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**Oxidative desulfurization utilizing activated carbon supported phosphotungstic acid in the frame of ultrasonication**

Journal:	<i>ACS Omega</i>
Manuscript ID	ao-2021-05935y
Manuscript Type:	Article
Date Submitted by the Author:	23-Oct-2021
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3 **Oxidative desulfurization utilizing activated carbon supported phosphotungstic acid in the**  
4 **frame of ultrasonication**  
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21 **ABSTRACT**  
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24 Desulfurization technology is essential to remove sulfur content in diesel oil to achieve clean fuel  
25 products. In this study, oxidative desulfurization under an ultrasonic bath was utilized in  
26 conjunction with a synthesized activated carbon supported phosphotungstic acid (HPW-AC)  
27 catalyst. This research focuses on the extent of desulfurization on a simulated diesel oil, containing  
28 2.3 % S from benzothiophene (BT) and dibenzothiophene (DBT) mixed in actual fuel oil. The  
29 effects of ultrasonication time (30 min to 90 min), reaction temperature (40 °C to 70 °C) and  
30 catalyst dosage (6 wt% to 18 wt%) were examined for the oxidation of the simulated diesel oil  
31 containing BT and DBT. A 2<sup>k</sup> full factorial design was implemented in the experimental runs to  
32 evaluate the parameters by the analysis of variance. Results showed that the curvature of the model  
33 was not significant (p-value = 0.3134). Thus, further optimization runs were no longer required to  
34 fully analyze the model. The best conditions for sulfur conversion can be attained at 30 min, 70 °C  
35 and 18 wt% HPW-AC catalyst dosage. Furthermore, the basic diesel oil properties (density,  
36 viscosity and calorific value) were compared before and after the desulfurization process. Results  
37 indicated that the simulated diesel oil retained essentially the same properties prior to its treatment.  
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3 This proves to show a promising result that can further be improved for its applicability in future  
4 industrial practice.  
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10 Keywords: activated carbon, benzothiophene, dibenzothiophene, diesel oil, oxidative  
11 desulfurization, ultrasound  
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## 17 **1. Introduction**

