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ORIGINAL RESEARCH PAPER

Oxidative Desulfurization of Liquid Hydrocarbon Fuel: Experimental and Mathematical Modeling Study

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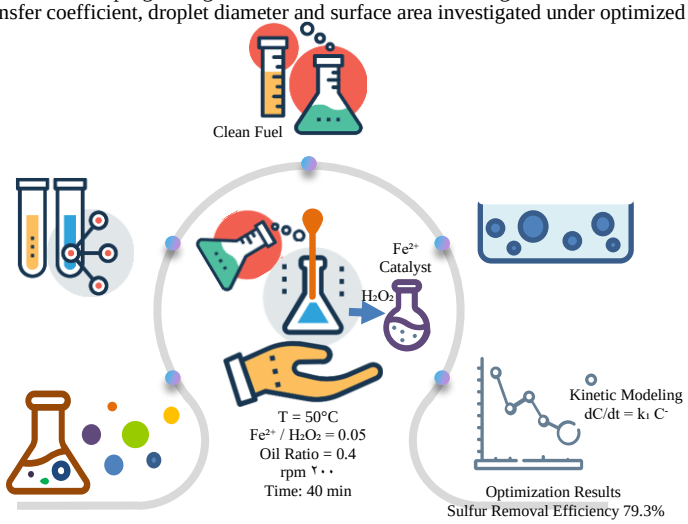
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A B S T R A C T

The positive increment trend in the world of continuously production of low sulfur content fuel as a transportation feed is under progressing. This issue is feasible by oxidative desulfurization as one of the most promising approaches. To cope with the difficulties and limitations of hydrotreating units, integration with oxidative desulfurization can be a vital solution. This assay presented Fenton process as a treatment method and explain a comprehensive analysis of different parameters and characteristics of this method on a model fuel of toluene. So contains experimental and modeling results for optimizing the reaction parameters to Fe^{+2}/H_2O_2=0.05 molar ratio, T=50°C, agitation speed= 200 rpm, oil volume ratio=0.4 and reaction time of 40 min under acidic pH. Then mass transfer characteristics estimated and process progressing studied. Since the oxidation occurred under estimated conditions, 79.3% efficiency achieved in the first-order kinetics. Parameters optimized for toluene as a model fuel nutriment by DBT as a sulfur contamination and oxidized under hydrogen peroxide as the oxidizing agent and ferrous ions as the catalyst. Which temperature and oil volume fraction play the most important roles in the progressing of the reaction. Kinetics modeling and calculations of reaction time constant, mass transfer coefficient, droplet diameter and surface area investigated under optimized condition.



1. Introduction

Due to stringent environmental regulations for reduction of sulfur oxides, refineries and petrochemical companies faced to decrease sulfur compounds in their fuel products. Also alternative products such as biofuels, bio gas, diesel and gasoline from GTL are not attractive from economical point of view. Hence crude oil as feed of the refineries and petrochemical processes contains vast ranges of pollutants and ingredients. Those are as sulfur and nitrogen compounds in the form of aromatic and nonaromatic hydrocarbons with different quantities which ranging of 0.05-5.0 wt.% also as high as 8 wt.% of organically bound sulfur compounds reported [1]. During the crude oil distillation, sulfur compounds end up to the gasoline and diesel as the most applicable fuels for transportation. Because of special distribution of organically bound sulfur in crude oil their percentage increases along with the boiling point of the fraction [2]. If these compounds remain in the crude oil fractions or does not remove entirely, will result in the formation and emission of polluting sulfur oxide during combustion. Resolve this problem and achieving environmental legislations of reaching “zero sulfur content” in hydrocarbon streams and fuels is vital. To gain this, various alternatives exists as traditional hydro desulfurization (HDS) and some new ones as bio

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desulfurization (BDS), ultrasound assisted oxidative desulfurization (UAOD) and oxidative desulfurization (ODS) etc. The research on desulfurization of liquid fuels getting started since 1928 when the first research article developed [3]. Therefore HDS was the first industrial method which used bud faced with series of difficulties [4]. ODS technology is received much attention for desulfurization of middle distillate and is proposed for removing some refractory slightly polar organo sulfur compounds (OSCs) that can't be removed by traditional processes such as HDS. One of the most potent techniques which is used as the famous treatment technologies are advanced oxidative processes (AOPs) with a great range of techniques. These physio-chemical approaches contain methods as UV/H_2O_2, UV/O_3, UV/TiO_2 and many others which are ozone-based or non-ozone-based. Although AOPs has a good background with a great effect in the field of treatment engineering process but has some disadvantageous. This properties are summarized in Table 1. Several oxidative desulfurization technologies are actually available and typically consist of two main steps: sulfur oxidation and separation. In the oxidation step, the hydrocarbon stream is contacted with an oxidant. In the vast background of this process various types of oxidants used in the contact of different catalysts[2, 6-8]. In the separation section there is some alternatives as extraction and adsorption. In the vast categories of AOPs, Fenton is one of them. This technique uses in many industries for treatment such as wastewater, ink, dies and suchlike administrative industries. This process still is under progress and coupled with many other technologies for better results [2, 9, 10]. However this technique has some limitations and nearby advantageous. The following steps are expected in the Fenton technique: pH adjustment (acidic environment), oxidation reaction, neutralization and finally coagulation [11]. Fenton process proceed as shown in Table 2. In the Fenton process H_2O_2 used as oxidation agent in contact with Fe^{+2} as the catalyst. Yongchuan Dai et al. evolve that in the acidic environment the decomposition rate of H_2O_2 into hydroxyl radicals accelerated so the reaction progress enhanced [9] . Also they investigated the effect of iron ions in the Fenton process and compared it with Cu^{+2} ions. They elicit that Fe^{+2} gain better results especially in the presence of ultra-sonication [10]. Bolla et al. examined different treatment systems with various sulfur content of fuels. But best results obtained in the presence of peracetic acid and Fenton process under high pressure condition. The oxidation process occurs in the heterophasic mixture because of the usage of hydrogen peroxide solution. Therefore this process contains both physical and chemical steps [2]. Besides a modeling attempt conducted for kinetics constant investigation of benzo- and dibenzothiophene under supplying of peroxyformic acid as the oxidizing agent which values of 2.255×10^{-1} and 1.206×10^{0} (m^3 $kmol^{-1}$ s^{-1}) under 40°C obtained, respectively. As discussed this oxidative reaction proceeds under a slow liquid-liquid reaction regime. Also chemical reaction plays the role of controlling step [12]. In BDS as one of the similar options for treating the fuels a modeling analysis in a model biphasic small-scale reactor investigated for desulfurization of DBT. In this study the power input per volume and impeller tip speed were the most effective parameters with values of 10,000 W/ m3 and/or vtip greater than 0.67, respective. Also Marcelis et al. developed a mathematical model in BDS to estimate the key parameter for proceeding the process in desulfurization of DBT under temperature range of 20-60 ◦C, at oil volume fractions of 10 and 25%. Also estimated the mass transfer rate of DBT in aqueous phase was in a factor of 10 up to 10^4 [1].

