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Using response surface methodology to optimize ultrasound-assisted oxidative desulfurization

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Abstract−Latest strict environmental regulations have restricted the sulfur content of diesel fuels; therefore, deep desulfurization of fuels is required. Ultrasound-assisted oxidative desulfurization (UAOD) is an alternative for conventional desulfurization methods which can remove sulfur compounds from fuels under mild process conditions. In this study, UAOD of gasoil using tungstophosphoric acid catalyst and tetraoctylammonium bromide as a phase transfer agent in the presence of hydrogen peroxide as an oxidant was optimized. The optimal design of experiments was generated based on central composite face-centered design of Response surface methodology (RSM) to study effects of four process variables such as oxidant volume, mass of catalyst, mass of phase transfer agent and the ultrasonic wave amplitude on the sulfur conversion of gasoil. In addition, a predictive model of sulfur conversion was obtained based on RSM. The optimal values of process variables were evaluated to be 21.96 mL of oxidant, 1 gr of catalyst and 0.1 gr of phase transfer agent to achieve the maximum sulfur conversion of 95.92%.

Keywords: Response Surface Methodology, Central Composite Face-centered Design, Optimization, Ultrasound-assisted Oxidative Desulfurization

INTRODUCTION

Transportation fuels such as diesel oil, jet fuel and gasoline contain high sulfur compounds which are a major source of air pollution. Sulfur compounds are also capable of being transferred to fuels during the refining process. Indeed, sulfur can be found as hydrogen sulfide, organic sulfides and disulfides, benzothiophene, dibenzothiophene, and their alkylated derivatives in diesel fuels. These compounds are converted to sulfur oxides (SO_x) due to the diesel combustion, which would contribute to acid rain and lead to air pollution and endanger public health and welfare.

Hence, stringent environmental regulations have been issued all over the word to limit the sulfur content of diesel fuels. For example, the U.S. Environmental Protection Agency (US EPA) stated that the sulfur content of diesel fuel had to be reduced from 500 ppm to 15 ppm by 2006. The similar regulation in Europe forced petroleum industries to lower the sulfur content of diesel fuels from 350 to 50 ppm by 2005 and to 10 ppm by 2009 [1].

Growing concerns about air pollution due to wide use of diesel fuels with high sulfur content have brought about great research activity in deep desulfurization of fuels. In recent decades, a traditional or conventional method known as hydrodesulfurization (HDS) technology has been widely used to remove sulfur in which aliphatic and acyclic sulfur-containing compounds are eliminated from diesel fuels using hydrogen. To achieve the lower sulfur content in fuels with HDS technology, the high reaction temperature and pressure, large reactor volumes and highly active catalysts are required. The studies in HDS field revealed that this process can efficiently remove mercaptans, thioethers, sulfides, disulfides and thiophene while it has shown some limitations in the treatment of alkylated aromatic sulfur compounds, such as 4, 6-dimethyldibenzothiophene(4, 6-DMDBT) [2]. To overcome the limitations of the HDS process, alternative unconventional desulfurization techniques have been developed among which oxidative desulfurization (ODS) is considered as one of the promising processes due to its mild process conditions, such as relatively low temperature, pressure and cost of operation compared with HDS, while it requires no hydrogen. In recent studies considerable effort has been made on application of the ODS process for sulfur removal from petroleum cuts, namely, gasoline, gasoil and diesel [3-14].

In ODS process sulfides are readily oxidized to sulfoxides and sulfones by a variety of oxidizing agents involving hydrogen peroxide, organic hydroperoxides like t-butylhydroperoxide (TBHP) and t-butyl hypochlorite (t-BuOCl) [3,6-8] and oxygen of air or ozone [8-14], in the presence of different catalysts [3,8,9]. Although ODS is known as an efficient desulfurization method, there are still numerous issues such as safety and economic problems which should be tackled.

To improve the efficiency of the ODS process, Mei et al. and Wan et al. used an innovative technology called ultrasound-assisted oxidation desulfurization (UAOD) in which the oxidation was conducted rapidly, economically and safely, under mild operational conditions [1,15]. A large number of articles have been reported in the literature dealing with the UAOD process [1,15-24]. The UAOD

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process can selectively oxidize sulfur content of diesel such as thiophenes to corresponding sulfoxides or sulfones, which are highly polar and thus they can be easily removed from the treated diesel based on their polarity by selective extraction or adsorption. The mechanism of UAOD process has been explained in several articles [17-19]. The oxidization system in this process includes fuel, catalyst, phase transfer agent and oxidant. A mixture of hydrogen peroxide and formic acid or acetic acid was widely used as an oxidizing agent in many studies [2-13]. In fact, the ultrasound energy immediately raises the local temperature and pressure of the reaction mixture, which consequently pushes up the conversion rate. The ultrasound waves of high intensity cause acoustic cavitation in liquid. The subsequent processes of formation and collapse of cavitation bubbles locally heighten the solution temperature and pressure. This process requires good dispersion of the solvent and fuel phases in which the ultrasound pulses generate this dispersion using the generation of very fine droplets, leading to an emulsion-like dispersion of the two phases [19-23].

The effective factors on UAOD process involving ultrasonic frequency and power, process time, the amounts of oxidants, catalysts and phase-transfer agent were investigated in several studies [15-23].

To scale up UAOD process in industrial scales, mathematical modeling and optimizing of this process are required. Literally, there are only a handful of studies dealing with optimization of UAOD and ODS. For example, Jose et al. employed the Box-Behnken method to optimize the oxidative desulfurization of thiophene using Cu/titanium silicate-1 [24]. Abghari et al. studied the effects of three factors on the efficiency of a Co-Mo catalyst in HDS process using response surface methodology (RSM) [25]. Another work investigated the use of UAOD to reduce sulfur content of gasoil using isobutanol as a phase transfer agent. Then, the optimum conditions of this process were evaluated using RSM in which impacts of three variables of time, amounts of oxidant and catalysts on sulfur removal were studied [26].