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19 Crude oils such as gasoline, kerosene, jet fuels, and diesel are invaluable in the technological  
20 advancement of industrial and transportation sectors. This type of fuel oils has an elemental  
21 composition of carbon, hydrogen, oxygen, nitrogen, sulfur, and other metals. In the aspect of sulfur  
22 content of the fuel oil, these are in the form of benzothiophene (BT), dibenzothiophene (DBT) and  
23 its alkylated derivatives [1]. Sulfur reaction in the combustion process forms sulfur dioxide and  
24 sulfur trioxide gas. The exposure of the sulfur dioxide to oxygen in saturated air can result in the  
25 formation of sulfuric acid, which leads to air pollution in the form of acid rain or acid deposition.  
26 Moreover, sulfur oxides are also commonly emitted from combustion of coal and in the process  
27 of burning fossil fuels [2]. Sulfur oxides from these sources can cause a detrimental impact on the  
28 environment and the health. In terms of the public health concerns, this can cause multiple chronic  
29 and acute respiratory tract ailments that include asthma, bronchitis, lung infection, and other  
30 inflammations of functional organs [3]. Sulfur oxides can also damage the catalytic converters  
31 inside vehicles that are responsible for volatile organic compounds, CO and NO oxidation  
32 reactions [4]. Thus, immediate actions to prevent the negative externalities of sulfur emissions  
33 towards society and environment resulted are essential. Currently, stringent environmental  
34 regulations to decrease the sulfur content to 10 ppm in fuel oils are implemented in China,  
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3 European Union, Japan and the United States [5]. Furthermore, even third world countries such as  
4 the Philippines are using sweet crude due to their implementation of its regulations in DAO No.  
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6 2015-04 which states that the fuel oils sold by petroleum companies should be under the Euro 4  
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8 standard- 50 ppm sulfur [6].  
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12 The process wherein the sulfur content of a fuel is reduced to an acceptable value is called  
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14 desulfurization. Desulfurization is classified as pre-combustion, wherein sulfur is removed before  
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16 burning the fuel, and post-combustion, wherein sulfur is removed after burning.  
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18 Hydrodesulfurization (HDS) is the conventional desulfurization of fuel oils [7]. However, there  
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20 are multiple drawbacks in this desulfurization technology. HDS requires high energy consumption  
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22 due to extreme conditions, which operate at high temperature (300 °C to 440 °C) and high pressure  
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24 (3 MPa to 6 MPa), and spends a considerable amount of hydrogen that translates to expensive  
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26 costs [8]. Moreover, the aromatic sulfur compounds such as thiophenes, BT and DBT have low  
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28 reactivities towards the HDS that presents a limitation to this process [9]. Therefore, various  
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30 studies regarding alternative processes have been developed to cover the limitations of the HDS.  
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32 The oxidative desulfurization process (ODS) is a promising technique due to operating at mild  
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34 conditions - room temperature and ambient pressure that addresses the problems associated to  
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36 HDS [10]. In addition, ODS has the capability of removing the aromatic sulfur compounds that  
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38 are almost unreactive in HDS [11]. Oxidative desulfurization involves a two-step process. The  
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40 first-step of the process is the conversion of the aromatic sulfur to their corresponding sulfones  
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42 [12] and the second-step is separation of the formed sulfones from the petroleum fuel [13,14] The  
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44 latter part involves the separation of the phases using liquid-liquid extraction [15]. Ultrasound-  
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46 assisted oxidative desulfurization (UAOD) is an improved method of ODS which has been an  
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48 interest in recent years. Ultrasound applied to the process of ODS assists the reaction by increasing  
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3 the mass transfer of the process through cavitation that leads to a more efficient desulfurization of  
4 diesel oil. UAOD aims to accelerate the oxidation that results to effective removal of sulfur  
5 compounds found in fuels.  
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10 The utilization of a catalyst is vital in the UAOD. One type of catalyst that is used in the  
11 desulfurization process is the heterogeneous catalyst. A heterogeneous catalyst is a catalyst that  
12 appears in different phases in chemical reactions. An advantage of this type of catalyst is its ease  
13 to separate from the resulting product. A heterogeneous catalyst widely used in UAOD is called  
14 heteropoly acid (HPA) that is known for incorporating polyoxometalate anions [16]. The HPA  
15 reacts with the hydrogen peroxide ( $H_2O_2$ ) oxidant to produce an intermediate that is more efficient  
16 in oxidizing the sulfur compounds in the fuel. Specifically, the phosphotungstic acid (HPW) is a  
17 highly effective HPA for oxidation reactions [17]. Furthermore, the catalyst performance can be  
18 further improved when supported by carbon materials. Carbon based substances help in the  
19 desulfurization of aromatic sulfur compounds [18]. The carbon substance acts as both catalyst and  
20 adsorbent in the process, making it very efficient. However, the aforementioned catalyst is still  
21 effective in terms of selectivity, but are more efficient when impregnated with activated carbon  
22 (AC) [19].  
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40 Thus, the focus of this study is to determine the optimal parameters in the desulfurization of  
41 simulated diesel containing 2.3% sulfur comprising of BT and DBT mixed in commercially  
42 available diesel oil. The catalyst used for the process is the synthesized activated carbon supported  
43 phosphotungstic acid (HPW-AC). This is characterized after the dry impregnation method. The  
44 varied variables are the ultrasonication time, temperature, and catalyst dosage to test the sulfur  
45 removal in the UAOD process. The fuel properties (density, viscosity and calorific value) are  
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3 tested in order to validate appropriate fuel standards before and after the removal of the sulfur  
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5 compounds.  
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## 7 **2. Methodology**

### 8 *2.1. Materials*

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10 Phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ : 99.9 % purity), benzothiophene (BT: 98 % purity),  
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12 dibenzothiophene (DBT: 98 % purity), toluene (99.9 % purity) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ : 30  
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14 vol%) were purchased from Merck Inc. Activated carbon was obtained from Fluka Analytical.  
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16 Acetonitrile was procured from Sigma-Aldrich. The diesel used for the simulated fuel was  
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18 acquired from a commercially available gas station.  
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### 23 *2.2. Catalyst preparation*

