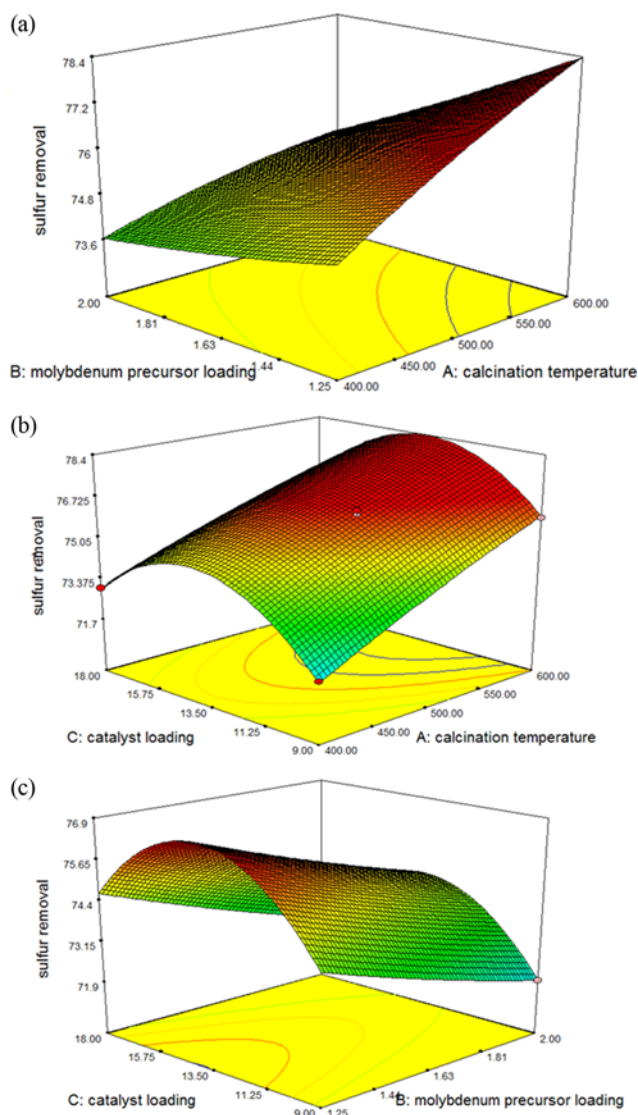


Fig. 9. 3-D surface plots of sulfur removal as a function of (a) calcination temperature and Molybdenum precursor loading, (b) calcinations temperature and catalyst loading and (c) catalyst loading and molybdenum precursor loading.

on sulfur removal while keeping the molybdenum precursor loading at 1.36 g. Fig. 9(b) clearly shows that as the catalyst amount and calcination temperature increased, the sulfur removal increased. Desulfurization reaction was intensified because more sulfur molecules were adsorbed on the more active center of the catalyst surface as also obtained by Wang et al. [16]. Meanwhile, as can be observed from Fig. 9(c), sulfur removal was increased with the increasing catalyst amount to its peak, but then decreased with a further increase in molybdenum loading precursor. The addition of a suitable amount of  $\text{MoO}_3$  loading enabled the catalyst to achieve the optimum state for sulfur removal, but the addition of  $\text{MoO}_3$  beyond a certain amount decreased the activity. This decrease can be attributed to metal agglomeration and formation of bulk metal particles leading to a decrease of the number of active sites. Additionally, bulk metal particles may block the pores and active sites of

the catalyst. Overall, the important degree of these parameters on sulfur removal was in order: calcination temperature > molybdenum loading precursor > catalyst loading.

### 8. Optimization Response and Verification Test

The main objective of the optimization was to determine the optimum conditions for  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst preparation in optimizing sulfur removal in commercial diesel. The factor setting can be adjusted to get the initial solution. The values of the independent variables are obtained by considering the starting values of calcination temperature, molybdenum loading precursor and catalyst loading of  $400^\circ\text{C}$ , 0.5 g, and 9 g/L, respectively. The sulfur removal was estimated as 77.23% within these optimum conditions (calcination temperature  $510^\circ\text{C}$ , molybdenum loading precursor 0.98 g and catalyst loading 11.18 g/L). An additional experiment was conducted under the optimum condition to confirm the agreement of the model and experimental results. The experimental value 77.8% is in great agreement with the predicted result, and hence validates the findings of response surface optimization.