The aim of the present study was to optimize UAOD of gasoil in which the influences of process variables on the sulfur conversion of gasoil were studied. To properly design experiments and study effects of parameters and their interactions with a minimum number of experiences, RSM was applied. Indeed, this method can significantly reduce the cost of expensive experimental methods by decreasing the number of experiments. RSM has been widely used in several studies to design the experiments in which one or more dependent variables, known as responses, are influenced by several independent variables [25-43]. In this study, effects of operational parameters such as oxidant volume, mass of catalyst, mass of phase transfer agent and ultrasonic wave amplitude on the sulfur conversion of the gasoil in a UAOD process were investigated. In addition, the optimum process variables to achieve the maximum sulfur conversion of gasoil were determined by RSM.

EXPERIMENTAL PROCEDURE

1. Instrument and Process

The apparatus was an Ultrasonic Processor VCX 750 (Sonics and Materials, Inc.) with the horn of 25.4 mm diameter in which the frequency of generator was 20 kHz. The power output of the generator can be set up to a maximum power of 750 W by adjustment of the amplitude. The quantity of the wave amplitude (as a percentage of the maximum amplitude) was given on the display and was kept constant by generator. The maximum amount of amplitude of the probe of this ultrasonic processor was 35 μm. In this study three levels of the wave amplitude, 40%, 70% and 100%, were tested. Löning et al. [43] showed that there is a theoretical relationship between power input and amplitude as follows:

$$P=\omega^2\beta m\xi^2 \quad (1)$$

where P, β, m and ξ were power input [W], total resistive constant leading to damping, inertia of the oscillator and amplitude [m], respectively.

An ultrasonic probe was dipped into the oil/reagents mixture for all the experiments in which the amplitude ratio could be diver-

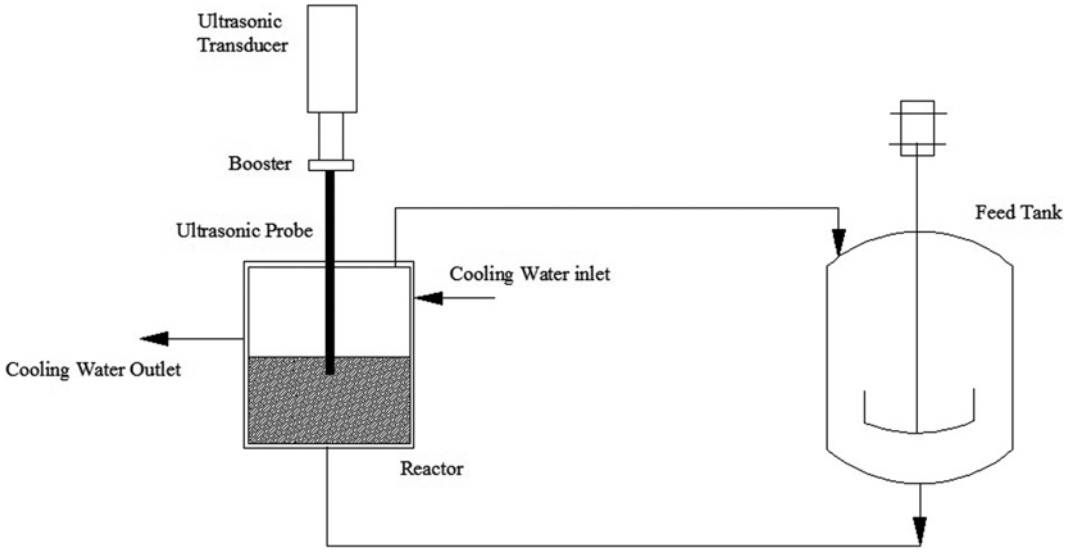

Fig. 1. Scheme of an ultrasound -assisted oxidative desulfurization process.

sified. The scheme of UAOD process in this study is shown in Fig. 1. This system includes the following sections: (i) the ultrasound transducer, (ii) reactor with a cooling jacket, (iii) feed tank. To control the temperature of the reactor and keep it constant, water was employed as a coolant which entered the jacket of the reactor and left it after regulating the temperature of the reaction. Additionally, a glass separator funnel was used for the solvent extraction step.

2. Reagents and Materials

Gasoil samples were desulfurized using the UAOD process in which the samples were provided by RIPI[1] authority. The total sulfur content of gasoil for experiments was approximately 250 ppm as sulfur.

Hydrogen peroxide (40 vol% solution) was used as an oxidant. A catalyst was required to expedite the production of hydroxyl radicals from hydroperoxide. Various studies reported that the use of transition metal catalyst, namely phosphotungstic acid, could significantly raise the sulfur conversion in UAOD and ODS processes [3,8,20]. Therefore, in this study, phosphotungstic acid catalyzed the UAOD process. However, the poor contact between gasoil and oxidant due to the low solubility of hydrogen peroxide in oil phase, is also considered as a problem in thte UAOD process. In the literature, to enhance the solubility of hydrogen peroxide in oil phase, a phase transfer agent (PTA) has been used in combination with the main catalyst. Based on these studies, the effective amount of PTA ranges between 0.2 and 50 gr/L [3,19]. Hence, in this work, to improve the kinetic of the oxidative desulfurization, tetraoctylammonium bromide was employed as a PTA.

