

An Innovative Approach for Oxidative Desulfurization Advancement through High Shear Mixing: An Optimization Study on the Application of Benzothiophene

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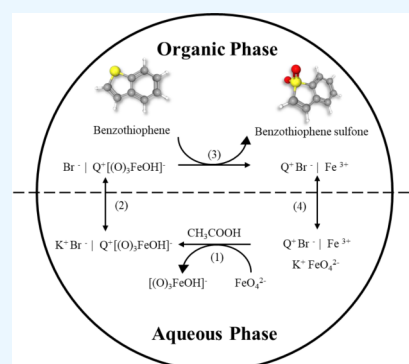
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ABSTRACT: Alternative fuels are being explored to mitigate the effects of petroleum-based fuels. Pyrolysis oil from waste tires is a promising alternative fuel; however, it contains very high concentrations of benzothiophene (BT) which are beyond the allowable sulfur limits of Taiwan and the Philippines. Mixing-assisted oxidative desulfurization (MAOD) is a method that removes sulfur from fuel oils by utilizing high-shear mixing and oxidants. In this paper, the oxidation of BT in a model fuel was studied to determine optimal process conditions. Crude Fe(VI) prepared from sludge was used as the oxidant. Using the Box–Behnken design under response surface methodology, the significance of the following independent variables was studied: mixing speed (4400–10 800 rpm), phase transfer agent (PTA) amount (100 to 300 mg), Fe(VI) concentration (400–6000 ppm), and mixing temperature (40 to 60 °C). The results from a comprehensive statistical analysis showed the increase of sulfur conversion with high levels of Fe(VI) concentrations and PTA amounts together with low levels of agitation speeds and temperatures. The BT to BT sulfone conversions from experimental runs ranged from 17% to 64%. The optimum sulfur conversion of 88% for the BT model fuel was reached at the maximum levels of Fe(VI) concentration and mixing speed, along with the minimum levels of PTA concentration and temperature. The optimal MAOD variables were applied to a high-sulfur pyrolysis oil sample, which resulted in a sulfur reduction of 55%. The produced fuel oil meets the sulfur requirements of Taiwan and the Philippines for industrial heating oils. Therefore, the findings of the study support the effectiveness of sludge-derived Fe(VI) in the MAOD of BT in the model fuel and pyrolysis oil under mild process conditions.



1. INTRODUCTION

Fossil fuel-derived oils have been conventionally used to accompany the increasing demand for heat and power generation, especially in transportation and industries. However, due to the rapid depletion of materials and the negative environmental effects of fossil fuels, researchers are exploring alternative fuels with lower environmental impacts than fossil oil sources. These alternative fuels include pyrolysis oil from biomass, waste plastic, and waste tires. In this study, pyrolysis is a process wherein waste tires are subjected to high temperatures (above 300 °C) in the absence of oxygen to facilitate main chain degradation and cross-linking disconnection.¹ Main chain degradation occurs in C–C bonds and is accompanied by hydrogen transfer. Meanwhile, the bond fragments with sulfur radicals recombine and form new bonds.² After the heating process, char and volatile products are produced. The volatile products then undergo condensation, which separates gaseous products from pyrolysis oil.³ Pyrolysis oil is reported to be useful due to its similar characteristics to diesel, particularly in density and calorific value, after undergoing treatment.⁴ Although pyrolysis oil is not applied as a transportation fuel, it has shown promising applications in

industrial usage, specifically as a boiler fuel and heavy oil generator. It also serves as potential feedstock for the production of carbon black.⁵ However, a disadvantage of utilizing pyrolysis oil from waste tires is the high amount of sulfur compounds, especially benzothiophene (BT).⁶

Exposure to sulfur compounds can cause several problems, which include respiratory problems in humans and growth problems in plants. Environmentally, the release of these compounds in the atmosphere may strengthen acid rain and reduce atmospheric visibility.⁷ Due to these potential issues, laws have been set by governments to limit the sulfur concentration in fuels for industrial usage. In 2020, Taiwan set its sulfur limit for heating oils to 5 000 ppm.⁸ In the Philippines, special-grade industrial fuel oils have a sulfur limit of 10 000 ppm.⁹ To reduce the sulfur concentration in fuel, the

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process of hydrodesulfurization (HDS) is commonly used because it is efficient in removing acyclic and aliphatic sulfur compounds, particularly thiols, sulfides, and disulfides. However, HDS can also decrease the lubricating properties of fuels as it involves the removal and hydrogenation of selected aromatics.¹⁰ Furthermore, HDS was found to be ineffective in converting sterically hindered heterocyclic thiophenic compounds, such as BT and dibenzothiophene (DBT), and their alkyl derivatives.¹¹

With this, alternative desulfurization processes were introduced, one of which is oxidative desulfurization (ODS). ODS promotes the oxidation of aromatic compounds to their resulting sulfones and/or sulfoxides with the aid of an oxidant. The advantage of ODS over HDS is its use of mild operating conditions, such as atmospheric pressure and temperatures below 100 °C.¹² Following the oxidation stage, oxidized sulfur compounds can be easily extracted through adsorption, extraction of solvent, or distillation, as they are significantly more polar than hydrocarbons.¹³ Phase transfer agents (PTAs) are also added to the reaction mixture to aid the transfer of the materials between the two phases. Various catalysts are also studied to improve the efficiency of the process. Common heterogeneous catalysts used in the ODS process include transition metal oxides, polyoxometalates, and ionic liquids.¹⁴ Metal–organic frameworks are also widely studied for their high surface area, thermal stability, and excellent recyclability.¹⁵

Modifications to the ODS process have been made to improve the rate of sulfur removal under optimal conditions. A common modification is ultrasound-assisted oxidative desulfurization (UAOD). UAOD utilizes ultrasound irradiation to increase cavitation and provide more sites for reaction, promoting mass transfer and accelerating oxidation.¹⁶ However, in a commercialized setting, the UAOD method would demand high energy and numerous devices, such as amplifiers and sono-reactors.¹⁷ Mixing-assisted oxidative desulfurization (MAOD) is a modification in ODS that utilizes high shear mixing to enhance contact between the two phases by creating small droplets through molecular diffusion and achieving sulfur conversion.¹⁸