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25 The HPW-AC was prepared by using the dry impregnation method. Initially, the AC was  
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27 pretreated by washing with 0.1 M HCl and water to achieve pH 7.0. The activated carbon is then  
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29 dried for 24 h at 120 °C. The HPW of 1 g was dissolved in distilled water separately. These were  
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31 then impregnated on the AC by adding the solution on the AC in a dropwise manner. The system  
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33 was then dried for 24 h then transferred in a crucible and then dried for 8 h at 120 °C. After 8 h,  
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35 the dried system was calcined in a Vulcan® Box Furnace with Programmable Controls Model 3-  
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37 550 for 4 h at 350 °C. The samples were tested using a field emission scanning electron microscopy  
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39 (FESEM: Helios Nanolab 600i) and a Fourier transform infrared spectroscopy (FTIR: Thermo  
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41 Scientific Nicolet 470 FTIR spectroscope) after undergoing calcination to determine the  
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43 characterization of the synthesized catalyst.  
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### 49 *2.3. Experimental method*

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51 For the simulated diesel oil, this was synthesized by mixing 300 mL of Shell Fuelsave Diesel with  
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53 11.53 g of BT and 17.52 g of DBT that produced 2.3% sulfur by weight diesel. The simulated  
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3 diesel was stored in glass containers at room temperature in a dry place. The concentration of H<sub>2</sub>O<sub>2</sub>  
4 and ultrasound amplitude were constant at 30 wt% peroxide and 47 kHz, respectively, in the  
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diesel was stored in glass containers at room temperature in a dry place. The concentration of H<sub>2</sub>O<sub>2</sub> and ultrasound amplitude were constant at 30 wt% peroxide and 47 kHz, respectively, in the UAOD process. The parameters which were investigated were reaction temperature (40 °C to 70 °C), ultrasonication time (30 min to 90 min) and catalyst dosage (6 wt% to 18 wt%).

The HPW catalyst was placed inside a 150 mL beaker. The catalyst was presaturated by 10 mL of fuel for 5 min. The H<sub>2</sub>O<sub>2</sub> solution was then added to a predetermined amount of catalyst and the fuel mixture with a fuel to oxidant ratio of 1:1. The beaker with the solution was then placed in the Cole Parmer Model 8894 Cleaning Unit and allowed to undergo oxidative desulfurization at various reaction time. After a specified reaction time had elapsed, the separation of the organic phase (desulfurized fuel) from the aqueous phase was done by the use of the Hermele Small Centrifuge Z 206 A at 4000 rpm at 20 min. The recovered organic phase was filtered before it was subjected to sulfur analysis. The gas chromatograph coupled with flame ionization detector (GC-FID) was then used for the determination of the sulfur content of the desulfurized fuel. The percent oxidation was evaluated using **Eq. (1)**.

$$\% \text{ Sulfur oxidation} = \frac{S_i - S_f}{S_i} \cdot 100 \quad (1)$$

where  $S_i$  denotes to the initial sulfur concentration of the diesel oil and  $S_f$  refers to the sulfur concentration after undergoing oxidation reaction at a predetermined time interval.

A 2<sup>k</sup> full factorial design with four center points was employed for the determination of the effects of the UAOD parameters on the oxidation process. The curvature was obtained and analyzed to determine the significance of the factors and for possible identification of further optimization. The factorial design generated by the Design Expert software includes eight runs for three factors with additional four center points. Thus, the 2<sup>k</sup> full factorial design has a total of 12 experimental runs.

## 2.4. Determination of diesel oil properties

The oxidized sulfur compounds (sulfones) were completely removed from the fuel prior to the determination of fuel properties. This was through the extraction process using acetonitrile as the solvent. The process involved a one-step extraction in a separatory funnel with a feed to solvent ratio of 1:1.

