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Parametric Screening Analysis for the Oxidative Desulfurization of Diesel Oil

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This research utilized a real raw diesel oil to be subjected in an innovative desulfurization technique. The novelty of this study is in the use of screening analysis in the ultrasonication enhancement of sulfur oxidation in actual fuel. This addresses the research gap in literature that have yet to compare and completely analyze all factors in the ultrasound-assisted oxidative desulfurization (UAOD) method. Specifically, the effects of ultrasonication via amplification and irradiation time, material usage of tetraoctylammonium bromide, hydrogen peroxide, polyoxometalate catalyst and the process parameters of fuel to oxidant molar ratio and temperature were examined. A definitive screening design (DSD) using the JMP 11.0 was utilized for a statistical screening analysis to determine the essential and non-essential parameters in the UAOD. Upon the oxidation of sulfur compounds in diesel oil, results suggested that the enhancement technique via ultrasonication, polyoxometalate catalyst and temperature were the only significant factors based on the p-value < 0.05. The aforementioned factors are essential due to being able to instigate an oxidation reaction of sulfurs into its sulfone forms. Based on the generated DSD experimental runs, sulfur conversion can range from 36.41 % to 92.69 %.

1. Introduction

Fossil fuel derived-oil is still relevant in its use in recent times. However, this would risk the stability and sustainability of the environment. Various researchers have developed desulfurization techniques to control harmful environmental impacts coming from fossil fuel derived-oil. Diesel oil is one of the fossil fuels that is derived from petroleum. Diesel fuel pertains to heavy fuel that is often used in heavy machineries and vehicle. A drawback in using untreated diesel oil is its high organic sulfur compound (OSC). This is also a common major problem in transportation fuels that cause air pollution, such as SO_X and particulate matter (PM) upon combustion. These compounds also have the ability to poison the catalyst in emission controls and cause drastic air pollution leading to acid rains (Yu et al., 2021). The removal of OSCs is an essential step to produce clean fuels.

Several desulfurization technologies have already been established. These are the hydrodesulfurization, biocatalytic-desulfurization, adsorptive desulfurization and oxidative technology. Out of all the technologies mentioned the oxidative desulfurization process has drawn a significant attention in the recent years. Advantages of using this particular process are for the reason of having its mild reaction conditions (operating at low reaction temperature and pressure) and that this does not use up any expensive and corrosive hydrogen in the process of removing the sulfur content as oppose to HDS (Chen et al., 2021). Oxidation reactions are more stable as oppose to biocatalytic-desulfurization (Chen et al., 2013). Wearing and erosion of the adsorbent remains a limitation in adsorptive desulfurization that would not be cost effective (Muzic, 2013). Despite the progress in oxidative desulfurization, the long reaction time to reach high desulfurization efficiency of this process still remains a drawback (Shafiq et al., 2021).

An innovative oxidative desulfurization technology called the ultrasound-assisted oxidative desulfurization (UAOD) has been investigated to increase the efficiency of oxidative reactions (Ghahremani et al., 2021). This type of technology provides a selective removal of the OSC from the hydrocarbons by combining the different processes such as selective oxidation, solvent extraction, and solid adsorption. However, there is a research gap in the investigation of all the possible parametric effect in the UAOD system. Studies such as Dana et al.

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(2020) only focused on the reaction time and oxidant to fuel molar ratio while Houda et al. (2020) analyzed the effect of oxidant concentration and catalyst dosage. The novelty of this study highlights an extensive statistical analysis through the of the definitive screening design (DSD) in JMP 11.0 to appropriately identify significant factors in UAOD. In this research, the UAOD system account for 7 process parameters of irradiation time, amplification, phase transfer agent, catalyst, oxidant concentration, fuel to oxidant ratio and reaction temperature. An actual raw diesel oil is also used in this study as opposed to the conventionally tested simulated diesel oil in literature.

2. Experimental

In order to appropriately oxidize sulfur compounds in diesel oil, it is essential to test and take appropriate measurements in the oxidizing agent, phase transfer agent and catalyst. The succeeding subsections describes the specific detail of the screening design of the variables in the UAOD setup.

2.1 Materials

Diesel oil (2,199.6 ppm sulfur) was obtained from Taichin Global Co. (Taoyuan, Taiwan). Hydrogen peroxide (H_2O_2, 50 % concentration) was acquired by G-Watt Co., Ltd. (Taiwan). Sodium phosphotungstate hydrate ($Na_3PW_{12}O_{40}\cdot xH_2O$) was supplied from Alfa Aesar (Taiwan). Tetraoctylammonium bromide ($C_{32}H_{68}BrN$, 98 % purity) was procured from Hungyao (Taiwan). All chemicals utilized were of analytical grade and without further purification step.