Commonly used oxidants in ODS include hydrogen peroxide,¹⁹ oxygen gas,¹⁰ and ferrate.²⁰ H₂O₂ is particularly utilized since it is cheap, easily available, and environmentally friendly.²¹ A study in 2014 utilized H₂O₂ and compared the capability of the sulfur conversion of UAOD and MAOD.¹⁷ The study findings indicated that both systems achieved a conversion rate of 99% for DBT and 98% for BT. The optimized conditions for the MAOD reaction were found to be 10 000 rpm mixing speed, 70 °C reaction temperature, and 30 min reaction time. Oxygen gas has also been studied due to its wide availability and low cost. Noncatalytic ODS of kerosene and diesel fractions was also optimized using oxygen gas in the presence of water. In this process, a bubble reactor was maintained at 180 to 200 °C and 2.5 to 3.0 MPa. The study revealed that water had a positive effect in balancing the oxidation intensity for the hydrocarbon medium but had no effect on the removal of sulfur compounds from the oil fractions. The mercaptan sulfur removal degree reported in the study was 62%.¹⁰ Meanwhile, Fe(VI) or potassium ferrate (K₂FeO₄) is known for its high stability, selectivity, and a high reduction potential of 2.2 V in an acidic medium and is considered environmentally friendly.²² One study explored the effectiveness of commercial Fe(VI) as an oxidant in the MAOD of sulfur compounds and real diesel oil.²⁰ The

researchers optimized the process by varying agitation speed (7600 to 14 000 rpm), temperature (50 to 70 °C), and mixing time (10 to 30 min). The optimal parameters were determined to be 12 198 rpm, 52.22 °C, and 15.42 min for BT, and 8,704 rpm, 51.26 °C, and 14.43 min for DBT. Confirmatory runs resulted in mean conversion rates of 84.35% for BT and 93.68% for DBT in model fuels. The same parameters were applied to diesel oil wherein sulfur conversion reached 58.03% and 93.15% using BT and DBT optimal conditions, respectively. The study also highlighted the impact of the temperature on the system, finding that higher temperatures favor the formation of Fe(VI) complexes. However, increasing the temperature to 70 °C may lead to reduced oxidation activity due to the low thermostability of Fe(VI) at this temperature.

Despite the effectiveness of commercial Fe(VI), its availability is very limited and costly. Therefore, different methods for synthesizing Fe(VI) from various sources are being explored. One method is called the wet oxidation method, wherein raw materials containing Fe(III) are oxidized using hypochlorite and hydroxide solutions.²³ One potential raw material for this method is drinking water treatment sludge (DWTS). In the drinking water treatment process, Fe is used as an oxidant and a disinfectant, particularly in sludge dewatering, anaerobic fermentation, sludge minimization, and pollutant removal.²³ The produced DWTS contains high concentrations of Fe(III) compounds, which can be used to derive Fe(VI). A recent study reported the effect of Fe(VI) derived from DWTS as an oxidant in the UAOD of organosulfur compounds and optimized sulfur conversion by varying ferrate concentration (100 to 300 ppm), PTA concentration (100 to 300 mg), organic to aqueous phase ratio (10:30 to 30:10), and sonication time (10 to 30 min). The applied optimum parameter values of 100 ppm ferrate, 100.01 mg PTA, 30:10 organic to aqueous phase ratio, and 13.32 min resulted in 43.91% BT conversion in a model fuel.¹¹

Previous studies have established that increasing various variables, such as ferrate concentration, PTA concentration, agitation speed, and mixing temperature, does not necessarily translate to an increase in sulfur conversion. For instance, excessive concentrations of ferrate and PTA may produce a low sulfur conversion due to the nature of compounds and steric hindrance.¹⁸ Additionally, in the frame of MAOD, the increase in agitation speed increases the rate of mass transfer; however, elevated mixing speeds may also cause the formation of whirlpools, which slow down the rate of desulfurization.²⁴

A recent paper by the authors has synthesized Fe(VI) from drinking-water treatment sludge (DWTS) and applied it in the MAOD of DBT. The results showed that the maximum DBT conversion in model fuel reached 99.6%. Furthermore, the high levels of Fe(VI) concentration and low levels of PTA concentration and agitation speed favored sulfur oxidation. The application of the optimized parameters in pyrolysis oil desulfurization reached 53.2%.²⁵

From previous studies, the desulfurization of BT was found to be harder to achieve than DBT due to its lower electron density, which translated to a rate constant that is eight times slower.²⁶ Thus, this paper is a continuation of the previous study, as the effect of using Fe(VI) from drinking-water treatment sludge in the MAOD of BT has not been explored.

The novelties of this study are as follows:

- 1 usage of Fe(VI) derived from DWTS to oxidize BT in an MAOD system;
- 2 optimization of Fe(VI) concentration, PTA concentration, mixing speed, and mixing temperature to achieve the maximum BT conversion using the Box–Behnken design under the response surface methodology (BBD-RSM); and
- 3 application of the optimal variables in the MAOD of a high-sulfur pyrolysis oil sample and comparison of its performance with the optimal variables obtained from the MAOD of DBT.

2. METHODS

2.1. Materials. The model sulfur compound BT (98% purity) was purchased from Alfa Aesar (Taiwan). Glacial acetic acid, tetraoctylammonium bromide (TOAB; 98% purity), toluene (0.99 mass fractions), sodium hydroxide pellets ($\geq 99\%$), and potassium hydroxide pellets ($\geq 99\%$) were obtained from Sigma-Aldrich (USA). Nitric acid (69%) and sodium hypochlorite (6–12%) were acquired from Merck (USA) and Nihon Shiyaku (Japan), respectively. DWTS was sourced from the Changhua No. 3 Water Purification Plant located in Changhua City, Taiwan. The pyrolysis oil from waste tires was procured from Kao Hsing Chang Company, Taiwan.