### 2.4.1. Density

A pycnometer was used to determine the density of the simulated diesel oil. The pycnometer was dried then an analytical balance was used to accurately weigh the mass of the empty and dried pycnometer. After the measurement of the corresponding weight, water was introduced as a standard solution. The pycnometer was filled with water and weighed once again. This process was repeated for both the simulated diesel oil before and after the UAOD process.

### 2.4.2. Viscosity

The viscosity of the diesel, both treated and untreated, was determined using the falling sphere method. The liquid was poured into a graduated cylinder, then the height was determined. A small sphere was obtained and then its mass and radius were measured to obtain the density of the ball. The ball was then released from the highest point of the liquid. The time it took for the ball to reach the bottom point of the liquid was then measured. **Eq. (2)** shows the formula for the calculation of the viscosity ( $\mu$ ) of the diesel oil samples.

$$\mu = 2(\rho_b - \rho_l)gr^2/(9v) \quad (2)$$

where  $\rho_b$  refers to the ball density,  $\rho_l$  signifies the liquid density,  $g$  denotes the gravitational acceleration of 9.81 m/s<sup>2</sup>,  $r$  indicates the radius of the ball and  $v$  means the velocity of the ball.

### 2.4.3. Calorific value



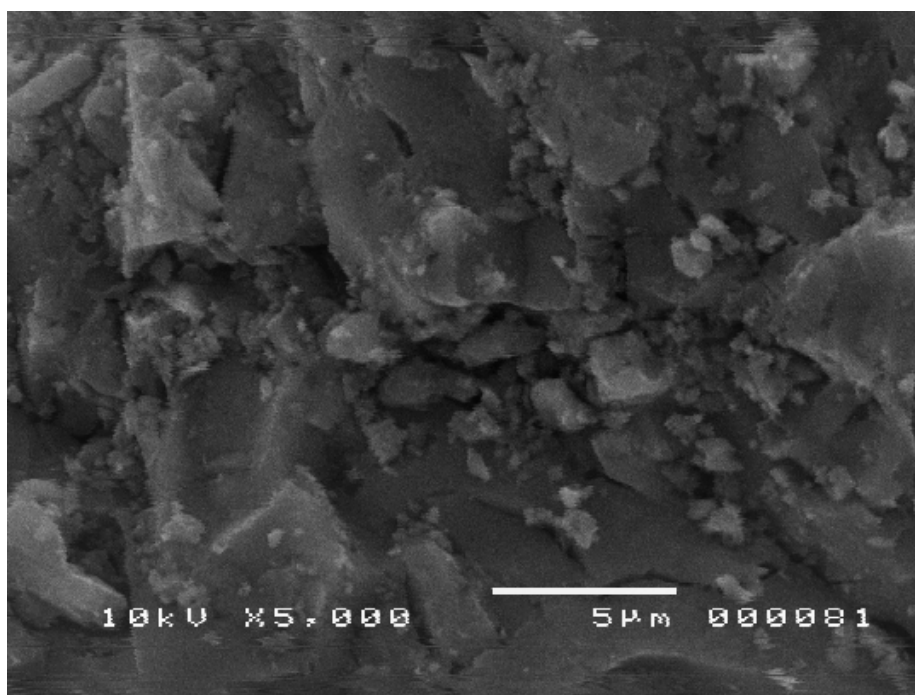
The higher heating value (HHV) of the solutions was determined empirically using **Eq. (3)** for the American Petroleum Institute (API) that leads to **Eq. (4)** for the calculation of HHV in kJ/kg.

$$API = \frac{141.5}{S.G.} - 131.5 \quad (3)$$

$$HHV = 42,890 + 93(API - 10) \quad (4)$$

### 3. Results and discussion

#### 3.1. Surface morphology of the HPW-AC catalyst



**Fig. 1** Scanning electron microscope image of activated carbon supported phosphotungstic acid. The surface morphology was determined through the SEM in order to confirm a successful impregnation of HPW in the synthesized catalyst. **Fig. 1** depicts the micrograph of the catalyst sample after undergoing the impregnation of HPW onto AC at a magnification of five-thousand times. It can be observed that there are traces of scattered HPW presented as the small-sized particles. This was consistent with a study made by Gildo et al. [20] that utilizes the same type of

catalyst sample. The same small-sized particles made up of HPW were larger in number and more scattered throughout the surface of the AC.