2.2 Instrumental analysis

An ultrasound apparatus (Sonic VCX, USA) equipped with a titanium probe tip (25 mm diameter and 122 mm length) was utilized and operated at 500 W and 20 kHz frequency. A Kubota 2420 Centrifuge was used with a setting of 3,000 rpm until only two phases are left. The sulfur content of diesel oil was analyzed using a SLFA-2100 X-ray fluorescence sulfur-in-oil analyzer (Horiba). SLFA-2100 Sulfur-in-oil analyzer or also known as the total sulfur analyzer (TSA) from Horiba, Taiwan. This is with compliance to the ASTM D4294 method that was used for analyzing diesel oil samples

2.3 UAOD methodology

The procedure for the oxidation through UAOD utilizes the combination of a specified amount of tetraoctlyammonium bromide as the phase transfer agent and sodium phosphotungstate hydrate as the polyoxometalate catalyst. These were added unto a set volumes of untreated diesel oil and hydrogen peroxide in a Pyrex beaker. The mixture was heated at a specific temperature setting. In the UAOD setup, the mixture was to be irradiated by ultrasound at frequency of 20 kHz with varying amplification for a specified time interval. After ultrasonication, the emulsified mixture was broken by a centrifugation step until a visible division of the oil phase and the aqueous phase. The oil phase was then withdrawn for analysis in a sulfur-in-oil analyzer.

2.4 Experimental design

Table 1: Variables and ranges for the definitive screening design for UAOD

Variables	Units	Ranges		
		Lower	Mid	Upper
X_1	min	6	18	30
X_2	%	20	40	60
X_3	mg	100	300	500
X_4	mg	10	255	500
X_5	%v/v	30	40	50
X_6	mL : mL	50:50	70:30	90:10
X_7	°C	30	50	70

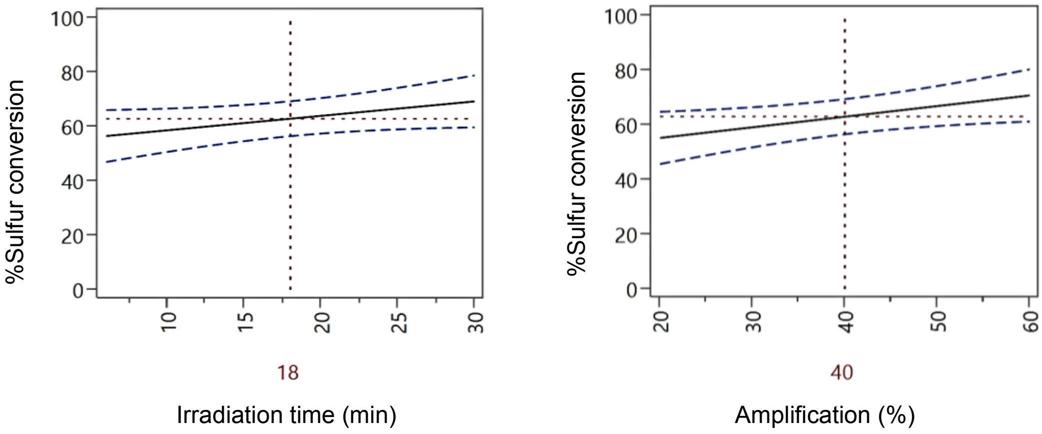
The screening analysis technique applies the concept of the DSD available on the JMP 11 statistical software. In this study, DSD utilizes the combinatory build of analysis for seven factors and three levels as shown in Table 1 in the UAOD analysis of diesel fuel. The irradiation time, amplification, tetraoctylammonium bromide, polyoxometalate catalyst, hydrogen peroxide concentration, fuel to oxidant ratio and temperature are the seven parametric variables to be analyzed. A total of 17 runs were generated for the screening studies.

3. Results and discussion

A parametric analysis followed by the statistical results on the DSD are discussed in the succeeding sections.