At the end of irradiation time, a two-phase product was generated involving oil and aqueous phases in which the oil phase contained sulfones (produced by the oxidation reaction). Sulfones can be easily extracted from the treated gasoil by the liquid-liquid extraction using polar solvents such as dimethyl formamide, N-methylpyrrolidone, acetonitrile or water. In this study, the 99.5% pure acetonitrile (MeCN) as a solvent was used to extract the sulfones from oil phase. Based on the recent studies, we assumed that the solvent-to-oil (S/O) ratio was 1 : 1 by weight [17,18,20,22,23]. Moreover, water was considered as a facilitator of the extraction steps as well as a solvent to reduce the viscosity of gasoil, which was added to gasoil with 1 : 1 volumetric ratio.

3. Experiment Methodology

Reactions related to UOAD were performed combining different amounts of hydrogen peroxide, PTA and phosphotungstic acid as a catalyst directly into the feed tank containing 100 mL of gasoil and 100 mL of water. Afterwards, this mixture, called feed, was put into the reactor. The feed was irradiated with a 20 kHz frequency probe for 20 minutes that was vertically dipped into the feed. The wave amplitude ratio could be varied based on the experimental design. Different experiments were carried out to study influences of the oxidant volume (ranging from 6 to 26 mL), mass of a catalyst (ranging from 0.2 to 1 gr), mass of PTA (0.02 to 0.1 gr) and the ultrasonic wave amplitude (40-100%) on the sulfur conversion of gasoil.

The ultrasound-assisted oxidation generated heat; thus an external heat source was not required. The temperature of the reactor was kept constant at 65±5 °C using water as the coolant circulating through the jacket of the UOAD reactor.

After ultrasound treatment, a product mixture was obtained including aqueous and oil phases in which the oil phase contained the sulfones. Phase separation was spontaneously achieved in less than 1 min. These oil/aqueous phases were separated by decanting. Afterwards, the treated gasoil was extracted from the oil phase three times with a polar solvent of acetonitrile by using a glass separator funnel with manual and vigorous shaking for 10 minutes based on the procedure described in the prior studies [18,20,22, 23]. The sulfur conversion was calculated based on the sulfur concentration remaining in the treated gasoil via Eq. (2):

$$\text{S Conversion \%} = \frac{\text{Total sulfur content in the feed} - \text{Total sulfur content in the treated gasoil}}{\text{Total sulfur content in feed}} \times 100 \quad (2)$$

Note that the amount of the gasoil lost with the aqueous phase and sulfones in the extraction steps was negligible.

EXPERIMENTAL DESIGN

We assumed that the sulfur conversion of gasoil in UAOD process was affected by at least four independent factors: the volume of oxidizing agent, mass of catalyst, the mass of PTA and the ultrasonic wave amplitude. The tests were carried out under different conditions of these four factors at three levels, which were defined based on central composite face-centered (CCF) design of RSM. According to the CCF design for four factors, only 31 different experiments were required. These 31 experimental points included 2^4=16 factorial points (a cube's vertices), 2×4=8 axial points, and 7 center points that were coded with the value of 0. Center points in CCF design are usually repeated 4-7 times to get a proper estimate of experimental error. Each independent coded variable had three levels of −1, 0, and +1. Table 1 shows the high and low level of these four independent variables.

The critical range of each independent variable was defined based on several preliminary experiments and results of the conducted studies in this field. To optimize the gasoil desulfurization using UOAD process and to obtain the optimal values of these four independent variables, RSM was applied. RSM fitted experimental data from the CCF design into a quadratic second-order polynomial as given in Eq. (3). The design was generated by Minitab15 software and the unknown parameters of this mathematical model were estimated by least-square regression analysis.

$$Y = \beta_0 + \Sigma_{i=1}^{4}\beta_i X_i + \Sigma_{i=1}^{4}\beta_{ii} X_i^2 + \Sigma_{i<j}^{4}\beta_{ij} X_i X_j + \varepsilon \quad (3)$$

Table 1. Low and high levels of the independent variables

Independent variables	Coded levels		
	−1	0	1
Volume of oxidant (ml)=x_1	6	16	26
Mass of catalyst (gr)=x_2	0.25	0.625	1
Mass of PTA (gr)=x_3	0.02	0.06	0.1
Ultrasonic wave amplitude, %=x_4	40	70	100

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where Y is a response defined as the sulfur conversion, β_0, β_i, β_{ii} and β_{ij} are coefficients of the intercept, linear, square and interaction effects, respectively, and ε denotes the error. Generally, modeling and experimental errors are two sources of error. The main difference between these two types of error is generated by the response. In physical experiments, inaccuracy can be due to the measurement errors, while in computer-based simulations the numerical noise is resulted from an incomplete convergence of iterative processes. As this research was based on experimental data, the error ε was only due to the weakness of experiments [30,31,41,42]. The coded values of independent factors of this study were defined as follows:

$$X_1 = \frac{x_1 - \bar{x}_1}{1/2(x_{1H} - x_{1L})} = \frac{x_1 - 16}{10} \quad (4)$$

$$X_2 = \frac{x_2 - \bar{x}_2}{1/2(x_{2H} - x_{2L})} = \frac{x_2 - 0.625}{0.375} \quad (5)$$

$$X_3 = \frac{x_3 - \bar{x}_3}{1/2(x_{3H} - x_{3L})} = \frac{x_1 - 0.06}{0.04} \quad (6)$$