### 3.2. FTIR analysis of the HPW-AC catalyst

The synthesized HPW-AC catalyst sample was subjected in an FTIR analysis to validate the proper impregnation of HPW. The FTIR analysis of this study was compared to the results obtained from Sajankumarji Rao et al. [21] and Chen et al. [22] as summarized in **Table 1**. In the previous studies, the peak numbers at 1084  $\text{cm}^{-1}$  and 1080  $\text{cm}^{-1}$  represent the phosphorus-oxygen (P-O) bond, the peak numbers 983  $\text{cm}^{-1}$  and 985  $\text{cm}^{-1}$  signify the tungsten-oxygen bond, 890  $\text{cm}^{-1}$  and 896  $\text{cm}^{-1}$  denote the corner-shared oxygen's bond and the 798  $\text{cm}^{-1}$  and 804  $\text{cm}^{-1}$  indicate the edge-shared oxygen's bond. It can be seen from the characterization results that the HPW confirms a successful impregnation onto the AC. This has also validated the HPW was spread about the AC and that the Keggin structure of the acid was maintained.

**Table 1** FTIR peak numbers in  $\text{cm}^{-1}$  and their corresponding bonds

Bond	HPW [12]	HPW [22]	HPW-AC (This work)
P - O	1084	1080	1078.49
W - Ot	983	985	984
W - Ob - W	890	896	893.29
W - Oc - W	798	804	807.90

### 3.3. Ultrasound-assisted oxidative desulfurization parameters for simulated fuel

The implementation of the appropriate design of experiments was used to completely analyze the effects and interactions of the UAOD parameters based on its overall percent sulfur oxidation. A 2k factorial design experiment was done to determine the level of significance of each parameter affecting the response of percent oxidation. This was also done to determine the significance of the curvature of the model in the UAOD process. Further optimization is needed should the

curvature of the model be proven significant. The 2k factorial runs with four center points as formulated by the Design Expert software are listed in **Table 2**.

**Table 2** UAOD experimental runs with the resulting sulfur oxidation

Run No.	Temperature (°C)	Ultrasonication time (min)	Catalyst dosage (wt%)	Percent oxidation (%)	BT Removal (%)	DBT Removal (%)
1	55	60	12	33.03	19.43	42.81
2	40	30	6	37.39	18.39	52.30
3	55	60	12	31.98	17.50	42.55
4	40	90	18	34.41	15.23	49.54
5	40	30	18	38.86	20.13	53.77
6	55	60	12	33.46	18.88	44.19
7	70	90	6	31.10	18.89	39.48
8	70	30	18	39.74	20.15	55.50
9	55	60	12	33.00	19.11	43.07
10	70	90	18	36.18	18.78	49.72
11	70	30	6	27.95	17.99	34.05
12	40	90	6	31.45	17.95	41.08

Results indicate that the highest run with an oxidation of the simulated diesel oil reached 39.74 % under the conditions of the highest temperature setting (70 °C), lowest residence time (30 min) and the highest catalyst dosage (18 wt%). On the other hand, the lowest oxidation performance of the simulated diesel oil attained only 27.95 %. The conditions were at the lowest catalyst dosage of 6 wt%, highest temperature setting of 70 °C and the lowest residence time of 30 min. This