Table 1. Fenton process properties.

Advantageous	Disadvantageous
Environmentally friendly materials	Achieving to the best result unless coupling the process
Low cost for reagents preparation and reactor design	Unsafety because of acidic based of hydrogen peroxide
Presenting a good result although in a short time	Production of large amount of sludge
Affecting on the vast range of pollutants	Treatment of produced sludge
No energy input for hydrogen peroxide activation	Effective on the special pH range (2-4)
No mass transfer limitation due to its homogeneous catalytic nature	Consumption of iron ions more rapidly than their regeneration
No form of energy involved as catalyst	Deactivated of iron ions due to complexion with some iron complexing reagents such as intermediate oxidation products.

See Ref. [20].

The aim of this study is to explore the possibility of fuel desulfurization by means of Fenton process and also enhance its efficiency by changing different reaction conditions to approach the regulations. For this important issue and also economical emphasizes Taguchi experimental design applied, optimum conditions and the most effective parameter was determined. Thereafter some mathematical modeling results presented in order to describe the mass transfer phenomena in the oil droplet interface. Also investigation of capability of a defined model for the similar process is under estimation.

Table 2. Steps in Fenton process.

Initiation step Hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals	$\mathbf{Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + OH^- + OH^-}$
Propagation step Reduction of produced ferric spices with hydroxyl radical and ferrous ion regeneration	$Fe^{2+} + OH^- \rightarrow Fe^{3+} + OH^-$ $RH + OH^{\circ} \rightarrow H_2O + R^{\circ}$ $R^{\circ} + Fe^{3+} \rightarrow Fe^{2+} + R^+$

2. Experimental

2.1. Chemicals

The organosulfur compound used in this experiment is dibenzothiophene (DBT, $C_{12}H_8S$, Merck). Hydrogen peroxide (H_2O_2, 34.5 wt. %) and $FeSO_4.7H_2O$ as the catalyst are used directly without purification. Toluene (C_7H_8) as the base of model fuel and methanol (CH_3OH) for the extraction are supplied by Merck and used without further purification.

2.2. Analytical Method for Sulfur Content Analysis

Total sufur content of the fuel was measured by an Analytical Jena EA3400 TS/TN Germany Analyzer. To determine the sulfur content in the fuel, nearly 100 µl of the extracted fuel injected into the apparatus. Then combustion started at the temperature of 1050°C in the two stages combustion tube and after a period of about 5 minute the residual amount of sulfur in the fuel will be monitored.

2.3. Experimental Procedures

2.3.1. Oxidation

In each experimental run 25 ml of toluene nutrient with DBT as a sulfur compound was introduced into a reactor equipped with thermocouple and mechanical mixer. Which produce a solution of 900 ppm sulfur content. An appropriate amount of $FeSO_4.7H_2O$ as the catalyst added to the reactor and maintain under certain temperature for considered reaction period. When H_2O_2 as the oxidizing agent supplied in the reactor, the reaction started. Which is "zero time" for oxidation of the fuel. Then this solution kept under certain conditions including agitation at a constant rate of 100 rpm, atmospheric pressure and specific adjusted temperature in the water bath. After a certain time it removed from the water bath and cooled in the room temperature for next step.

2.3.2. Extraction

For solvent extraction general procedure was as follows: after the oxidation reaction completed, the fuel should be extracted to remove the oxidized sulfur compounds. So it taken in the separated funnel with the equal amount of water and methanol as the extractive solvent, 12.5 ml for each one respectively, and solvent to fuel oil volume ratio equal to 1. It should be shaken for about 20 minutes and rested for equal time to separate organic and aqueous phase. Then the dispersion formed was allowed to separate into two distinct phases. After that the lower layer removed and upper layer collected for more analyzes. The progress of the oxidation reaction ceased by adding an appropriate amount of Na(OH) to the sample bottles. The performance of the oxidation-extraction reactions and the effect of changing different parameters on the sulfur removal were characterized by measuring the residual amount of sulfur compound in the fuel after oxidation and extraction step over a defined period of time. Flowchart of whole experimental procedures elicited in Figure. 1.

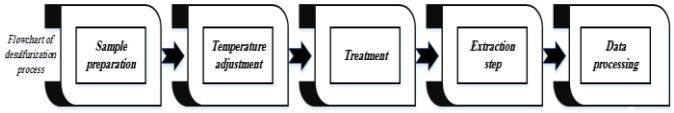


Figure 1. Flowchart of experimental procedure.

2.4. Taguchi design of experiment

Taguchi method is an acceptable method in design and optimization of experiments. The concept of "quality engineering" is the optimization of processes of engineering experiments by suchlike methods. It is a statistical method which emphasis on the cost considerations which joined with statistical concepts. In Taguchi's experiments orthogonal arrays are used to assure the reproduction of the effects of parameters. Also in Taguchi various types of "signal to noise" (S/N) ratios are applied in order to measure variability around the target performance. By this technique and applying orthogonal arrays (OAs) experimental errors can be controlled and minimized in comparison with the other classical methods available for experiment design. In this study three different levels defined for three considered parameters so OA L9 (3×3) was chosen and applied for experimental design. In Table 3 effective parameters with corresponding levels presented. These experiments designed by the Qualitek-4 software for automatic design and analysis of Taguchi Experiments. Based on these factors and defined levels, 9 experiments should be done corresponding to L9 OA.