Table 2. Central composite face-centered design with four independent variables

Run	X_1	X_2	X_3	X_4
1	−1	1	−1	1
2	0	0	1	0
3	0	1	0	0
4	0	0	0	1
5	1	1	1	−1
6	1	1	−1	−1
7	1	−1	−1	1
8	−1	−1	1	−1
9	1	0	0	0
10	0	0	0	−1
11	1	−1	−1	−1
12	−1	−1	1	1
13	−1	1	−1	−1
14	1	1	−1	1
15	−1	−1	−1	1
16	−1	−1	−1	−1
17	1	−1	1	−1
18	0	0	−1	0
19	0	−1	0	0
20	−1	1	1	1
21	−1	1	1	−1
22	1	1	1	1
23	−1	0	0	0
24	1	−1	1	1
25	0	0	0	0
26	0	0	0	0
27	0	0	0	0
28	0	0	0	0
29	0	0	0	0
30	0	0	0	0
31	0	0	0	0

$$X_4 = \frac{x_4 - \bar{x}_4}{1/2(x_{4H} - x_{4L})} = \frac{x_4 - 70}{30} \quad (7)$$

In Eqs. (4-7), variables x_1-x_4 were defined according to Table 1. Moreover, $\bar{x}_i$, x_{iL}, x_{iH} were the middle, the lowest and the highest values of each independent variable, respectively. Table 2 shows the values used for the CCF design.

RESULTS AND DISCUSSION

1. Analysis of Variance (ANOVA)

Table 3 presents three different values for each variable (oxidant volume, mass of catalyst, mass of PTA and ultrasonic wave amplitude) and corresponding values of sulfur conversion from 31 different experiments.

For a quadratic model of the sulfur conversion of gasoil, coefficients of Eq. (3), so-called second-order response surface model, were estimated by using Minitab15 software. Table 4 indicates the regression results in which the coefficients of Eq. (3) and their probability values were listed. It was assumed that all coefficients

Table 3. Experiments results for sulfur conversion of gasoil

Run	x_1	x_2	x_3	x_4	Y (%)
1	6	1	0.02	100	64.77
2	16	0.625	0.1	70	86.50
3	16	1	0.06	70	88.19
4	16	0.625	0.06	100	86.68
5	26	1	0.1	40	81.60
6	26	1	0.02	40	78.63
7	26	0.25	0.02	100	90.22
8	6	0.25	0.1	40	57.29
9	26	0.625	0.06	70	85.47
10	16	0.625	0.06	40	77.69
11	26	0.25	0.02	40	74.26
12	6	0.25	0.1	100	62.89
13	6	1	0.02	40	63.25
14	26	1	0.02	100	90.99
15	6	0.25	0.02	100	62.53
16	6	0.25	0.02	40	57.37
17	26	0.25	0.1	40	75.83
18	16	0.625	0.02	70	84.89
19	16	0.25	0.06	70	84.07
20	6	1	0.1	100	66.56
21	6	1	0.1	40	64.56
22	26	1	0.1	100	94.41
23	6	0.625	0.06	70	63.10
24	26	0.25	0.1	100	92.23
25	16	0.625	0.06	70	84.91
26	16	0.625	0.06	70	84.90
27	16	0.625	0.06	70	84.91
28	16	0.625	0.06	70	84.90
29	16	0.625	0.06	70	84.91
30	16	0.625	0.06	70	84.91
31	16	0.625	0.06	70	84.91

Table 4. Estimated regression coefficients for sulfur conversion using data in coded variables

Term	Coefficient	Standard error	F-value	Prob (F)	Remarks
Constant	84.9072	0.006093	13935.999	0.000	Significant
X_1	11.1844	0.004841	2310.392	0.000	Significant
X_2	2.0150	0.004841	416.242	0.000	Significant
X_3	0.8311	0.004841	171.684	0.000	Significant
X_4	4.4889	0.004841	927.278	0.000	Significant
X_1X_1	−10.6189	0.012749	−832.909	0.000	Significant
X_2X_2	1.2261	0.012749	96.168	0.000	Significant
X_3X_3	0.7911	0.012749	62.048	0.000	Significant
X_4X_4	−2.7189	0.012749	−213.263	0.000	Significant
X_1X_2	−0.3731	0.005135	−72.669	0.000	Significant
X_1X_3	0.4119	0.005135	72.216	0.000	Significant
X_1X_4	2.7031	0.005135	526.455	0.000	Significant
X_2X_3	0.3519	0.005135	68.530	0.000	Significant
X_2X_4	−0.9019	0.005135	−175.647	0.000	Significant
X_3X_4	0.1131	0.005135	22.032	0.000	Significant

regardless of their probability values were included in a response surface model, which resulted in a coded second-order model of sulfur conversion as follows:

$$Y=84.91+11.18X_1+2.02X_2+0.83X_3+4.5X_4-10.62X_1^2+1.23X_2^2+0.79X_3^2-2.72X_4^2-0.37X_1X_2+0.41X_1X_3+2.70X_1X_4+0.35X_2X_3-0.90X_2X_4+0.11X_3X_4 \quad (8)$$

Additionally, the uncoded second-order quadratic model was obtained as follows:

$$y=22.98+3.88x_1+0.26x_2-76.32x_3+0.47x_4-0.11x_1^2+8.72x_2^2+494.7x_3^2-0.003x_4^2-0.09x_1x_2+1.03x_1x_3+0.009x_1x_4+23.46x_2x_3-0.08x_2x_4+0.094x_3x_4 \quad (9)$$

To calculate the unknown coefficients of a polynomial in a regression, it is assumed that the coefficients equal zero. Therefore, the smaller the probability value for each parameter, the more significant they are in an estimated model. It denotes that when the probability value of a factor is greater than 0.05, the influential degree of this factor is less than 95% confidence level [41,42].

According to the regression results summarized in Table 4, the probability values of all the parameters including X_1, X_2, X_3, X_4, their quadratic terms and their interaction terms were less than 0.05, which showed all the terms were significant in the sulfur conversion equation.