2.2. Oxidant Preparation. The method of K_2FeO_4 preparation was adapted from the study by Arcega et al.¹¹ A sludge sample weighing 8.5 g was dissolved in 8.5 mL of 2 M HNO_3 . The mixture was stirred for 1.5 h at 100 rpm. In another flask, a mixture of 1:2 NaOH:NaOCl was vigorously stirred in a cold-water bath. The combination of the predissolved sludge and the NaOH–NaOCl mixture was continuously stirred at 400 rpm for 1 h. After this, 250 mL of saturated KOH was added, and the solution was stirred for 40 min at 400 rpm. This was followed by centrifugation at 4 000 rpm for 20 min. The top dark purple liquid was extracted and prepared for the MAOD experiment. The concentration of the Fe(VI) product was tested by using ultraviolet–visible spectroscopy at 510 nm.

2.3. MAOD Experiment. The experiment was conducted in a 400 mL beaker in which predetermined concentrations of 50 mL of the BT model fuel, 50 mL of the K_2FeO_4 oxidant, and PTA were added. To maintain the optimal conditions, glacial acetic acid was added dropwise until pH of 5 was achieved and the temperature was controlled using a heating mantle. The mixture was agitated for 30 min in a T 25 digital ULTRA-TURRAX mixer under varying Fe(VI) concentrations, PTA concentrations, mixing speed, and mixing temperature. The pH and temperature of the system were closely monitored to ensure that controlled conditions were maintained. After the completion of the reaction, the mixture underwent a cooling phase and was subsequently centrifuged at 4 000 rpm for 20 min. The model fuel was extracted for instrumental analysis.

2.4. Statistical Analysis. The experimental design under BBD-RSM is presented in Table 1. The four independent variables tested were the following: ferrate concentration (X_1 : 400 ppm to 600 ppm), PTA concentration (X_2 : 100 to 300 mg per 50 mL⁻¹ model fuel), mixing speed (X_3 : 4 400 rpm to 10 800 rpm), and mixing temperature (X_4 : 40 to 60 °C).

The general form of the quadratic equation to optimize the process is given by eq 1.

Table 1. Box–Behnken Design Variables for the Study

Factors	Levels		
	Low (-1)	Medium (0)	High (+1)
Fe(VI) concentration (ppm), X_1	400	500	600
PTA concentration (mg/50 mL model fuel), X_2	100	200	300
Mixing speed (rpm), X_3	4,400	7,600	10,800
Mixing temperature (°C), X_4	40	50	60

$$y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j \quad (1)$$

where y is percentage sulfur conversion, X_1 to X_k are the four operating variables, and β_1 to β_k are unknown variable coefficients. The experimental results were investigated by analysis of variance (ANOVA) and Design Expert v.22.

2.5. Instrumental Analysis. The BT model fuel was quantitatively analyzed using a gas chromatograph with a sulfur chemiluminescence detector (GC-SCD, Agilent Gas Chromatograph, 7890A, CA, USA) to ensure precision in measuring sulfur concentrations. The column was stabilized for 1 h prior to its usage to ensure constant temperature throughout the equipment. The column temperature upon starting the analysis was set at 150 °C for 1 min, and heating was done at 20 °C min⁻¹ for 4 min until the temperature reached 220 °C. The inlet was operated with 18.243 psi and 28.2 mL min⁻¹ total flow in split mode with a 20:1 split ratio. The column utilized in the analysis was an Agilent 19091S–433 with a flow of 1.2 mL min⁻¹. A total sulfur analyzer (Horiba SLFA-2100) was used to measure sulfur concentrations of the pyrolysis oil sample, before and after desulfurization.

3. RESULTS AND DISCUSSION

3.1. Effects of Fe(VI) Concentration and PTA Concentration. A proposed mechanism for oxidation involves the formation of a more reactive complex, $[O_3Fe(OH)]^-$, from Fe(VI) and acetic acid. This complex bonds with the quaternary ammonium cation (Q^+), forming $Q^+[O_3Fe(OH)]^-$.¹⁸ This compound creates an emulsion that enables the oxidation of BT to its sulfoxide and sulfone forms. Throughout the mixing process, the oxidant exhibits an evident color change from purple to brown, indicating the reduction of Fe(VI) to Fe(III). However, due to current limitations, detailed characterization of the oxidant and stability of the complex was reserved for further experimentation.

Figure 1 presents the effects of (a) Fe(VI) Concentration and (b) PTA concentration on BT conversion in a model fuel. It was observed that using 400 to 500 ppm Fe(VI) concentration resulted in an increase in oxidation. This increase is attributed to the presence of more complex Fe(VI) ions in acidic media, such as monoprotonated Fe(VI), which are responsible for oxidizing BT.²⁷ However, increasing the Fe(VI) concentration to 600 ppm resulted in a lower sulfur conversion. Previous studies reported similar results and attributed it to the basic shift in the system pH due to the high Fe(VI) concentration, as more ions are present to react with H^+ and water.¹⁸ Meanwhile, it is observed that BT oxidation decreased from 45.8% to 36.4% with an increase in the PTA amount from 100 to 300 mg. This is attributed to the formation of thicker and more turbid layers as the level of PTA increases. From a similar ODS study using commercial Fe(VI),