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3 implies that the HPW-AC catalyst plays a key role in enhancing sulfur conversion and selectivity  
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5 in the oxidation reaction.  
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8 Based on the percent oxidation obtained from the 12 experimental runs, this resulted in conversions  
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10 ranging approximately between 28 % to 40 %. The percent oxidation values were relatively close  
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12 to each run. Generally, the percent oxidation values were not that high compared to past literature  
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14 associated with the use of ultrasonic irradiation on oxidative desulfurization on various simulated  
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16 fuel oils [10]. This may be attributed to the difference of using solely one type of hydrocarbon as  
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18 a solvent in past literature. In this study, actual diesel oil comprising of various hydrocarbons was  
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20 utilized a mixed with sulfur compounds. This can affect the overall performance due to the  
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22 emulsification process that decreases the oxidation rate of sulfur compounds [23]. Analyzing the  
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24 results based on the percent oxidation is however too broad and incomplete. The sulfur-containing  
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26 compound that contributes more to either the overall percent oxidation or to the remaining sulfur  
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28 in the simulated diesel oil after oxidation is essential to be traced and determined. Thus, a more  
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30 desirable and in-depth discussion of the results for the percent removal of each sulfur compound  
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32 in the simulated diesel (BT and DBT) is also presented.  
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37 **Table 2** also shows each percent BT and DBT removal based on the overall percent sulfur  
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39 oxidation. It is observed that the DBT percent removal is substantially higher than the percent  
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41 removal of the BT. Therefore, the main contributor on the overall percent sulfur oxidation is based  
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43 on the DBT. However, it cannot be concluded that the contributor for the remaining sulfur is solely  
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45 in the BT compound. This is due to the amount of DBT remaining in each oxidized simulated fuel  
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47 is also relatively close with respect to the amount of BT remaining after undergoing the oxidation  
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49 process. This is consistently seen in the trend for all of the tested runs. The disparity of the  
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51 oxidation performance of BT and DBT can attributed to the difference between the electron  
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densities of the sulfur compounds. The DBT electron density (5.758) is higher compared to the BT electron density (5.738) [24]. This signifies that the electrons of DBT are less compact that leads to appropriate facilitation of oxidation reaction as opposed to the BT. Furthermore, the reactivity of both compounds can also be compared based on their rate constant. The DBT reaction rate (0.0574) was determined to be higher than that of BT (0.046) from the study of Jiang et al. [24]. It was found that of all the sulfur compounds, the DBT had the least activation energy. Thus, further validating the ease of oxidation for DBT against BT due to requiring lesser energy to activate the oxidation reaction towards the UAOD system in the simulated diesel oil.

### 3.4. Analysis of variance (ANOVA) for UAOD

Based on the percent oxidation response, an ANOVA was obtained. This is to verify the level of significance of each parameter and its respective interactions towards the percent oxidation response. This can also determine whether a response surface method is still essential for optimization. **Tables 3 and 4** lists the variables removed and the ANOVA, respectively, as formulated and obtained by Design Expert software.

**Table 3** Variables and interactions removed from the UAOD model

Removed	Estimate	Coeff=0	Prob >  t	R-Squared	MSE
AC	-0.6525	-2.94	0.0605	0.9649	1.15
B-Ultrasound Temp	-0.8925	-2.36	0.0779	0.9162	2.19
ABC	-1.03	-1.96	0.1076	0.8519	3.23
AB	1.25	1.96	0.0972	0.7567	4.55
A-Ultrasonication Time	-1.35	-1.79	0.1164	0.6452	5.80
BC	1.56	1.83	0.1052	0.4973	7.30