Table 3. Effective parameters and levels.

Factors	Levels		
Fe^{+2}/H_2O_2 (molar ratio)	0.05	0.07	0.09
T (°C)	60	70	50
Time (min)	20	30	40

3. Mathematical Modeling

3.1. Experiments

Additional experiments done in the same reactor based on the optimum conditions obtained from experimental section of 50°C temperature, molar ratio of Fe^{+2}/H_2O_2 equal to 0.05 and reaction time of 40 min. The STR reactor is under three different agitation speed and oil volume fractions, respectively. The sample preparation conducted after addition of catalyst to the model fuel concentrated with DBT. So oxidation reaction started after surcharging of oxidant and extraction step conducted as explained before, thereafter. Total

sulfur concentration of the upper layer is measured by an Analytical Jena EA3400 TS/TN Germany Analyzer. In Table 4 three different levels of the factors illustrated. For each run the "Qualitek-4 software" and the corresponding L_9 OA used similarly.

Table 4. Taguchi design of experiment needs in mathematical modeling.

Factors	Levels		
Agitation speed, N (rpm)	100	200	400
Oil volume fraction (φ_o)	40	50	70

3.2. Time constant Calculations

A mass transfer model with chemical reaction in a liquid-liquid system which consists in an aqueous acid phase (aq) and an organic phase (o) is schematically represented via oxidation of DBT by Fenton reaction. This process simulate via a time constant (τ_o) as a criteria for analytical analyzes. Droplet size affected through stirring which also has an influence on the time constant. Also parameters with great effects on the average droplet diameter as reactor operating conditions, physical properties and the volume fraction of the dispersed phase investigated. The inverse product of mass transfer coefficient (k_o) and specific surface area (a_{ow}) of the oil phase provide a volumetric mass transfer coefficient in the time constant definition. Which can be obtained from (Eq. 1) [1]:

$$\tau_o = \frac{1}{K_o\, a_{ow}} \tag{1}$$

This model is characterized based on three vital dimensionless numbers. Reynolds (Re), Sherwood (Sh) and Weber (We) number which represent hydrodynamic of the liquid phase, mass transfer characteristics and estimation of droplet diameter, respectively. The fundamental elements of these numbers shown in Table 5. In this dimensionless numbers the input variables are temperature dependent. Also oil phase volume fraction (φ_o) and type of organic phase (ξ) has significant effect on the input variables.

Table 5. Important dimensionless numbers.

Dimensionless Number	Applicability	Factors Description
$\mathbf{Re} = \frac{\rho_1 v d}{\mu_1}$	Hydrodynamic of the liquid	Density (ρ_1), dynamic viscosity (μ_1), velocity (v), diameter (d)
$\mathbf{Sh} = \frac{k_o l}{D_o}$	Characteristics of the mass transfer	Mass transfer coefficient (k_o), diffusivity coefficient (D_o), specific length (l)
$\mathbf{We} = \frac{\rho_1 v^2 l}{\sigma_{ow}}$	Estimate the diameter of the droplet	Density (ρ_1), velocity (v), specific length (l), surface tension (σ_{ow})

In this study dispersion of the oil phase occurred via three different agitation speed. Formation and stability of emulsions in the complex solutions depends on the energy input. The energy capacity (ε) is an acceptable criteria to relate between input mechanical energy (P) into the mass content of the reactor since agitation conducted special amount of energy to the solution. This parameter calculated by the equation following (Eq. 2) [1]:

$$\varepsilon = \frac{P}{\rho_1 V_1} = N_P \frac{\rho_1 N^3 D^5}{\rho_1 \left(\frac{\pi}{4}\right) T_S^2 H} \tag{2}$$

Where N_P represents power number, N shows the impeller speed with D as the diameter size in the reactor with liquid height of H and reactor diameter of T_S. Dynamic viscosity affected from variations in temperature and volume ratio. When the volume ratio of oil increases the solution viscosity increases subsequently and effect on the droplet size. Also droplet distribution is influenced from shear force in the mixture. Massodi et al. [14] presented an specific formula for biphasic solutions with equal mixing speed but here mixing rule applied for solution viscosity. In this attempt a paddle impeller used with NP=1.94. In order to calculate solution density (ρ_1), the mixture rule applied (Eq. 3) :

$$\rho_1 = \varphi_o \rho_o + (1 - \varphi_o)\rho_w \tag{3}$$

ρ_o implies the organic phase density in contact with the aqueous phase of density ρ_w. Availability of o/w surface area depends on the droplet diameter and actually affects on both mass transfer rate and reaction rate. Specific surface area (a_{ow}) defined as the total surface area of the oil droplets per cubic meters dispersion and so calculated by (Eq. 4) [23 in 1adv]:

$$a_{ow} = \frac{6\varphi_o}{d32} \tag{4}$$

The Sauter mean diameter, d_{32}, is the size of a droplet which has the same volume-to-surface area ratio as the entire population of droplets. Therefore the Sauter mean diameter gives important information about the available interfacial area of the drops in the distribution. There is some uncertainties for droplet size distribution in the mixture so it is difficult to relate a clear relationship of the Sauter mean diameter (d_{32}) with physical parameters. Also it can be recalled that there is a linear relationship between (d_{32}) and (d_{max}) [15]. Typically, a function of (d_{32}) to oil volume fraction is depicted as followed in (Eq. 5) [16].

$$\frac{d_{32}}{D} = 0.057(1 + 0.9\varphi_o)(We_{STR}^{-\frac{3}{5}}) \tag{5}$$

In the STR reactor droplet formation and characteristics' are subjected to the turbulent condition, applied pressure and shear force. These factors affect on the droplet distribution, deformation and breakage, if exceed interfacial tension force [1]. The Weber number is a good criteria for these relationships which depicted in Eq. 6. Maximum droplet diameter emerged in the mixture is presented in Eq. 7.