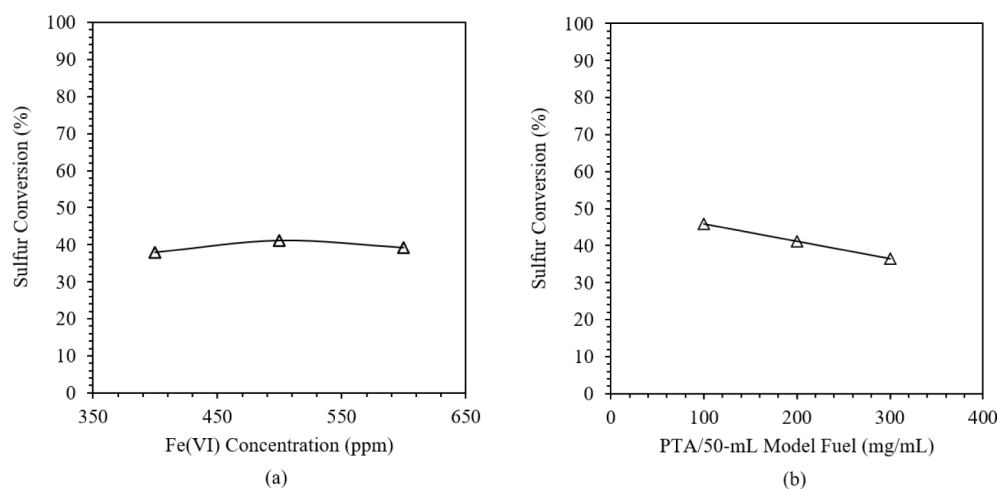


Figure 1. Effects of (a) Fe(VI) concentration and (b) PTA concentration on % S conversion of BT.

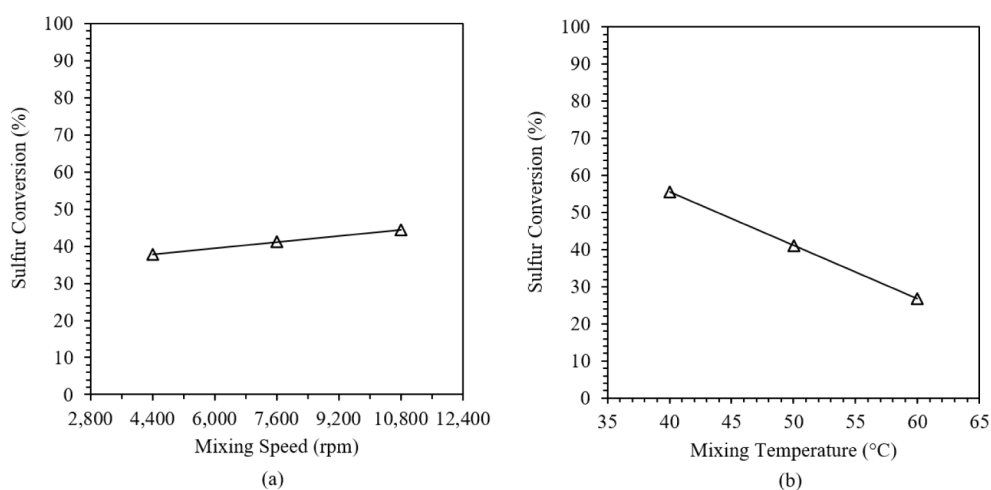


Figure 2. Effects of (a) mixing speed and (b) mixing temperature on the % S conversion of BT.

it was reported that the high concentration of alkyl groups from the PTA may cause steric hindrance in the system, preventing the oxidation of BT.¹⁸ Additionally, brominated byproducts are formed in the MAOD of BT due to the reaction of TOAB with BT. These unwanted byproducts are caused by side reactions that may compete with the desired oxidation reaction of BT to BTO.

In comparison to the previous desulfurization study, it is notable that BT desulfurization resulted in a significantly lower sulfur conversion. In application to DBT, the same system produced the maximum sulfur conversion of 97.3% and 98.7% in the one-factor analysis using Fe(VI) concentration and PTA concentration, respectively.²⁵ This significant contrast is due to the selectivity of oxidative desulfurization to DBT and BT. The reactivity of the refractory compounds is associated with their electron density. A previous study reported that DBT has a higher electron density than BT, with a reported oxidation rate constant of $0.0460 \text{ L mol}^{-1} \text{ min}^{-1}$, eight times that of BT.²⁶ This implies that DBT undergoes oxidation much faster and explains the lack of brominated byproducts in the MAOD of DBT.²⁸

3.2. Effects of Mixing Speed and Mixing Temperature. The effects of the (a) mixing speed and (b) mixing temperature on BT conversion are illustrated in Figure 2. An increasing trend was observed for BT conversion where results

increased from 37.8% to 44.5% and from 4 400 rpm to 10 800 rpm. The mass transfer resistance in the system is reduced as the agitation speed increases to 10 800 rpm and more Fe(VI) ions are transferred in the interface to react with the sulfur compounds, translating to a higher sulfur conversion.²⁴ On the other hand, a decreasing trend of BT oxidation was observed for an increase in temperature, wherein sulfur conversion lowered from 55.5% to 26.8% and from 40 to 60 °C. The low sulfur conversions at increasing temperatures may be attributed to the increased reaction of Fe(VI) with water, which produces Fe(III) and O_2 and reduces its high oxidation potential.²⁹

Figure 3 presents the reaction products in the BT model fuel after undergoing MAOD, as identified using GC-SCD. At the peak times of 3.622 and 4.976 s, the compounds

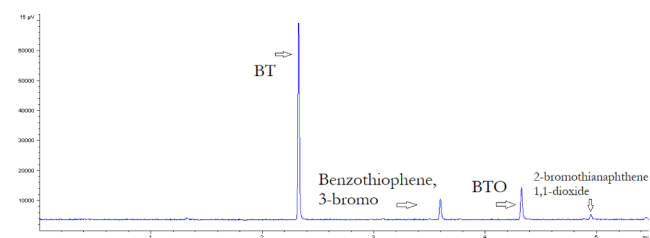


Figure 3. Reaction products after the MAOD of BT.