**Table 4** Analysis of variance for UAOD

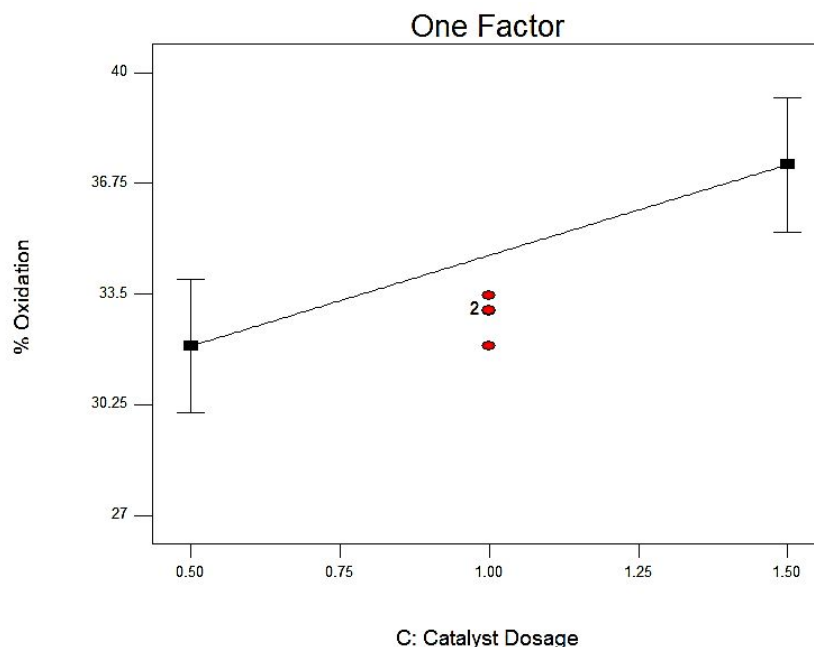
Source	Sum of Squares	df	Mean Square	F-value	p-Value Prob > F	
Model	56.71	1	56.71	7.76	0.0212	significant
C-Catalyst						
Dosage	56.71	1	56.71	7.76	0.0212	
Curvature	8.33	1	8.33	1.14	0.3134	not significant
Residual	65.74	9	7.30			
Lack of Fit	64.56	6	10.76	27.29	0.0103	significant
Pure Error	1.18	3	0.3942			
Cor Total	130.78	11				
Model	56.71	1	56.71	7.76	0.0212	significant
C-Catalyst						
Dosage	56.71	1	56.71	7.76	0.0212	
Curvature	8.33	1	8.33	1.14	0.3134	not significant
Residual	65.74	9	7.30			

The ANOVA included only one variable – catalyst dosage. This explains the aforementioned results of the 12 experimental runs that had the lowest and highest oxidation performance at its lowest (6 wt%) and highest (18 wt%) catalyst dosages, respectively. It could be seen that the model has a p-value of 0.0212. This implies that the generated model utilizing the variable is significant. Results also indicate that there is only a 2.12 % chance that a large F-value that can be caused by the noise associated with the experimental runs. However, the curvature was determined to be not significant (p-value = 0.3134). Thus, a response surface method is not essential to fully analyze the model and further optimization is not recommended.

### 3.5. Determination of the effects of UAOD parameters to sulfur removal

The effects and interactions of the parameters on the percent oxidation were analyzed in the UAOD process. **Fig. 2** shows the interaction plot of the response against the significant parameter. It is observed that the catalyst dosage had a significant effect on the percent oxidation, which was determined in the aforementioned section of the ANOVA in the UAOD system. It was observed that as the catalyst dosage increased, the percent oxidation increases. This is attributed to the higher

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3 dosage of catalyst for a reaction can result to the acceleration of oxidation reactions in the  
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5 compounds in contact with the catalyst molecules [25].  
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**Fig. 2** Model graph of the catalyst dosage in relation to the percent oxidation for the UAOD process

On the other hand, insignificant factors of the ultrasonication time and temperature have the implication of the percent oxidation even at large changes in its parameters does not substantially change the results. Therefore, further modifications in these parameters have little to no effect on the percent oxidation. The effect of the ultrasonication time in this study was concurrently observed in the study conducted by Shayegan et al. [26]. It was found that the overall oxidation changed is minimal as the time increases by a considerable duration. It was also observed in the study by Ja'fari et al. [27] that further exposing the process after 20 min had no significant effect on the desulfurization efficiency in terms of the sulfur content. This was due to the occurrence of hydrogen peroxide decomposition that forms water [26]. This phenomenon is also responsible for the behavior of the percent oxidation with respect to the ultrasonication temperature. The study of

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3 Shayegan et al. [26] found that the percent oxidation plateaued due to the positive and negative  
4 effects of the temperature counterbalancing each other. Although the reaction rate increases for a  
5 reaction theoretically at higher temperature, the hydrogen peroxide decomposes and cavitation  
6 collapse occurs that instigates a negative effect towards oxidation performance [28].  
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### 12 *3.6. Optimum parameters for UAOD*