$$We = \frac{c_1\, \rho_w \varepsilon^{2/3} d_{max}^{5/3}}{\sigma_{ow}} \tag{6}$$

$$\frac{d_{max}}{D} = c_2(We_{STR}^{-\frac{3}{5}}) \tag{7}$$

Details about Weber number and its derivation explained in literatures [15, 17]. Finally, a suitable scale for comparing the main path of desulfurization is mass transfer coefficient (k_o). For this issue Eq. 8 recommended:

$$k_o = \frac{Sh_o D_o}{X} \tag{8}$$

Here, the characteristic length (X) of the oil droplet is equal to d_{32} and diffusion coefficient (D_o) of DBT in aqueous phase at considered temperature is calculated by Wilke-Chang equation (Eq. 9) [18]:

$$D_o = 7.4 \times 10^{-8} \frac{(xM)^{0.5} T}{\eta V^{0.6}} \tag{9}$$

Here x donate association parameter, M molar volume of solute at normal boiling point, η viscosity of solution and T relate to the temperature in K. In this study Sherwood number for rigid and spherical particles was applied. Also interfacial tension of the mixture obtained by Pallab Ghosh presentation [19].

Another important dimensionless number is Hatta number which defined as follow [12] (Eq. 10):

$$Ha_j = \frac{\sqrt{\nu_j k_j C_i^{\circ} D_o}}{k_o} \tag{10}$$

Which ν_j indicate stoichiometric coefficient of the spices, k_j is reaction constant, C_i° concentrations of each spices. This number imply a good criteria for estimation of the main path of desulfurization. Hatta number provide a good comparison between the maximum chemical conversions in the mass transfer interface to the maximum diffusion flux in the same area.

4. Results and Discussion

4.1. Experimental Results

4.1.1. Analysis of Variance

To optimize the effective parameters of desulfurization using ODS, Taguchi design experiments applied which is a useful approach. As illustrated in Table 6 the analysis of variance (ANOVA) summarized the results of sulfur removal. Form ANOVA analysis the parameter with most contribution percent (P %) has the most effect on the removal efficiency. As it is showed in the following table the most effective parameter is temperature which has the main effect on the sulfur removal efficiency. Also the magnitude of difference between the average effects (L_2 - L_1) represents the relative influence of the factor to the variability of results which temperature represent higher difference respect to others.

Table 6. Analysis of variance for sulfur removal (ANOVA) and Main effects in experimental part.

Factors	DOF (f)	Sum of squares	Variance (V)	F-ratio (F)	Pure sum (S´)	Percent P (%)	L_2-L_1
Fe^{2+}/H_2O_2	2	62.626	31.313	2.096	32.749	3.206	6.344
Temperature	2	861.903	430.951	28.848	832.026	81.471	-11.811
Time	2	66.846	33.423	2.237	36.969	3.62	0.844
Other error		29.876	14.938			11.703	

4.1.2. Interactions

Another capability of Taguchi design method is that all possible interactions among two factors can be calculated. In Table 7 interaction pairs are shown in descending order of their severity index (SI, 0-100%). In this table "Col." shows the column that should be reserved if this interaction effect were to be studied. On the other hand "Opt." indicates factors level desirable for the optimum condition. Also from ANOVA analysis the most effective level for each parameter is shown in Figure. 2, 3 and 4.

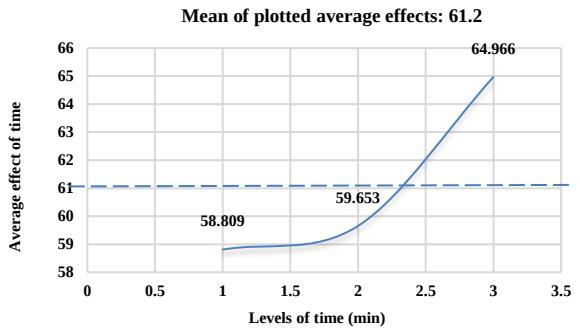


Figure 2. Main effect of reaction time.

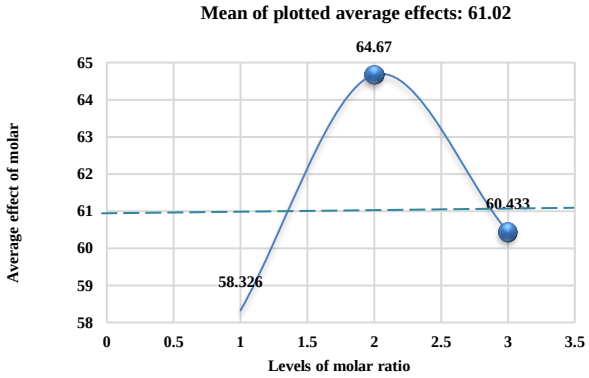


Figure 3. Main effect of molar ratio.

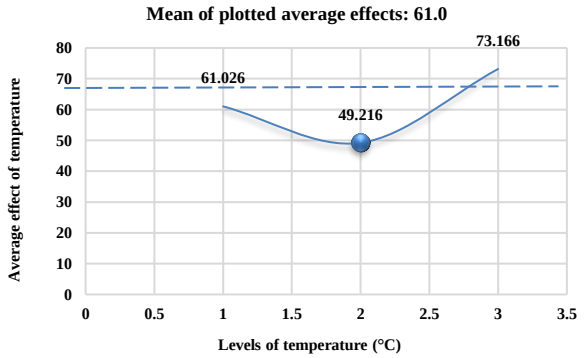


Figure 4. Main effect of reaction temperature.

Table 7. Interaction between factor pairs.