benzothiophene, and 3-bromo and 2-bromothianaphthene 1,1-dioxide were observed. The formation of these brominated minor products is caused by the reaction of BT with TOAB which was used as the PTA in the MAOD process. As temperature increases, there is also a higher collision frequency between PTA and BT, which can increase the rate of unwanted side reactions in the system. As a result, this decreases the reaction of BT into BTO, translating to a lower %S conversion. A similar ODS study reported the presence of the same brominated byproducts using H₂O₂ as an oxidant and TOAB as the PTA over different polyoxometalate catalysts under a temperature range of 30 to 70 °C.³⁰

3.3. Statistical Analysis. A total of 27 runs were performed for the study under BBD-RSM. As presented in Table 3, BT sulfur conversions were observed from 16.5 to 63.7%. The fit summary of linear, two-factor, quadratic, and cubic models is presented in Table 2. The coefficient of

Table 2. BBD-RSM Variables with Corresponding Percent Conversions

Fe(VI) Concentration (ppm)	PTA (mg/50 mL model fuel)	Agitation Speed (rpm)	Mixing Temperature (°C)	BT Percent Conversion (%)
500	100	4,400	50	40.0
400	200	7,600	40	43.7
400	200	4,400	50	54.1
600	200	4,400	50	21.9
500	200	4,400	60	24.4
600	200	7,600	60	16.5
500	300	4,400	50	33.3
500	200	7,600	50	42.6
500	200	7,600	50	50.0
500	300	7,600	40	61.6
500	200	4,400	40	49.0
500	100	7,600	60	44.2
600	200	10,800	50	53.1
400	100	7,600	50	32.2
500	200	10,800	60	30.1
600	300	7,600	50	20.9
600	100	7,600	50	49.6
500	300	10,800	50	46.9
500	100	7,600	40	54.1
400	300	7,600	50	32.1
400	200	7,600	60	25.4
500	300	7,600	60	17.3
500	200	7,600	50	47.8
500	100	10,800	50	48.2
400	200	10,800	50	20.8
500	200	10,800	40	63.7
600	200	7,600	40	57.9

determination, expressed as R^2 , refers to the statistical evaluation of the model's quality. The resulting adjusted R^2 and predicted R^2 metrics are indicative of the goodness of fit within the generated model equation. The results in Table 3 indicate a high R^2 of 0.9083 for the quadratic model, as determined through the ANOVA test. The model's capacity for prediction is supported by a predicted R^2 value of 0.7754, demonstrating its effectiveness in calculating sulfur reduction based on the Fe(VI) concentration, PTA concentration, mixing speed, and mixing temperature. The quadratic model was also determined to be the best fit for the sulfur conversion data with a probability value (p -value) of 0.0063 and a

Table 3. Fit Summary for BT Models Using BBD-RSM

Source	Sequential p -value	Lack of Fit p -value	Adjusted R^2	Predicted R^2	
Linear	0.0011	0.1150	0.4650	0.3018	
2FI	0.0011	0.2626	0.7904	0.6393	
Quadratic	0.0063	0.5010	0.9083	0.7754	Suggested
Cubic	0.4910	0.4195	0.9149	-0.1072	Aliased

significant lack of fit derived from the Fisher variance ratio (F -value) of 0.500 in comparison with the cubic, linear, and two-factor interaction models.

The coefficients of independent variables (β_1 to β_k), based on the independent variable responses defined in Table 1 (X_1 , X_2 , X_3 , and X_4), were determined using the experimental data of sulfur conversion. The quadratic response surface model that predicts %S conversion is presented in eq 2. A positive sign in the model equation implies that sulfur conversion is increased by increasing the levels of the independent variables. Meanwhile, a negative sign denotes the reduction of sulfur conversion as a result of increasing the tested variables.

$$\begin{aligned} \%S \text{ conversion} = & 91.47349 + 0.651718X_2 - 0.027452X_3 \\ & + 0.949615X_4 - 0.000537X_1X_2 \\ & + 0.000057X_1X_3 - 0.001328X_1X_4 \\ & - 0.0086X_2X_4 - 0.000253X_1^2 \end{aligned} \quad (2)$$

The ANOVA of the BT quadratic model is presented in Table 4. This analysis determines the level of importance of the individual process variables to validate the generated quadratic equation. The residual values show the degree of unexplained variation in the response. Meanwhile, the lack of fit assesses the extent to which model predictions differ from the observed values. The indicated pure error measures the differences between replicate runs, while the row of corrected total sum of squares (correlation total) defines the overall variation around the mean of the observations. For each process variable and interaction, the sum of squares, degrees of freedom, mean square, F -value, and p -value are listed. The sum of squares defines the sum of squared differences between the overall average and the variance explained by the source in each row. Meanwhile, the degrees of freedom pertain to the number of estimated parameters used to compute the sum of squares. The mean square, also known as variance, is computed by dividing the sum of squares by the degrees of freedom. The F -value and p -value are also utilized to assess the significance levels of a specific process variable and its interactive variables with respect to the sulfur conversion parameter in the context of the MAOD system. A high F -value implies that the variability of the response can be explained by the quadratic model, indicating the significance of the coefficient term. Meanwhile, a p -value of less than 0.05 indicates that the model and the coefficient terms are statistically significant.³¹ The ANOVA for the reduced quadratic model is presented in Table 5. The results show that the significant terms in the model were X_2 , X_3 , X_4 , X_1X_2 , X_1X_3 , X_1X_4 , X_2X_4 , and X_1^2 . These variables are identified to have a strong significance as supported by their p -values (<0.0500). Moreover, the specific process variables of X_4 and X_1X_3 were found to be extremely significant in strongly influencing the sulfur conversion response based on their high F -values ($X_4 = 145.85$ and