The accuracy of an achieved quadratic model could be determined by the residual plots. To check the normality assumption, the normal probability plot of the residual was drawn. If the trend of the residual plot is approximately a straight line, then the residuals are normally distributed [34]. Fig. 2 displays the normal probability plot of the residual for sulfur conversion of gasoil which is approximately a straight line.

The determination coefficient (R^2) and adjusted determination coefficient (Ra^2) for the quadratic model were found to be, 99.99% and 99.96%, respectively. The amount of R^2 suggested that more than 99.99% of the variations in the response variable of Y could be explained by this model. To examine a second-order model statistically, the corresponding analysis of variance (ANOVA) is given in Table 5. The extremely small probability value (far smaller than 0.050) means that the experimental data are properly fitted by the quadratic model, which is higher than the 95% confidence level. For this study, the F-value for regression was calculated to be 27.04, which was significantly higher than tabulated $F_{9, 5, 0.05}$ (4.77) [24]. Thus, the estimated second-order quadratic model is considered to be statistically significant.

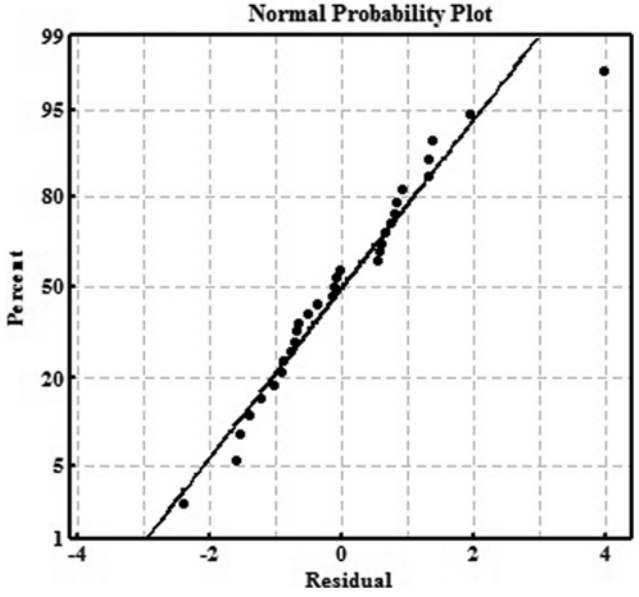

Fig. 2. Normal probability plot of sulfur conversion.

2. Effects of Individual Factors on Response

To investigate and compare the influence of each factor on the sulfur conversion of gasoil at a point of a design space, the perturbation plot was applied as shown in Fig. 3.

The influence of each variable was evaluated and plotted against the response (sulfur conversion) while other variables were kept

Table 5. The analysis of variance of the second-order model

Source Y	D. F.	Seq. SS	Adj. SS	Adj. MS	F-value	P-value
Regression	14	3792.57	3792.57	270.90	642206.93	0.00
Linear	4	2699.87	2699.87	674.97	1600121.72	0.00
X_1	1	2251.65	2251.65	2251.65	5337909.03	0.00
X_2	1	73.08	73.08	73.08	173257.66	0.00
X_3	1	12.43	12.43	12.43	29475.45	0.00
X_4	1	362.70	362.70	362.70	859844.75	0.00
Square	4	955.64	955.64	955.64	566376.59	0.00
X_1X_1	1	935.88	292.63	292.63	693737.29	0.00
X_2X_2	1	0.58	3.90	3.90	9248.29	0.00
X_3X_3	1	0.00	1.62	1.62	3849.99	0.00
X_4X_4	1	19.18	19.18	19.18	45481.04	0.00
Interaction	6	137.05	137.05	22.84	54150.62	0.00
X_1X_2	1	2.23	2.23	2.23	5280.79	0.00
X_1X_3	1	2.71	2.71	2.71	6434.59	0.00
X_1X_4	1	116.91	116.91	116.91	277154.59	0.00
X_2X_3	1	1.98	1.98	1.98	4696.42	0.00
X_2X_4	1	13.01	13.01	13.01	30851.94	0.00
X_3X_4	1	0.20	0.20	0.20	485.41	0.00
Residual error	16	0.01	0.01	0.00		
Lack-of-fit	10	0.01	0.01	0.00		
Pure error	6	0.00	0.00	0.00	0.001	0.001
Total	30	3792.57				

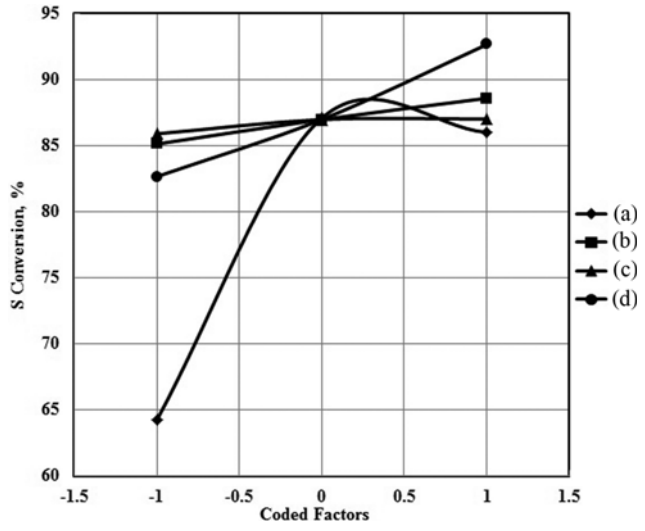

Fig. 3. Perturbation plot for sulfur conversion, (a) volume of the oxidant, (b) mass of the catalyst, (c) mass of PTA, (d) ultrasonic wave amplitude.

constant. According to Fig. 3, the volume of oxidant (graph a) showed the highest and the most significant effect on the sulfur conversion of gasoil compared with other factors. After the maximum point in graph a, the sulfur conversion decreased with a rise in the volume of oxidant. The ultrasonic wave amplitude (graph d) stood on the second place. Based on graph d of Fig. 3, the wave amplitude influenced the sulfur conversion of gasoil positively. The mass of catalyst (graph b), mass of PTA (graph c) and the wave amplitude showed similar effects on the sulfur conversion. These parameters exerted positive effects on the response variable. So every increase in each of these three independent variables could raise the sulfur conversion of gasoil. Additionally, the mass of PTA (graph c) had the lowest effect on the response. This fact can be understood from the statistical data summarized in Table 4. The parameters with larger F-value exerted the greater influence on a response equation as described by Kafuku et al. [37].