Interacting factor pairs (order based on SI)	Columns	SI %	Col.	Opt.
Mole * Temperature	1 * 2	19.99	3	[3, 3]
Temperature * Time	2 * 3	9.43	1	[3, 2]
Mole * Time	1* 3	7.5	2	[3, 2]

4.1.3. Effect of Temperature

As it was mentioned in the analysis results of Taguchi design, temperature was the most key factor affecting the reaction. As can be observed from Figure. 5, a rise in the reaction temperature from 40 to 50°C leads to a remarkable increase in the sulfur removal. Sulfur removal substantially increases from 62.04% at 40°C to 73% at 50°C and then decrease to 39% at 70°C. This behavior of efficiency enhancement is expected and can be explained by an increase in the oxidation reaction rate of sulfur-containing fuel. Therefore leading to a higher percentage conversion of the sulfur compound due to strong dependence of reaction rate on the reaction temperature. On the other hand the main reason of the removal efficiency decreasing in the higher temperature as 70°C is the hydrogen peroxide decomposition at such a high temperature. Based on Eq. 11 hydrogen peroxide decomposed and produce water and oxygen. The more decomposition the more water production which cause decrementing the reaction rate by decreasing efficient contact between two phases. Also it should be mentioned that the effect of different temperature levels on the sulfur removal is presented in Figure. 4.

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (11)$$

4.1.4. Effect of Oxidant TO Catalyst Molar Ratio (Fe^{+2}/H_2O_2)

The most significant parts of ODS process is the utilization of an oxidant. Table 8 illustrate all the mechanism happens in the Fenton reaction. Based on (R1) the hydrogen peroxide can be decomposed into hydroxyl radical by Fe^{2+} in aqueous solution. Hydroxyl radicals ($HO^{\cdot}$) generated by the processes can oxidize the majority of organic compounds. The most utilization of Fe^{+2} can cause the most production of $OH^{\cdot}$ so based on (R3) more excited R. produced which improve the chance of oxidation. Hydrogen peroxide is the most effective oxidant which used in the ODS. Beside its advantageous, the water as the only byproduct of H_2O_2 has a double-edge effect on the process. Its positive effect is environmentally friendly characteristic but the negative effect is decreasing the efficient contact between two phases. So as can be seen (Figure. 6) by increasing the molar ratio of catalyst to oxidant, the sulfur removal increased. Also it should be mentioned that this reaction conducted under 70°C which hydrogen peroxide is very capable for decomposition. So better molar ratio is 0.07 at this condition as presented in previous results in Figure 3.

Table 8. Fentons reactions.

$Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + OH^- + OH^{\cdot}$	(R1)
$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^-$	(R2)
$RH + OH^{\cdot} \rightarrow H_2O + R^{\cdot}$	(R3)
$R^{\circ} + Fe^{3+} \rightarrow Fe^{2+} + R^+$	(R4)

See Ref. [20].

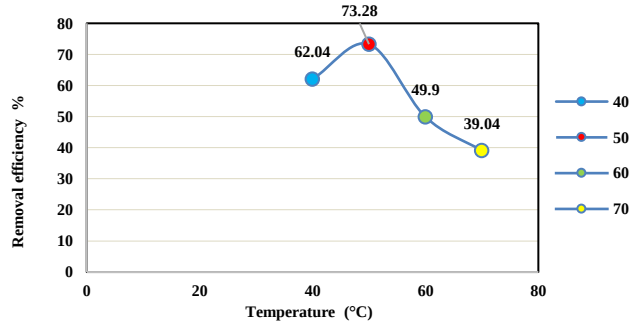


Figure 5. Effect of reaction temperature on the sulfur removal (test conditions: molar ratio: 0.05, time: 40 min).

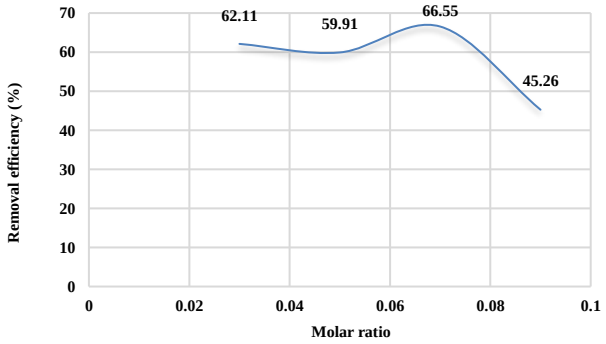


Figure 6. Effect of Fe^{+2}/H_2O_2 molar ratio on the sulfur removal (test condition: T: 70°C, time: 30 min).

4.1.5. Effect of Reaction Time

It can be observed that by increasing the reaction time from 20 min to 40 min, sulfur removal increased. It showed in Figure. 2, although from Taguchi results it requested that better result attains at 40 minute. However from Table 6 it revealed that time has the least effect (0.844) on the removal efficiency.

4.1.6. Effect of pH of the Aqueous Phase

The decomposition rate of hydrogen peroxide into hydroxyl radicals was reported to be pH dependent on the aqueous phase when the reaction was catalyzed by the metal ion. Also the ionization species is strongly dependent on pH value. Moreover, in an aqueous acidic solution, the redox potential is +1.77 V and +2.8 V for hydrogen peroxide and hydroxyl radicals, respectively. These values reduces to +0.88 V and +2.0 V in basic solution, respectively (Dai et al. 2011). Therefore it is advantageous to the ODS process for the aqueous phase to be at low pH values because generation of the hydroxyl radical takes place at the acidic pH range while at neutral pH range; the feryl ion (FeO^{2+}) mechanism predominates. It involves the non-radical pathway summarized as follows:

$$H_2O_2 + Fe^{2+} \rightarrow FeO^{2+} + H_2O \qquad (R5)$$

$$H_2O_2 + FeO^{2+} \rightarrow O_2 + H_2O \qquad (R6)$$

For the solution of hydrogen peroxide, the pH value is approximately 3.3 which is low enough for achieving best result and providing a good environment for oxidation. Results of experiments under test conditions of 30 min, 70°C and 0.05 molar ratio of Fe^{2+}/H_2O_2 present that sulfur removal doesn't change appreciably after adding HCl and adjusting the pH value at 2.07, because hydrogen peroxide can produce this acidic environment per se.