Table 4. ANOVA for the BT Quadratic Model

Source	Sum of Squares	d f	Mean Square	F-value	p-value	
Model	5033.52	14	359.54	19.39	<0.0001	significant
X ₁ -Fe(VI) Concentration	11.21	1	11.21	0.6048	0.4518	not significant
X ₂ -PTA	263.20	1	263.20	14.20	0.0027	significant
X ₃ -Agitation Speed	134.00	1	134.00	7.23	0.0197	significant
X ₄ -Temperature	2468.20	1	2468.20	133.11	<0.0001	significant
X ₁ X ₂	204.49	1	204.49	11.03	0.0061	significant
X ₁ X ₃	1040.06	1	1040.06	56.09	<0.0001	significant
X ₁ X ₄	133.40	1	133.40	7.19	0.0200	significant
X ₂ X ₃	7.29	1	7.29	0.3932	0.5424	not significant
X ₂ X ₄	295.84	1	295.84	15.96	0.0018	significant
X ₃ X ₄	20.25	1	20.25	1.09	0.3166	not significant
X ₁ ²	440.04	1	440.04	23.73	0.0004	significant
X ₂ ²	34.91	1	34.91	1.88	0.1951	not significant
X ₃ ²	19.68	1	19.68	1.06	0.3232	not significant
X ₄ ²	14.01	1	14.01	0.7557	0.4017	not significant
Residual	222.50	12	18.54			
Lack of Fit	193.62	10	19.36	1.34	0.5010	not significant
Pure Error	28.88	2	14.44			
Cor Total	5256.03	26				

Table 5. ANOVA for a Reduced BT Quadratic Model

Source	Sum of Squares	d f	Mean Square	F-value	p-value	
Model	4951.41	8	618.93	36.57	<0.0001	significant
X ₂ -PTA	263.20	1	263.20	15.55	0.0010	significant
X ₃ -Agitation Speed	134.00	1	134.00	7.92	0.0115	significant
X ₄ -Temperature	2468.20	1	2468.20	145.85	<0.0001	significant
X ₁ X ₂	204.49	1	204.49	12.08	0.0027	significant
X ₁ X ₃	1040.06	1	1040.06	61.46	<0.0001	significant
X ₁ X ₄	133.40	1	133.40	7.88	0.0116	significant
X ₂ X ₄	295.84	1	295.84	17.48	0.0006	significant
X ₁ ²	412.21	1	412.21	24.36	0.0001	significant
Residual	304.61	18	16.92			
Lack of Fit	275.73	16	17.23	1.19	0.5493	not significant
Pure Error	28.88	2	14.44			
Cor Total	5256.03	26				

$X_1X_3 = 61.46$). The lack of fit F -value of 1.34 and p -value (0.5010) also imply that the lack of fit has no significant relationship with the pure error.

3.4. Diagnostic Plots for the Response Surface

Model. The diagnostic plots illustrate the statistical performance of the MAOD system in relation to sulfur conversion in the BT model fuel using Fe (VI). The following diagnostic plots were generated by Design Expert v22 following model selection, as presented in Figure 4(a) normal probability, (b) residuals versus run number, and (c) predicted versus actual response for sulfur conversion. The normal probability plot in Figure 4a indicates that the internally studentized residuals follow a normal distribution, as specified by the data points lying close to the normal line in red. This highlights the suitability of the generated response surface quadratic model for the data. Moreover, there are no definitive patterns in the plot, such as an S-shaped curve, which may indicate that a response transformation is needed. Thus, the generated equation is adequate to model without requiring transformation.

The residuals versus run number plot, as presented in Figure 4b, checks for a serial correlation among responses that may have been influenced by variables, such as time. The findings

reveal a scattered distribution of data points with internally studentized residuals from the experimental runs falling within the range of ± 3 . Therefore, the chosen quadratic model demonstrates a favorable outcome, as there are no potential outliers in the experiment. Consequently, there is no requirement to repeat the experimental runs considering the errors and noise associated with the MAOD system.

Finally, the comparison between the predicted and actual response values is presented in Figure 4c. The predicted values correspond to the approximated sulfur conversion derived from the generated quadratic models, whereas the actual values represent the calculated sulfur conversions from the experimental runs. The BT model was observed to have responses along the diagonal line, indicating that the model can strongly predict the sulfur conversion response in the MAOD system with adequate accuracy.

3.5. Optimization. The 3D response surface graphs show significant interaction between two variables in the model, as indicated by the ANOVA results. Figure 5a shows the 3D response surfaces for the BT model with respect to the Fe (VI) concentration and PTA concentration. Meanwhile, Figure 5b presents the response with interacting variables of Fe (VI) concentration and agitation speed. Figure 5c illustrates the 3D