3. Effect of Factors Interactions on the Response

Table 4 reveals that the interaction between the oxidant volume (x_1) and the ultrasonic wave amplitude (x_4) had the largest positive effect on the sulfur conversion in comparison with other interactions terms. Then, interactions of the mass of catalyst (x_2) and the ultrasonic wave amplitude (x_4), oxidant volume (x_1) and mass of catalyst (x_2) exerted higher negative impacts on the response variable, respectively. The interactions of oxidant volume (x_1) and mass of PTA (x_3), mass of catalyst (x_2) and mass of PTA (x_3) and mass of PTA (x_3) and ultrasonic wave amplitude (x_4) showed the least positive effects on the sulfur conversion of gasoil in this set of experiments.

Effects of interactions terms on the sulfur conversion of gasoil as the response surface plots are presented in Figs. 4-9. These figures were drawn using Minitab 15 and based on Eq. (8). Figs. 4-6 indicate the interactions between x_1 and x_2, x_1 and x_3 as well as x_1 and x_4. It was observed that the sulfur conversion of gasoil grew with increasing oxidant volume initially, and then it diminished with further rise above the maximum point. It suggested that the surfeit of oxidant could inhibit the chain reactions by scavenging carbonyl free radicals, which reduced the production of peroxide

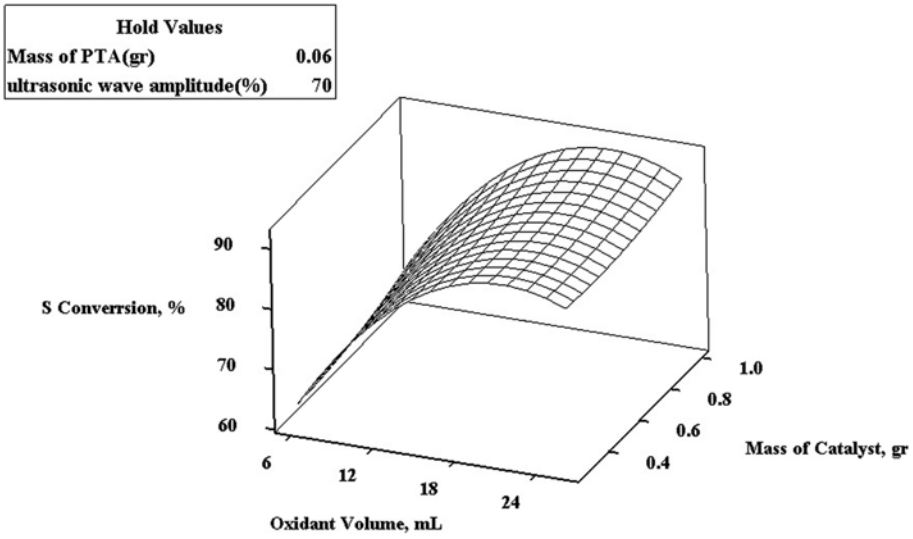

Fig. 4. Surface plot of sulfur conversion at mass of PTA=0.06 gr, ultrasonic wave amplitude=70%.

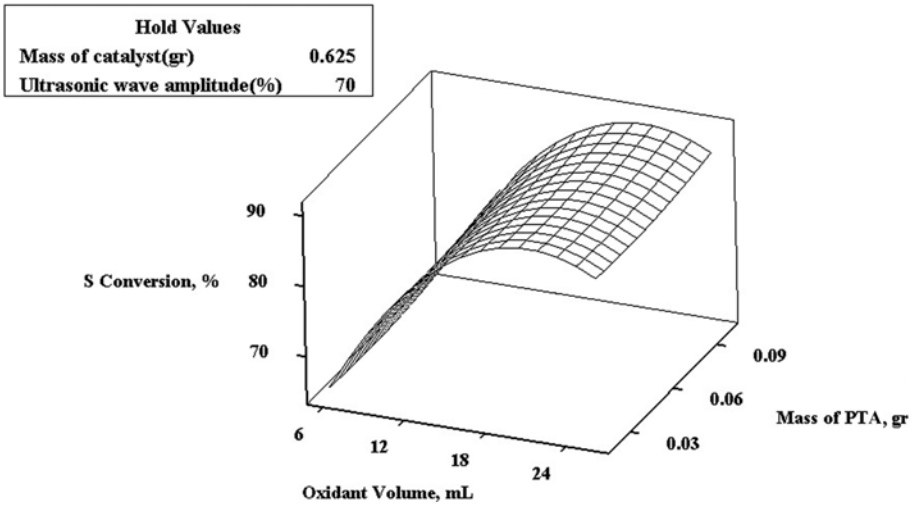

Fig. 5. Surface plot of sulfur conversion at mass of catalyst=0.625 gr, ultrasonic wave amplitude=70%.