3.1 Analysis of irradiation time and amplification towards sulfur oxidation

Figure 1a shows a trend of 56.61 % to 69.34 % sulfur conversion from 6 min to 30 min. This is due to the irradiation time can help facilitate the liquid-liquid interfacial area of two immiscible liquid through emulsification that would accelerate mass transfer process (Lu et al., 2014). On the other hand, ultrasonic irradiation for UAOD applies in controlling the wave amplitude in order to accelerate the chemical processes and at the same time decrease reaction duration. In Figure 1b, the sulfur conversion improved from 55.21 % to 70.74 % from the amplification from 20 % to 60 %. This is attributed to the oxidation of sulfur compounds that occurs in the bulk of the oxidizing phase which would require a good dispersion as supported in the studies of Tang et al. (2013). This proves to show that the ultrasonic amplitude would be an important variable for desulfurization process.

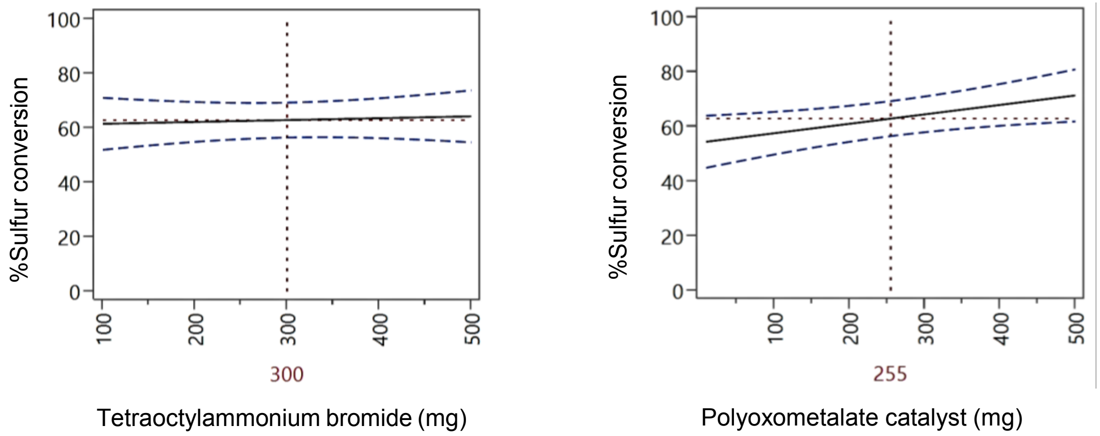


(a) (b)

Figure 1: Effect of (a) irradiation time and (b) amplification on sulfur conversion

3.2 Analysis of tetraoctylammonium bromide and polyoxometalate catalyst towards sulfur oxidation

The presence of the tetraoctylammonium bromide would be required in order to promote emulsification reaction. At a tetraoctlyammonium bromide dosages from 100 mg to 340 mg, the sulfur conversion improves from 61.60 % to 64.34 % as consistently seen in Figure 2a. The increasing trend occurred due to the emulsion of the two immiscible liquid mixtures. One of the liquids is totally dispersed into small droplet which forms throughout the other liquid with the aid of the phase transfer agent. Emulsion reaction system together with the reaction media could overcome reagent incompatibility problems due to high concentrations of both hydrophilic and hydrophobic compounds (Sachdeva and Pant, 2010).



(a) (b)

Figure 2: Effect of (a) tetraoctlyammonium bromide and (b) polyoxometalate catalyst dosages on sulfur conversion

Polyoxometalate catalysts in mild conditions are studied to be effective in combination of the hydrogen peroxide oxidant that exhibits fast reversible multi electron redox reaction. In Figure 2b, the polyoxometalate catalyst from 10 mg to 500 mg have improved the oxidation of sulfur in diesel oil from 54.49 % to 71.46 %. This is associated to the catalytic reactivity in the oxidation process. When hydrogen peroxide reacts with the polyoxometalate catalyst in the UAOD system, this would result to the formation of peroxometal complexes that bears the active oxygen and are effective species for epoxidation.

3.3 Analysis of hydrogen peroxide concentration, fuel to oxidant and temperature towards sulfur oxidation

The organic phase consists of the various thiophenic sulfur compounds its derivatives in actual fuel oil samples. The aqueous phase refers to the amount of oxidizing agent used. It is important to know the fuel to oxidant ratio to find the condition for equilibrium concentration and the influence of the oxidizing agent to the sulfur compounds. It is observed at fuel to oxidant ratio from 50:50 to 90:10 would only have a minimal increase in sulfur conversion from 62.61 % to 63.33 %. This implies that sulfur conversion is already appropriate at its minimum level as observed in Figure 3b. Figure 3c indicates an increase in sulfur conversion from 49.48 % to 76.47 % from temperature settings of 25 °C to 75 °C, respectively. This is associated with the conversion of refractory cyclic sulfur compounds increases with higher reaction temperature (Sachdeva and Pant, 2010). The reaction rate at higher temperature increases due to the lower interfacial tension in the organic and aqueous phase that promotes higher sulfur conversion (Lu et al., 2014).