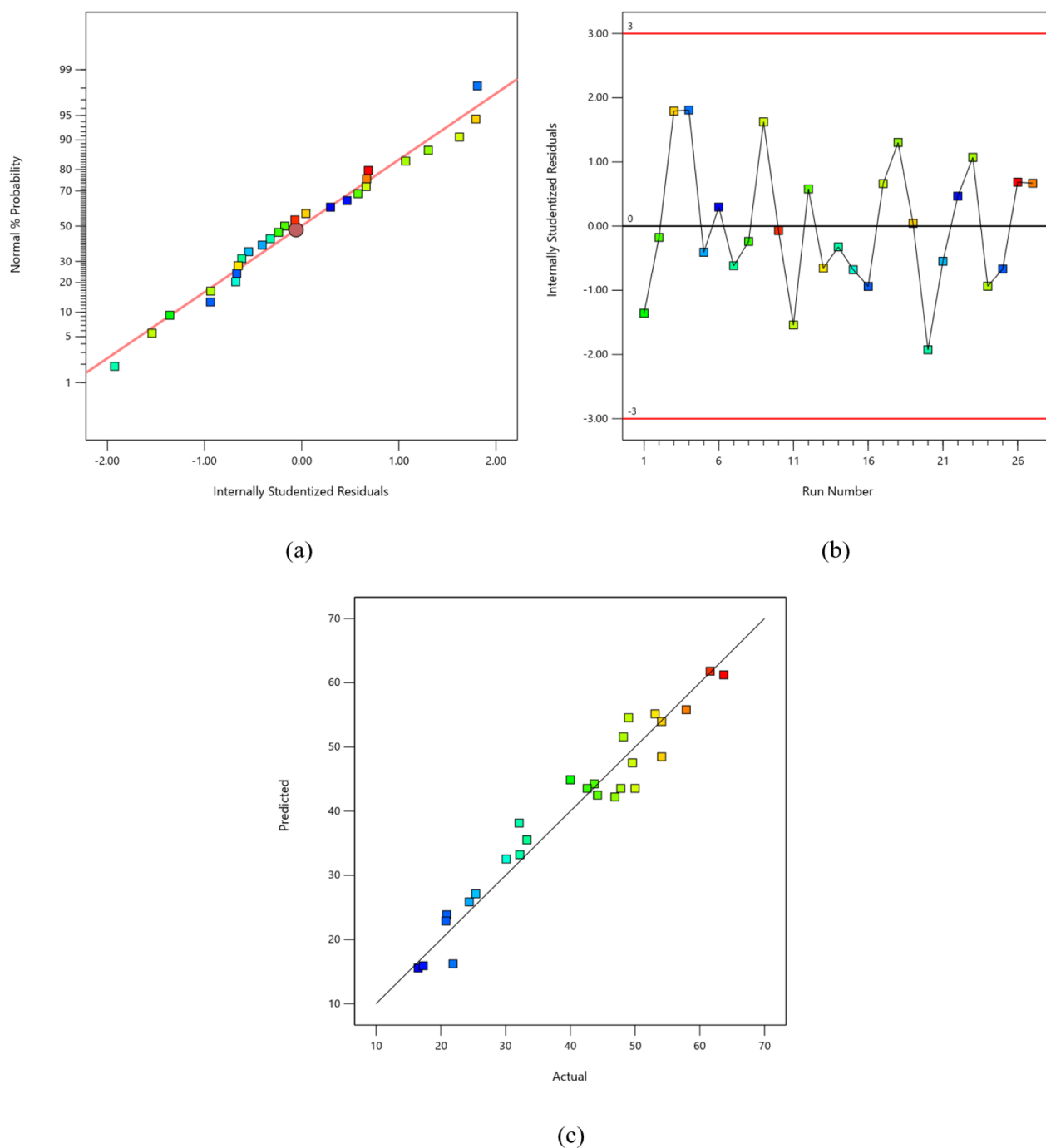


Figure 4. Diagnostic plots for the BT model: (a) internally studentized residuals, (b) residuals versus run number, and (c) predicted vs actual responses.

response surface with respect to the Fe (VI) concentration and temperature. Finally, Figure 5d presents the interaction between temperature and PTA concentration.

Figure 5a,b show an increasing trend in the BT response surfaces for Fe(VI) concentration, with the highest predicted responses ranging from 45% to 55% using 500 to 600 ppm Fe (VI). Meanwhile, Figure 5c projects the highest predicted sulfur conversion of 50% to 58% using 430 to 600 ppm Fe(VI). The trend suggests the significant effect of Fe(VI) concentration in the MAOD of a BT model fuel, wherein middle to high levels of Fe(VI) concentration are advantageous in generating Fe(VI) complexes to oxidize the model fuels.³²

From Figure 5a, a low concentration of PTA is sufficient to produce a high sulfur conversion, implying that the oxidant was efficiently transferred to the organic phase. However, a high concentration of PTA is also predicted to decrease sulfur conversion. This is due to the creation of more turbid and thicker layers which add to the external mass transfer limitations present in the system.¹⁸

Utilizing a low temperature of 40 to 45 °C is also beneficial for sulfur conversion, as observed in Figure 5c. This indicates that effective molecular collisions between the oxidant and BT result in the formation of BTO. Higher temperatures may be detrimental to the system, as the reaction of Fe(VI) with water