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14 Since the curvature was found to be not significant for the 2k factorial model, further optimization  
15 was no longer employed. Therefore, the best parameter for the UAOD process was determined at  
16 the highest sulfur conversion to desulfurize a 2.3% S diesel: 30 min (ultrasonication time), 70 °C  
17 (reaction temperature) and 18 wt% (catalyst dosage). This is within a 30 wt% hydrogen peroxide  
18 is used at a ratio of 1:1 with respect to the fuel. The obtained percent oxidation for the UAOD are  
19 relatively low. However, a study made by Gao et al. [29] described that as the sulfur content of  
20 diesel increases, the percent sulfur removal efficiency decreases. The percent oxidation of UAOD  
21 process ranges from 27.95 % to 39.74 %. The highest BT and DBT removal resulted in 20.15 %  
22 and 55.50 %, respectively. The low oxidation efficiency could have been due to the small amount  
23 of H<sub>2</sub>O<sub>2</sub> relative to a large initial amount of sulfur in the simulated diesel oil. Furthermore, the  
24 efficiency of the UAOD process can be affected by the samples that were placed in a bath type  
25 ultrasonicator. This inefficiency may be attributed by the unconformable and unevenly distribution  
26 cavitation. According to the study of Nascentes et al. [30], ultrasonic baths produce ultrasound at  
27 low intensity and is unevenly spread out in the bath. Thus, a disadvantage of this type of  
28 configuration is the low repeatability and scalability. A better alternative for using the bath type  
29 ultrasonicator is the probe type counterpart. The probe type ultrasonicator are able to produce  
30 highly localized cavitation which results to a more intense and efficient sonication process [31].  
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### 53 *3.7. Evaluation and comparison of fuel properties*

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3 The basic properties (density, viscosity and the calorific value) of the diesel oil were measured to  
4 confirm the property deviation before and after the UAOD process. The following properties were  
5 determined at a room temperature of 30 °C.  
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10 The initial density of the simulated diesel after the addition of the sulfur compounds was measured  
11 to 0.8670 g/cm<sup>3</sup>. After applying the UAOD process, the density of the treated diesel oil was  
12 measured to be 0.8546 g/cm<sup>3</sup>. It can be seen that after the UAOD process the value of the density  
13 only shown a minor reduction against its initial value. The change in density was correlated to the  
14 calorific value of the HHV in the diesel oil. A reduction of density implies that the calorific value  
15 increases based on **Eqs. (3) and (4)**. The calculated calorific value of the simulated diesel oil mixed  
16 with the sulfur compounds was 44.91 MJ/kg. The value that was calculated after undergoing  
17 UAOD was 45.14 MJ/kg. This indicates only a small deviation with the initial calorific value of  
18 the untreated diesel oil. For the viscosity of the diesel oil, the viscosities before and after the UAOD  
19 process resulted to 1.734 cP and 1.812 cP, respectively. The change in viscosity did not deviate to  
20 the original value. The results of the oil properties signifies that the diesel oil was preserved even  
21 after undergoing UAOD.  
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#### 37 **4. Conclusions**

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40 In this research, the UAOD process was able to remove sulfur contents of BT and DBT in the  
41 simulated diesel oil. The percent sulfur removal ranged from 27.95 % to 39.74 %. The response  
42 obtained from the initial 2k factorial design showed that the UAOD model was not significant.  
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44 Therefore, no further optimization was required in the UAOD process. The recommended  
45 parameters for UAOD were 30 min, 18 wt% catalyst dosage and 70 °C that attained a percent  
46 oxidation of 39.74 %. HPW-AC catalyst dosage showed to be the significant parameter in UAOD.  
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48 On the other hand, ultrasonication time and temperature were found to be insignificant. The low  
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3 efficiency for the UAOD process was due to the type and size of ultrasonicator used. In the aspect  
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5 of physical properties, the simulated diesel oil did not substantially change before and after the  
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7 UAOD process. This denotes that the UAOD process was able to retain the essential diesel  
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9 properties. This is an important finding for the practical application of UAOD in industries to  
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11 produce clean and efficient diesel oil. It can be recommended in future works that a probe type  
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13 ultrasonicator be utilized in conjunction with the HPW-AC catalyst to significantly improve sulfur  
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15 conversion.  
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