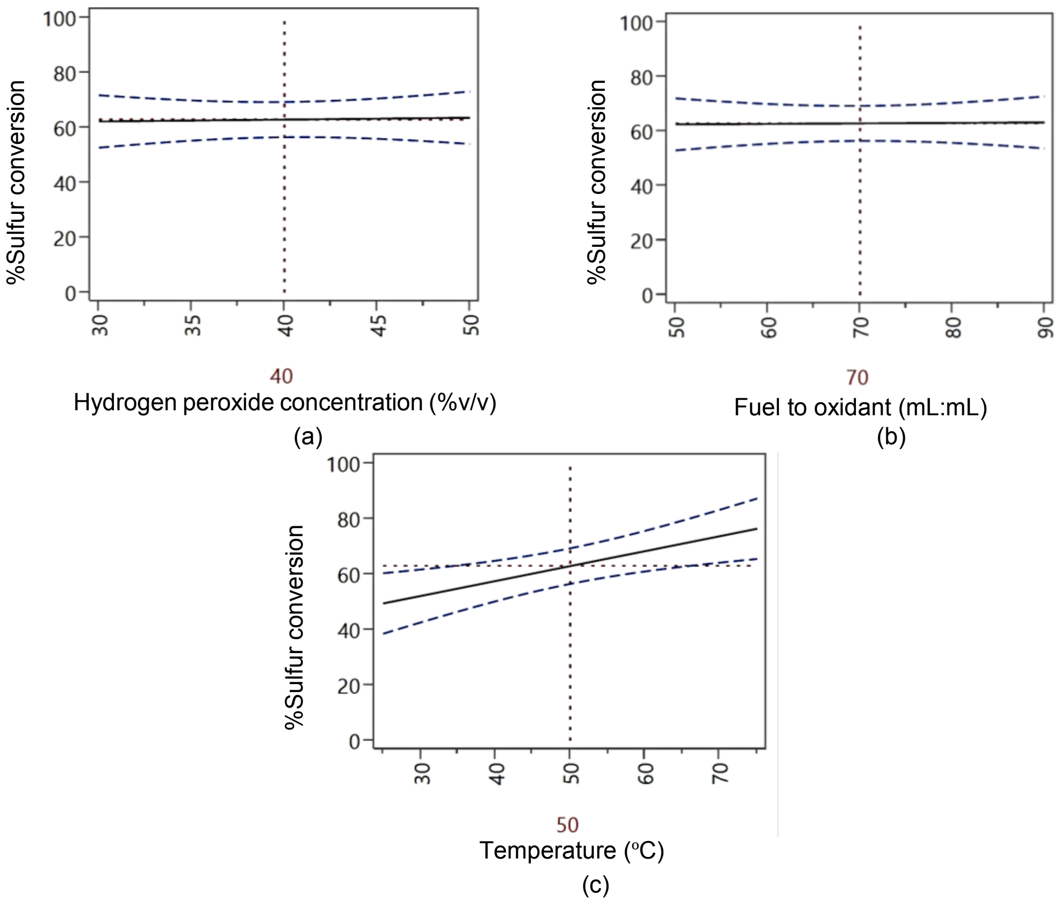


Figure 3: Effect of (a) hydrogen peroxide concentration and (b) fuel to oxidant and (c) temperature on sulfur conversion

3.4 Statistical analysis based on the DSD

A total of 17 runs were generated using the DSD upon varying seven variables for UAOD (irradiation time, amplification, tetraoctylammonium bromide, polyoxometalate catalyst, hydrogen peroxide concentration, fuel to oxidant ratio and temperature) in diesel oil. Table 1 shows the complete response of all the runs with respect to the percentage sulfur conversion in UAOD. The range for the response for percentage sulfur conversion in