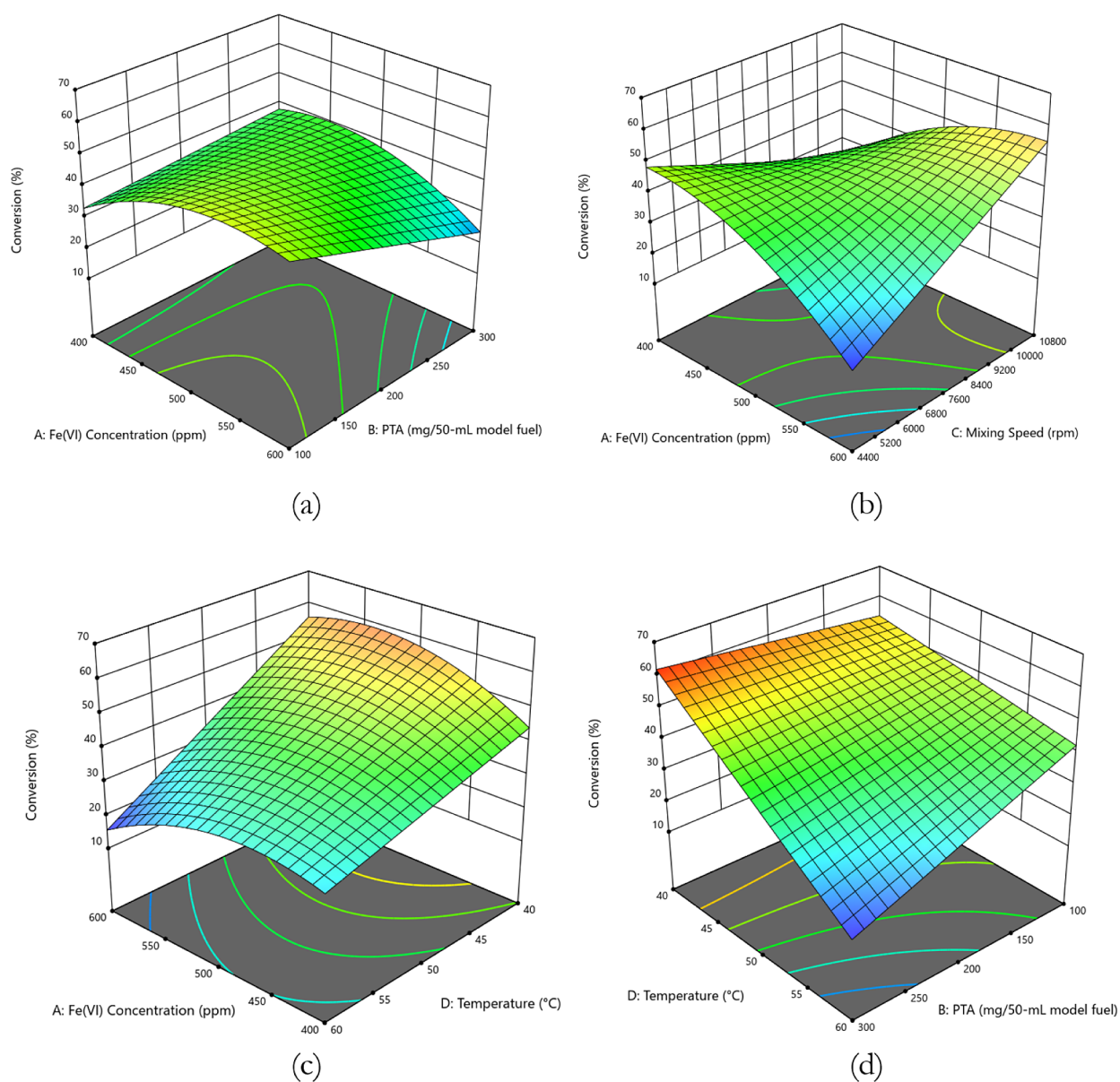


Figure 5. Model graphs of interacting variables for MAOD of BT model fuel: (a) Fe(VI) concentration and PTA 3D surface, (b) Fe(VI) concentration and agitation speed 3D surface, (c) Fe(VI) concentration and temperature 3D surface, and (d) temperature and PTA.

is promoted.³³ Furthermore, the production of brominated byproducts may be promoted as temperature increases. These unwanted side reactions lower the availability of BT to be oxidized to BTO, resulting in a lowering of sulfur conversion. Finally, from Figure 5b, a high level of agitation speed (10 000 rpm to 10 800 rpm) is advantageous for BT conversion as it increases the formation of emulsion. This shows that external mass transfer limitations are reduced with high agitation speeds. High shear mixing enhances the oxidation rate by promoting the formation of uniformly shaped droplets and reducing mass transfer resistance.²⁴

The optimal variables were obtained by setting the conversion to the maximum possible value in the model. The weights and importance for all variables were uniformly set. The optimal Fe(VI) concentration and PTA concentration were determined to be 600 ppm Fe(VI) and 101 mg PTA 50 mL⁻¹ model fuel. Meanwhile, the optimal mixing speed and temperature were found to be 10 800 rpm and 40.0 °C. The

predicted sulfur conversion for BT was 78.5% with a 95% confidence interval of 68.5 to 88.4%. In order to validate the developed quadratic model from the BBD-RSM, confirmatory runs were performed. The results indicated an average of 88.1% sulfur conversion, which falls within the determined confidence interval. This verified the precision of the response surface from the quadratic model equation under BBD-RSM.

3.6. Application to Pyrolysis Oil. The application of MOAD in a pyrolysis oil sample was performed using the conditions obtained from the optimization study using the model fuel. The original sulfur concentration of the pyrolysis oil sample was measured to be 8 804 ppm using a total sulfur analyzer. Following the MAOD process and solvent extraction, the sulfur concentration reached 3 990 ppm under the optimal BT conditions, resulting in a sulfur removal rate of 54.7%. The observed decline in desulfurization efficiency compared to that of the BT model fuel is attributed to the elevated presence of various sulfur compounds. In comparison, the optimized

parameters from the preceding study using DBT resulted in a lower sulfur removal rate of 53.2%. Since BT is more difficult to oxidize compared to DBT, the optimized parameters using the BT model fuel were more effective in targeting more sulfur compounds in pyrolysis oil, resulting in a higher desulfurization rate than that with the DBT optimal parameters. Furthermore, pyrolysis oil is known to have a higher sulfur content, comprising of thiophene, BT, DBT, and their derivatives.³⁰ With a significant amount of sulfur compounds and their derivatives competing for reaction, the optimal variables in the system may not be sufficient to achieve the predicted maximum sulfur oxidation.

4. CONCLUSIONS

K₂FeO₄ was prepared from a DWTS sample via the wet oxidation method and was successfully tested in the MAOD process of converting BT to BTO in a model fuel oil. BBD-RSM was employed to measure the effects of the Fe(VI) concentration, PTA concentration, agitation speed, and mixing temperature on sulfur conversion. The diagnostic plots and ANOVA validated the reliability of the generated quadratic model, indicating the goodness of fit and the reliable prediction of sulfur conversion. The 3D model graphs showed that sulfur conversion increased with the Fe(VI) concentration and PTA concentration. Meanwhile, low levels of agitation speed and temperature were favorable in the MAOD system. Actual sulfur conversions from experimental runs ranged from 16.5% to 63.7%. After MAOD and solvent extraction, the maximum desulfurization of 54.7% was reached under the BT optimal variables. The lower desulfurization results of the pyrolysis oil compared to those of the BT model fuel are attributed to the existence of more refractory sulfur compounds in the pyrolysis oil, such as thiophenes and their derivatives. Overall, the resulting S content confirms the effectiveness of MAOD in sulfur conversion using milder operating conditions compared to the conventional HDS method. Furthermore, the results support the promising applicability of MAOD in producing cleaner fuels via waste recovery for industrial applications. For future studies, it is recommended to test basic fuel properties before and after desulfurization for the future industrial applications of the MAOD system. In addition, the characterization of the oxidant, formation of the oxidant–catalyst complex, and kinetics of the reaction are proposed to be studied.

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Notes

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