### 9. The Mechanistic Study

DBT was used as a model compound to study the oxidative desulfurization process over TBHP- $\text{MoO}_3/\text{Al}_2\text{O}_3$  system at a time of interval 5 min, 15 min, 30 min and 45 min. The GC-FPD chromatogram of model compound of DBT extracted by DMF in the presence of catalyst is shown in Fig. 10.

The results of GC-FPD analysis in the model compound of DBT extracted by DMF of  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst showed that the desulfurization products were DBT sulfoxide and DBT sulfone. The desulfurization products of DBT sulfone increased as the reaction temperature was increased up to 30 min. This can be explained by describing interaction of oxidizing agents as time proceeds. TBHP and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  can interact with DBT to produce DBT sulfoxide and DBT sulfone. This reaction like any other reaction needs enough time to complete and promotes as time goes on. Best results are observed at 30 min. After a particular reaction time, the desulfurization products declined by rising reaction time, which means there is an optimum time for oxidation system to occur. This reduction in the desulfurization products might be due to loss of  $\text{MoO}_3$  active site, which accelerates the conversion of oxidized sulfur compound to DBT. In other words, the long time of reaction results in the loss of  $\text{MoO}_3$ , equilibrium change, and alteration of the reaction media from oxidizing to reducing one. So, carrying out the reaction in a long time could have no benefit in the TBHP-  $\text{MoO}_3/\text{Al}_2\text{O}_3$  system.

Based on these results, our proposed peroxidic oxidation mechanism of DBT on  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst with TBHP is shown in Fig. 11. The reaction pathway proceeds initially through the nucleophilic attack of TBHP on  $\text{MoO}_3/\text{Al}_2\text{O}_3$  to form species (1). The oxidation process must proceed by nucleophilic attack of the sulfur in the organosulfur compounds, (2) on the positively charged peroxomolibdate complex (1) to form DBT sulfoxide (3) and regenerated polymolybdate species, respectively. Subsequently, the sulfoxide (3) undergoes further oxidation to form DBT sulfone (4) [17]. It is possible to rationalize that phosphate would help withdraw electron density from the polymolybdate species, thereby conferring a higher electrophilic character to the Mo (VI) atoms [6]. The activation mechanism of peroxy oxygen is as proposed by García Guti-

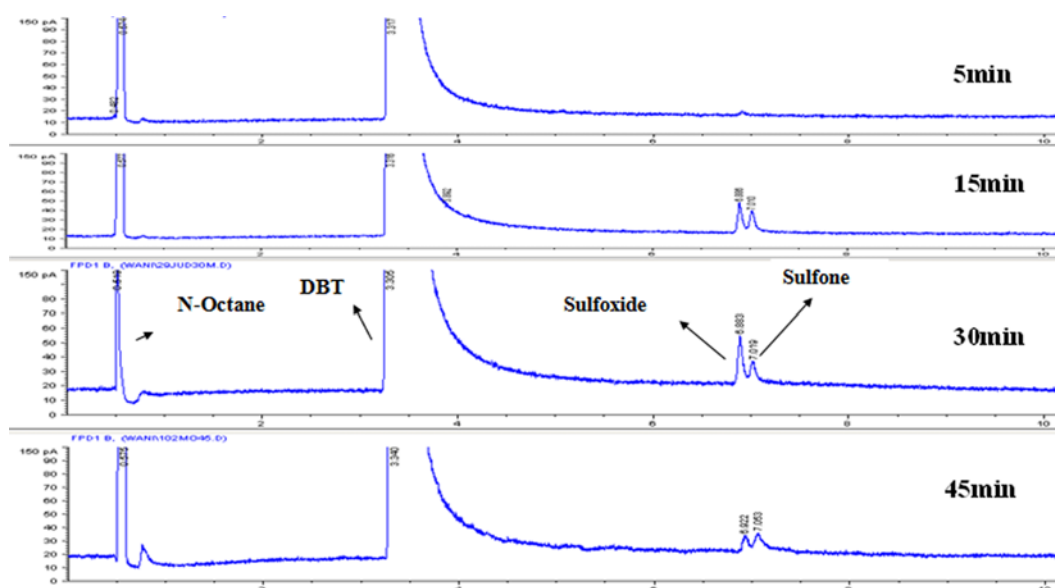


Fig. 10. Chromatograms of GC-FPD analysis for DBT oxidative desulfurization by TBHP after 5 min, 15 min, 30 min and 45 min using  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst in model diesel.