4.1.7. Optimization

The optimum table (Table 9) represents the predictive equation for performance at the optimum condition and any other possible condition. The numbers shown in Table 9 are calculated for the optimum condition. Maximum value predicted by software for optimum condition is 80.53% efficiency removal. To confirm the accuracy of the software, experiment conducted in optimal conditions and showed a 77.43% removal efficiency. This means that our design and selected optimal conditions had a very good accuracy.

Table 9. Optimum condition.

Factor	Level Description	Level	Contribution
Fe^{+2}/H_2O_2 (molar ratio)	0.07	2	3.526
Temperature (°C)	50	3	12.043
Time (min)	40	3	3.823

4.1.9. Effect of Fenton Process on the Fuel Properties

In order to find selectivity and effectiveness of the process, it is necessary to check fuel properties and performance of the fuel before and after desulfurization. Also it needs to be sure that this technology has no adverse effect on the fuel properties such as acidity and cetane number. However in this research a simple GC chromatography test was conducted on the desulfurized sample fuel after its oxidation-extraction process. As presented in the Figure 7. Fenton process has no adverse effect on the fuel and cannot change the nature of the fuel or produce another hydrocarbon. So this process can be a dependable in industrial applications.

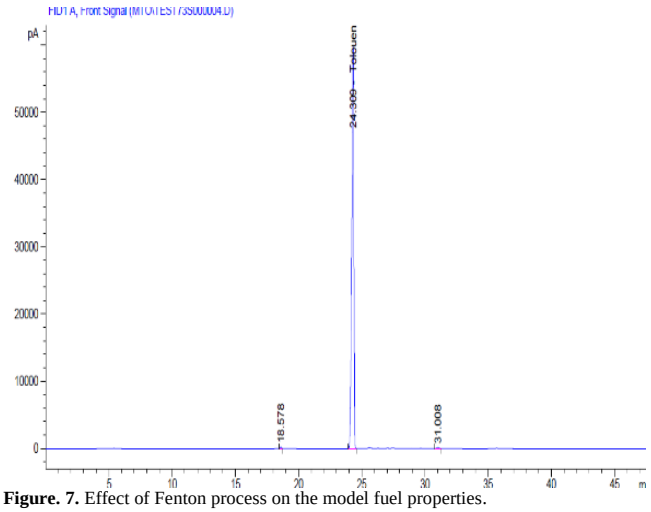


Figure. 7. Effect of Fenton process on the model fuel properties.

4.2. Mathematical Modeling

4.2.1. Experimental Results

4.2.1.1. Main Effect

Based on the Taguchi experimental design and analysis of ANOVA the contribution percent (P %) in Table 10 illustrates the most effective parameter for proceeding the process. Also the difference between the average effects ($L_2 - L_1$) approved this issue which shows the relative influence of the factor to the variability of results. So (φ_o) represent higher difference respect to the agitation speed. It emerges because any change in volume fraction can vary the volume in contact with the o/w interface and availability of oxidants. Therefore the chance of desulfurization revolve by variation in (φ_o) significantly than agitation speed. Also it reminisce that Fenton method is an oxidant based process so the amount of oxidant as a key parameter can have a deep effect in desulfurization which demonstrated by the Taguchi design.

Table 10. Analysis of variance for sulfur removal (ANOVA) in mathematical modeling.

Factors	DOF (f)	Sum of squares	Variance (V)	F-ratio (F)	Pure sum (S')	Percent P (%)	L_2-L_1
Oil volume fraction (φ_o)	2	411.769	205.884	110.427	408.04	96.472	11.409
Agitation speed (N, rpm)	2	3.733	1.806	1.001	0.004	0.001	-1.331

4.2.1.2. Interactions

In Table 11 Interaction pairs are shown in the order of their severity index (SI, 0 - 100%). The indicated levels in column as (1*2) must be replaced with the factor levels identified for the optimum condition because the interactions found significant in ANOVA (0.81%). Also from ANOVA analysis the most effective level for each parameter is shown in Figure. 8 and 9. Finally, for validating the results of the software analysis, two experiments carried out with the optimum conditions and most severity index condition, respectively. Which high efficiency goes to the results come from the experiments with the arrangement of levels with severity index, (1*2), 79.3%.

Table 11. Interaction between factor pairs.

Interacting Factor Pairs (Order Based on SI)	Columns	SI %	Col.	Opt.
Oil volume ratio*agitation speed	1*2	0.81	3	3*3

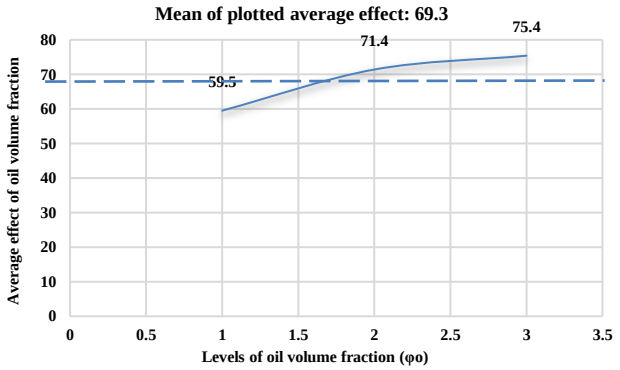


Figure 8. Main effect of the oil volume ratio.

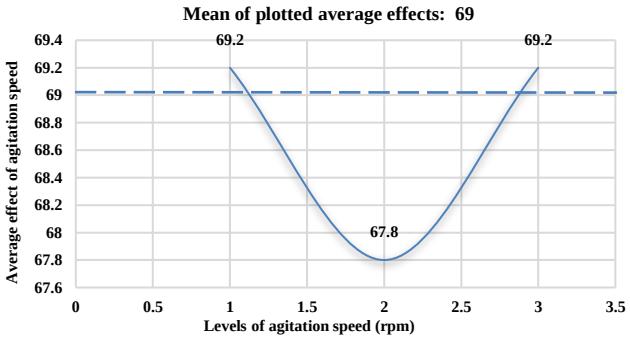


Figure 9. Main effect of the agitation speed.