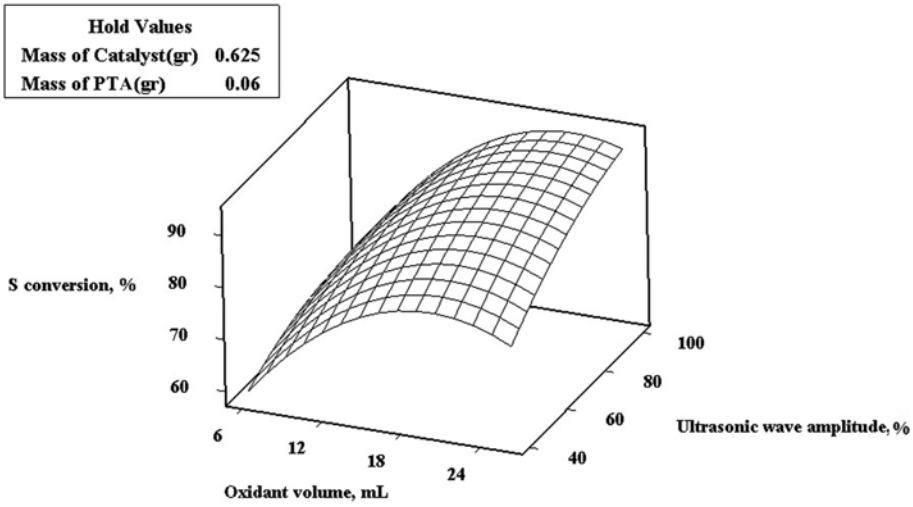

Fig. 6. Surface plot of sulfur conversion at mass of catalyst=0.625 gr, mass of PTA=0.06 gr.

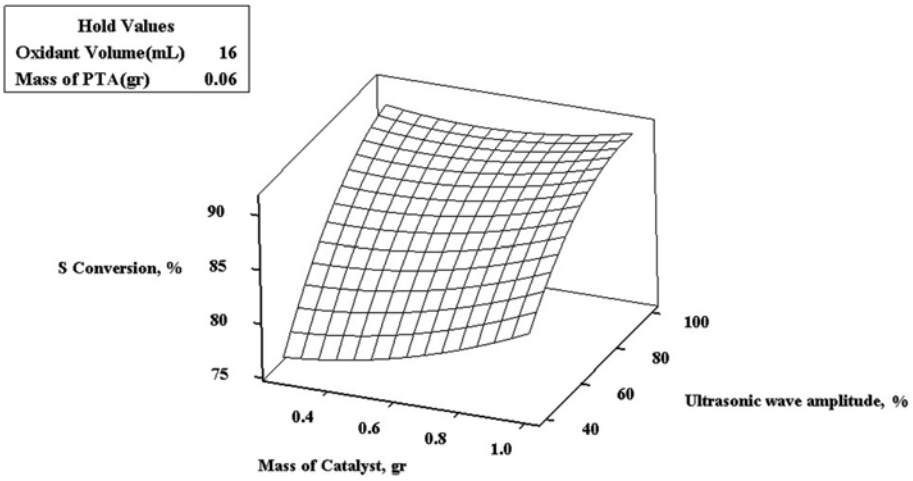

Fig. 7. Surface plot of sulfur conversion at oxidant volume=16 mL, mass of PTA=0.06 gr.

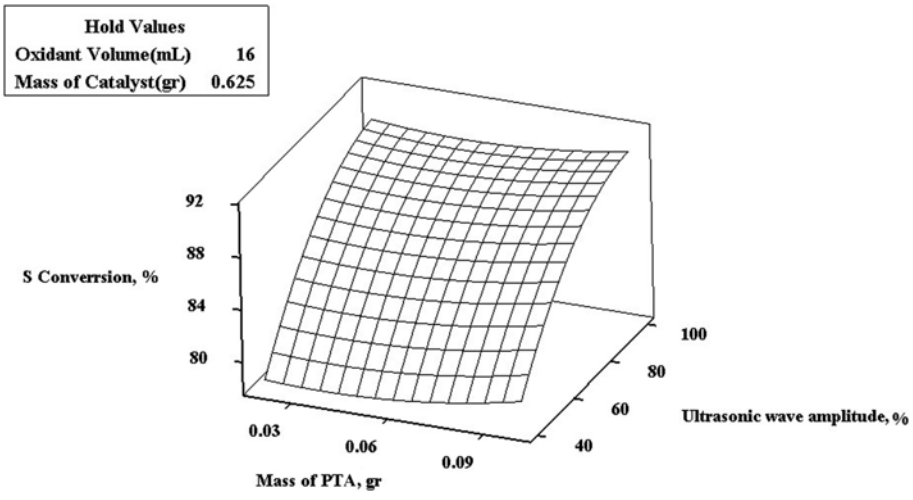

Fig. 8. Surface plot of sulfur conversion at oxidant volume=16 mL, mass of catalyst=0.625 gr.