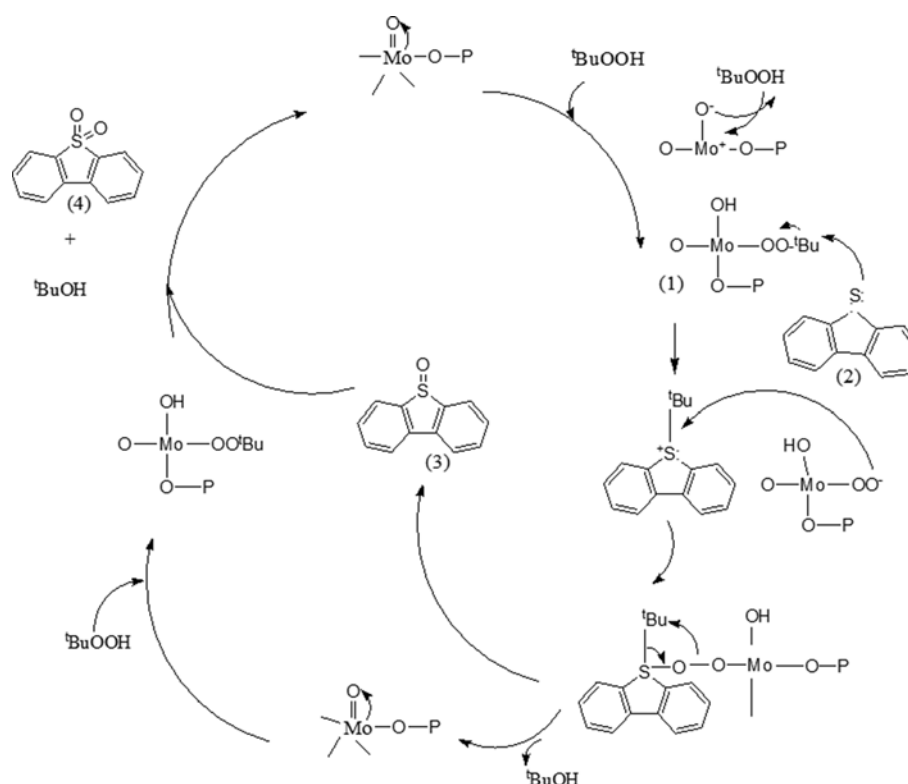


Fig. 11. A proposed cyclic mechanism for the oxidation of dibenzothiophene by TBHP in the presence of  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst.

érrez et al. [6,18] in which the peroxide reacts with DBT to produce DBT sulfoxide, and further oxidation produces the corresponding sulfone in presence of  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst.

## CONCLUSION

It is possible to reduce the level of sulfur in Malaysian commer-

cial diesel from 440 ppmw to 105 ppmw under mild conditions using a  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst calcined at  $500^\circ\text{C}$ . The screening of catalytic testing showed that the  $\text{MoO}_3$  catalyst provided a higher conversion of sulfur removal under mild condition. These results were also verified using Box-Behnken experimental design. The obtained model equation using BBD showed a high coefficient of determination ( $R^2=0.9987$ ), indicating that the predicted data well fit-

ted the actual data. According to the statistical design method, the optimal operation conditions were determined at calcinations temperature=510 °C, molybdenum loading precursor=0.98 g and catalyst loading=11.18 g/L. Verification experiment was performed at the optimum conditions, and the experimental value (77.8%) closely agreed with predicted value (77.23%). Based on our results, the reaction mechanisms for oxidation of sulfur compounds to the corresponding sulfones occur in the presence of  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst. The results indicate that alumina supported polymolybdate based catalyst has the potential to be used as a catalyst in Cat-ODS to meet the regulation of sulfur in diesel fuel.

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