4.2.2. Modeling Results

4.2.2.1. Time Constant Various Vs. Oil Volume Fractions

The time constant (τ_o) values of the DBT mass transfer vs. energy capacity and different oil volume fraction (φ_o) at 50°C is summarized in Figure. 10. The required time for the process to reach the 63% of the final value is defined as time constant. By enhancing energy capacity, the required time constant decreased which can be demonstrated via better emulsification and enhancing interfacial area. From the Figureure it is obvious when the oil volume ratio (φ_o) in the solution increased, the time constant also increased. This can be emerged from the origin of the desulfurization. It can be elicit that better desulfurization occurred in the lower oil fractions and so accessibility of more oxidant can improve the process. So the key path for the fuel treatment may be the oxidative desulfurization than mass transfer.

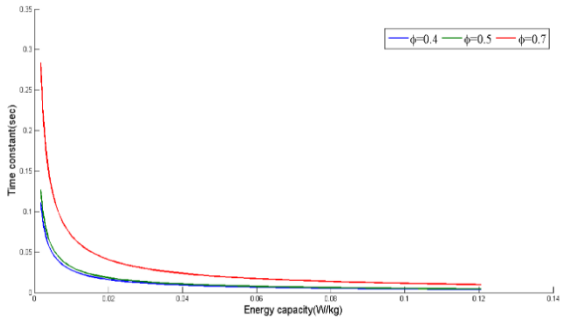


Figure 10. Time constant of DBT mass transfer for various oil volume fractions vs. energy capacity (T=50°C, time=40 min).

4.2.2.2. Energy Capacity Effect on Specific Surface Area and Mass Transfer Coefficient

Based on Figure 11 specific surface area enhanced by increasing energy capacity (ε) which can be resulted from the inverse relation between these two variables (Eq. 4 and5). Increasing mechanical energy can conquest to the interfacial tension force in the mixture. So producing of smaller particles facilitated and follow the ascending trend toward increasing the energy capacity. Accessioning the oil volume fraction, cause decrementing in specific surface area vice versa. It can be raised from increasing the fluid viscosity so cope with interfacial tension of this viscos flow faces with difficulties. Therefore chance of desulfurization decreased by charging the oil fraction.

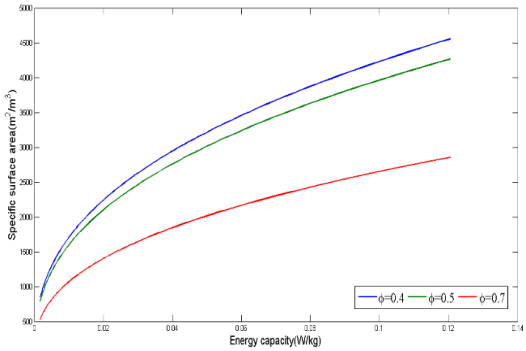


Figure 11. Specific surface area of various oil volume fractions (T=50°C, time=40 min).

In engineering mass transfer coefficient is a diffusion rate constant that relates the mass transfer rate, mass transfer area and concentration change as driving force. This can be used to quantify the mass transfer between phases, immiscible and partially miscible fluid mixtures or between a liquid and a porous solid. Quantifying mass transfer allows for design and manufacture of separation processes equipment that can meet specified requirements, estimate what will happen in real life situations (chemical spill), etc. Mass transfer coefficient can be estimated from many different theoretical equations, correlations and analogies that are functions of material properties, intensive properties and flow regime. Based on the Wilke-Chang equation and relation describes in Eq. 9 any change in viscosity affect inverse variation in diffusion coefficient and mass transfer coefficient. Great differences that obvious in Figure. 12 is a good criteria that illustrates solution viscosity variations for any oil volume fractions. Therefore the influence of viscosity on k_o is clearly demonstrated. Also increasing in oil volume fraction can increase fluid viscosity and so adverse effect on the mass transfer coefficient.

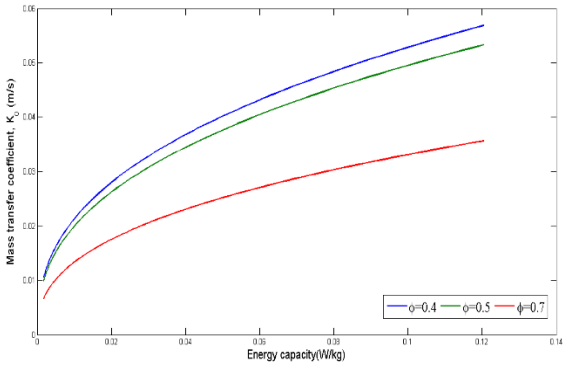


Figure 12. DBT mass transfer coefficient vs. energy capacity at 50°C and time=40 min.

4.2.2.3. Energy Capacity Effect on Droplet Diameter Estimation

Figure. 13 illustrates smaller droplets emerge in the low viscous mixture which provide a large specific surface area. It should be considered that high mixing intensities will produce high shear forces which can have negative effects on the operating condition. So estimation of optimal energy capacity will be resulted in enhancing efficiency in the economic manner. Also in the STR better distributions occurred in comparison to the non-agitated systems so agitation has a positive effect and increase specific surface area. Based on Eq. 2 any increment in agitation speed have a direct effect on energy capacity also We number will be enhanced. Therefore interrelations of agitation speed and droplet diameter in Eq. 5 demonstrated the results of the following graph (Figure 13).

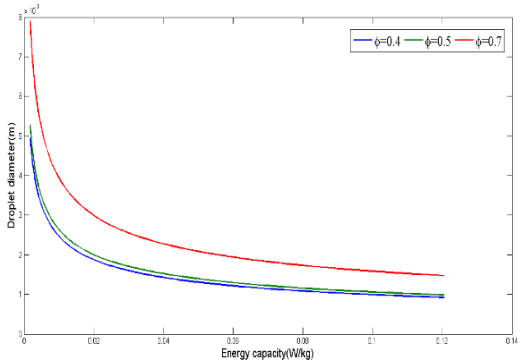


Figure 13. Droplet diameter vs. energy capacity at 50°C and time=40 min.