UAOD was in between 36.41 % to 92.69 %. Table 2a lists the summary of fit the DSD of the 17 runs in the UAOD. Results indicate a coefficient of correlation (R^2) and adjusted R^2 of 0.9378 and of 0.9004, respectively. A high R^2 value implies that the variation of the response has a strong correlation to the formulated model rather than in its random error. The RMSE value exhibited a small value of 5.62 %. This suggests that there is only a small random error associated to the response. In Table 2b, an analysis of variance (ANOVA) is shown for the UAOD process of the oxidation of sulfur to sulfones in diesel oil. Results confirms an extreme significance (p-value < 0.0001) in the formulated model. This implies that the DSD model is highly significant signifying a suitable fit towards the tested factors and response. On the other hand, Table 2c lists the parameter estimates of each factor in the model parameters of the UAOD process. A p-value less than 0.05 shows that the factors are statistically significant, while a p-value of greater than 0.05 designates a statistically insignificant factor towards the response. Specifically, the factors of irradiation time, amplification, polyoxometalate catalyst and temperature are statistically significant factors, while the other factors are statistically insignificant. Furthermore, the interaction of irradiation time with polyoxometalate catalyst and the amplification with temperature are significant in the UAOD process.

Table 1: Definitive screening design of experiment for UAOD

Run	X_1	X_2	X_3	X_4	X_5	X_6	X_7	% Sulfur Conversion
1	30	20	500	10	30	70:30	70	48.31
2	6	20	100	500	30	90:10	70	54.04
3	18	60	500	500	50	90:10	70	92.69
4	6	60	300	10	30	90:10	30	48.52
5	30	60	100	500	30	50:50	50	80.36
6	30	60	100	10	40	90:10	70	81.97
7	6	60	500	255	30	50:50	70	83.17
8	30	60	500	10	50	50:50	30	47.11
9	6	60	100	500	50	70:30	30	47.74
10	30	20	100	255	50	90:10	30	55.50
11	6	20	500	10	50	90:10	50	42.57
12	30	20	300	500	50	50:50	70	87.55
13	18	20	100	10	30	50:50	30	36.41
14	6	40	100	10	50	50:50	70	62.62
15	6	20	500	500	40	50:50	30	48.48
16	30	40	500	500	30	90:10	30	75.47
17	18	40	300	255	40	70:30	50	78.03

Table 2: (a) Summary of fit, (b) ANOVA and (c) parameter estimates for the UAOD System

(a)

R^2	0.9378
R^2 adjusted	0.9004
Root mean square error	5.62
Mean of response	63.27
Observations	17

(b)

Source	Degrees of freedom	Sum of squares	Mean square	F Ratio
Model	6	4758.25	793.04	25.11
Error	10	315.80	31.58	p-value
C. Total	16	5074.05		< 0.0001

(c)

Term	Standard error	T Ratio	p-value
Intercept	2.04	36.39	< 0.0001
X_1	6.37	3.33	0.0076
X_2	7.76	4.06	0.0023
X_4	8.49	4.44	0.0013
X_7	13.49	5.64	0.0002
X_1X_4	5.79	2.80	0.0187
X_2X_7	6.77	2.62	0.0256

4. Conclusions

In this study, results indicated the that the four essential parameters for UAOD are the irradiation time, amplification, polyoxometalate catalyst and temperature. This is attributed to a substantial increase towards sulfur conversion in diesel oil due to the formation of a more stable peroxometal complex that aids in the oxidation reaction of sulfur compounds through ultrasonic emulsification in fuel oil. This address the research gap in literature by statistically determining significant factors in UAOD that has yet to be determined in previous studies. Based on the statistical analysis through the DSD, the UAOD system of diesel oil showed a statistically significant effect towards the parameters of irradiation time (p-value: 0.0076), amplification (p-value: 0.0023), polyoxometalate catalyst (p-value: 0.0013) and temperature (p-value: 0.0002) in the UAOD. The results of this study proved to successfully screen insignificant factors towards accounting for the significant factors. Based on the DSD experimental runs, parameters at 18 min irradiation time, 60 % amplification, 500 mg of polyoxometalate catalyst and 70 °C reached a high sulfur conversion of 92.69 %. The novel results produced in this study can lead to practical implications of focusing on the four factors in UAOD. It is recommended in future works to further test the combinatorial parameters of irradiation time, amplification, polyoxometalate catalyst and temperature in optimization studies to determine its applicability in adherence to the standard regulatory limits of sulfur in diesel oil. This is essential to assess the practicability of identifying UAOD to be utilized in actual industrial practice in its succeeding studies.

Nomenclature

X_1 – irradiation time, min
X_2 – amplification, %
X_3 – tetraoctylammonium bromide, mg
X_4 – polyoxometalate catalyst, mg
X_5 – hydrogen peroxide concentration, % v/v
X_6 – fuel to oxidant ratio, mL : mL
X_7 – temperature, °C

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