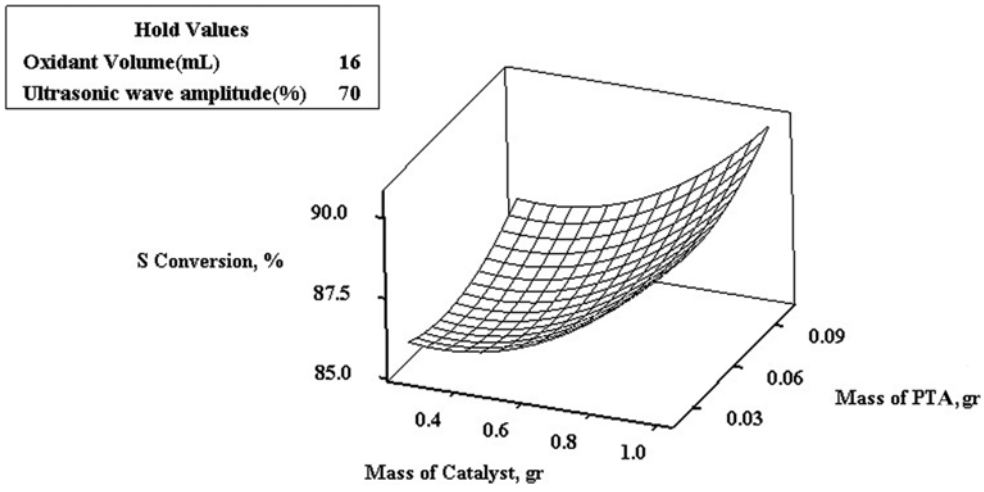

Fig. 9. Surface plot of sulfur conversion at oxidant volume=16 mL, ultrasonic wave amplitude=70 %.

and consequently the sulfur conversion. This result is consistent with the previous work [23]. Furthermore, every rise in mass of catalyst and mass of PTA as well as the ultrasonic wave amplitude could push up the sulfur conversion of gasoil in this process. Based

on Figs. 4-5 the impacts of mass of catalyst and mass of PTA on the sulfur conversion were small in comparison with that of oxidant volume. However, according to Fig. 6, ultrasonic wave amplitude showed a significant positive impact on the response.

Effects of interaction of x_2 and x_4 as well as interaction of x_3 and x_4 are shown in Figs. 7 and 8. The high level of wave amplitude in combination with the large amounts of catalyst and PTA led to an increased sulfur conversion. It is evident that wave amplitude of ultrasonic system raised the efficiency of desulfurization process more significantly than the two other factors. It was because the average ultrasonic power delivered to the probe was raised with raising the wave amplitude from 40% to 100%. The ultrasonic waves affected the reaction mixture due to the generation of cavitation phenomenon. An increased ultrasonic power at a fixed output frequency could strongly stir this mixture, which led to an accelerated reaction. Thus the sulfur removal of gasoil was improved with heightening the amplitude values.

The effect of the interaction term of x_2 and x_3 on the sulfur conversion is also presented in Fig. 9. The highest sulfur conversion of gasoil was obtained at the highest amounts of catalyst and PTA while mass of the catalyst exerted a more significant effect than mass of PTA on the response.

4. Optimization of Response

The response optimizer tool of Minitab software was used to optimize the obtained predictive model of sulfur conversion Eq. (9). Identifying the combination of input variable settings, the response optimizer tool of Minitab software is capable of optimizing a single response or a set of responses. The composite desirability is considered as an important factor used to indicate that the optimization can satisfy the requirements for all the responses in a set. As demonstrated by Jose et al., the individual desirability of both the seal strength and the variance in seal strength is 1 [24]. Thus, the combined or composite desirability of these two variables should be 1. To maximize the sulfur conversion using Minitab software, the starting values of four independent factors had to be set in software in which the composite desirability must be 1.

The supposed starting values of oxidant volume, mass of catalyst, mass of PTA and ultrasonic wave amplitude used in the response maximization were found to be 6 mL, 0.625 gr, 0.06 gr and 70%, respectively. The optimum values of the process factors for the maximum sulfur conversion are tabulated in Table 6. The predicted maximum sulfur conversion of gasoil was calculated to be 95.9%; furthermore, the corresponding composite desirability for this optimization equaled 1. According to Table 6, the optimum amounts of process variables were 21.96 mL of the oxidant, 1 gr of the catalyst, 0.1 gr of PTA and 100% of wave amplitude. Furthermore, the predicted amount of sulfur conversion at the maximum point was compared with the highest experimental sulfur conversion. The results reveal that the maximum experimental sulfur conversion is slightly lower than the maximum predicted conversion at the optimum point, which suggests that the achieved statistical model is adequate.

Table 6. Values of independent variables at the optimal point

Parameters	Values
Predicted sulfur conversion, %	95.92
Experimental sulfur conversion, %	94.5
Volume of oxidant (ml)=x_1	21.96
Mass of catalyst (gr)=x_2	1
Mass of PTA (gr)=x_3	0.1
Ultrasonic wave amplitude, %=x_4	100

Composite desirability=1.000000

CONCLUSIONS

The effects of four independent variables on the sulfur conversion of gasoil treated by the UAOD process were studied. The values of the sulfur conversion were evaluated for 31 different experiments designed by central composite face-centered design of response surface methodology (RSM). The experimental data resulted in a second-order quadratic model estimating the relationship between the four independent variables and the sulfur conversion of treated gasoil. The results revealed that mass of catalyst, mass of PTA and ultrasonic wave amplitude affected the sulfur conversion positively, while the volume of oxidant could raise the sulfur conversion until a special point; afterwards, every rise in the oxidant volume led to a decline in sulfur conversion. The obtained mathematical model in turn was employed to find the optimal conditions for the highest sulfur conversion of gasoil.

NOMENCLATURE

S : sulfur conversion [%]
Y : sulfur conversion response [%]
$\bar{x}_i$: mean values of uncoded variables [-]
x_i : values of uncoded variables [-]
$\bar{x}_{iH}$: high level of the i_{th} factor [-]
$\bar{x}_{iL}$: low level of the i_{th} factor [-]
X_i : values of coded variables [-]
P : input power [w]
ω : circular frequency [radian·S^{-1}]
β : total resistive constant leading to damping [-]
m : inertia of the oscillator [-]
ξ : amplitude [m]

Greek Letters

β_0 : intercept [-]
β_i : linear coefficient [-]
β_{ii} : squared coefficient [-]
β_{ij} : interaction coefficient [-]

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