4.2.2.4. Influence of Temperature

All the physical and chemical solution properties' affected by the temperature so the results change by temperature variations as depicted in the experimental results, Figure. 4 & 5. The considered criteria, time constant influenced directly and indirectly via each parameter. This claim demonstrated also by Figure. 14 of mathematical modeling which illustrate the mass transfer coefficient variations for different energy capacity intensities. Increasing temperature enhanced mass transfer coefficient by inter relations to the diffusion coefficient and so descend viscosity of the solution. Since mass transfer coefficient has more temperature dependency than interfacial tension as the parameters of time constant so variations illustrated in Figure. 14. Although mass transfer coefficient enhances while temperature rises but there is some chemical reactions which overcome this increment. Based on the experimental results best removal occurred in 50°C but mass transfer coefficient enhancement cannot overcome the excess production of water and hydrogen peroxide decomposition. Which causes less interfacial surface area so efficiency removal decreased.

4.2.2.5. DBT Desulfurization Pattern

Based on Eq. 10 and approved ranges described for this number which shown in the following table (Table 12) main desulfurization path identified. Mathematical modeling results estimated the basic parameters of the Hatta number. It should be recalled that all the parameters calculated in the organic phase and it is assumed that all the oxidized sulfur compound immigrate to the aqueous phase. From Figure. 15 it is obvious that this system is reaction limited for all three types of oil volume ratio. So the desulfurization process in limited by the reaction and Fenton process can manage the treatment phenomena. This means that mixing conducted in a suitable STR and availability of great surface area. But any parameter of Fenton method can affect on the desulfurization results and chance of desulfurization varied by any variations in Fenton variables as amount of reactants, temperature, reaction time and oil volume fraction etc. Also this issue can be estimated via other criteria as comparison of volumetric DBT flux to the o/w interface and DBT oxidative conversion rate.

Table 12. Desulfurization path.

Range	Description
Ha≫ 1	Mass transfer limited
Ha≪ 1	Reaction limited

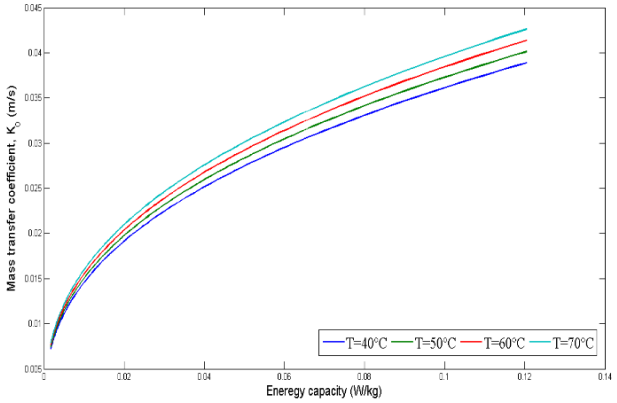


Figure 14. Mass transfer coefficient vs. energy capacity at oil volume fraction=0.5 and time-40 min.

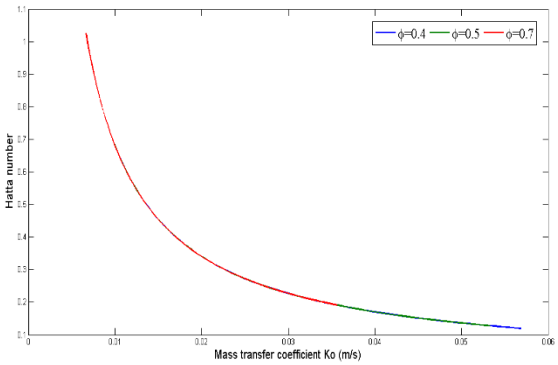


Figure 15. Hatta number vs. mass transfer coefficient (T=50°C, time=40 min).

5. Conclusions

A mathematical model was estimated for qualifying the main phenomena occurred in this oxidative desulfurization system. This process simulated based on theoretical and semi-empirical equations and used as a criteria for comparison between mass transfer limited variables and reaction limited ones.

As discussed oxidative desulfurization is a great method with profound effect on the sulfur content fuel. It hires much milder experimental conditions and consequently undesirable side reactions are minimized In the Fenton process hydrogen peroxide used as oxidant with great background as the most effective oxidative spice and high efficiency. It has economic preferences with non-polluting properties and environmentally friendly characteristics, high removal rate and many other great properties demonstrated. So increasing oxidant volume fraction can improve the process efficiency and then better results obtained. Because of STR, creation of fine dispersions and high energy-input achieved via agitation but based on experimental results it has less impact than φ_o for desulfurization. Based on the analytical results trend of all parameters is accurate. The assumptions and basic equations applied for this simulation all has high accuracy and demonstrated. This study conducted on a model fuel, toluene which nutrient with dibenzothiophene as a sulfur compound and treated under temperature range of 40-70°C. It was observed that differences in time constant is very negligible when energy capacity increases. Dynamic viscosity affected by the solution temperature or energy capacity intensity, in the other word. So time constant influence of it. Because of a close relationship of dynamic viscosity and diffusion coefficient. So mass transfer coefficient affected. Also temperature has a direct and indirect effect on the other parameters as diffusion coefficient, mass transfer coefficient and interfacial tension. But specific surface area receive negligible affect of temperature variations and more is obtained from hold-up of the organic phase.

Since validating the experimental and mathematical modeling results so applying the parameters in the optimum levels and priorities which designed by Taguchi can be a suitable tool for better results. Based on the Hatta number this system controlled by Fenton reaction so applying excess oxidant or catalyst, more residual time of solution in the STR and demolishing any interpreting limiting parameter to the oxidation process can reach a good advanced in the system efficiency. For this assay mixing happened in a suitable manner and no phase inversion occurred so other parameters should be optimized as discussed earlier. Also it is recommended that dispersion should remain Newtonian during the process otherwise non-Newtonian equations should be applied.

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