

Sulfur Removal of Hydrocarbon Fuels Using Oxidative Desulfurization Enhanced by Fenton Process

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Abstract—A comprehensive development towards the production of ultra-clean fuels as a feed stock is getting to raise due to the increasing use of diesel fuels and global air pollution. Production of environmental-friendly fuels can be achievable by some limited single methods and most integrated ones. Oxidative desulfurization (ODS) presents vast ranges of technologies possessing suitable characteristics with regard to the Fenton process. Using toluene as a model fuel feed with dibenzothiophene (DBT) as a sulfur compound under various operating conditions is the attempt of this study. The results showed that this oxidative process followed a pseudo-first order kinetics. Removal efficiency of 77.43% is attained under reaction time of 40 minutes with $(\text{Fe}^{+2}/\text{H}_2\text{O}_2)$ molar ratio of 0.05 in acidic pH environment. In this research, temperature of 50 °C represented the most influential role in proceeding the reaction.

Keywords—Design of experiment, dibenzothiophene, optimization, oxidative desulfurization.

I. INTRODUCTION

IRREGULAR production, low quality, and increasing use of various transportation vehicles cause a dramatic emission of hazardous materials from exhaust engines and air pollution, especially in big industrial cities. Extraction of crude oil is accompanied with various kinds of organic and non-organic compounds. During the last years, deep excavations cause ending up more pollutants to the crude oil, consequently the quality of later productions is affected. Different kinds of organic sulfur compounds (OSC), especially in the form of aromatics as sulfides, thiols, thiophenes, benzothiophene, dibenzothiophene, and their substituted derivatives exist in the crude oil. When distilled, these compounds end up with the gasoline and diesel which are the most important fractions of petroleum in transportation sector [1]. Thereafter, emission of NO_x , SO_x , PM_s , and many different kinds of pollutants can be a negative result of fuel's low quality, which is produced in the refineries. So, different types of environmental, health, and economic problems appeared during the last decades. Consequently, increasing in fuel demand and decreasing the

crude oil quality provide much more attention. Acidic rain, corrosion of buildings, damage to agricultural products, decreasing soil quality, poisoning catalytic convertor, and finally incrementing the API gravity are some of vast negative influences of fuel with low quality [2], [3]. On the other hand, in the future, it is anticipated that the demand of diesel fuel will increase in comparison to the gasoline fuels because of its high efficiency and economical importance. For this reason, development of methods with the production capability of ultra-clean fuels should be investigated in the theoretical and industrial scales. Nowadays, environmental stringent regulations have been issued to control the sulfur level in gas oil and diesel fuel. In EU, sulfur concentration in diesel is decreased from 50 $\mu\text{g/g}$ to 10 $\mu\text{g/g}$ between 2005 and 2010 [4]. In order to meet strict regulations, pre-nominated contaminants should be removed from the fuels to an expected level. For this reason, there are some traditional and modern technologies including hydrodesulfurization (HDS), ODS, biodesulfurization (BDS), ultrasound assisted oxidative desulfurization (UAOD), ionic liquid-catalysis, selective adsorption, and so on. In refineries over than 65 years, HDS as a traditional method has been used [2]. This technology has advantages as well as disadvantages from the industrial side of view. Special conditions such as long residence time, highly energy-intensive, negative operating conditions of high temperature (about 400 °C), and high hydrogen pressure (up to 100 atm) with the consumption of large amount of active metal catalysts (e.g., CoMo and NiMo) and finally limitations of treatment for refractory compounds like alkylated aromatic sulfur compounds as 4, 6 dimethyldibenzothiophene (4, 6-DMDBT), benzothiophene (BT) and dibenzothiophene (DBT, special) are a series of difficulties that HDS copes with. In contrast, high removal efficiency recorded for mercaptans, thioethers, sulfides, disulfides, and thiophene [5], [6]. Additionally, deep HDS technique can be a good solution for these limitations which are cooperated with the negative properties. This technology includes unsuitable inherent properties considering that it operates at very severe conditions such as reduction of catalyst life time, consumption much amount of H_2 , instability of fuel color and light, reduction of lubricant performance, and yield loss [1]-[5], [7]-[12]. That is why ODS is recommended as a better solution for the treatment process [8], [4]. Concerning about ODS, it consists of two main steps; oxidation and extraction. While oxidation reaction begins, OSCs are converted to their sulfoxides and/or sulfones in the presence of oxidant under

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mild condition of temperature and pressure [1]-[13]. Moreover, ODS follows a mechanism where undesirable side reactions are minimized [14]. It organizes a biphasic system in which the upper phase contains diesel fuel with highly polarized sulfones. Aqueous phase is separated by the gravity and it is extracted with the appropriate non-miscible solvent or adsorbent [9]-[11]. Sulfones are applicable in several industries extensively as agrochemicals, pharmaceutical products, lubricants, and so on. ODS has many advantages relative to the conventional HDS method such as capability to carry out in a liquid phase [3], [11], [13], applying effective oxidant, reactivity of the most refractory compounds like BT, DBT, and their derivatives [1], [3], [11], [13], non-expensive hydrogen residence time based on extensive efficiency of catalyst supply [2], and complementary chemistry due to conventional method [13]. On the contrary, there are still some issues that should be considered for ODS as to be a promising method; namely safety and economy of the process [15]. Moreover, Fenton as a branch of advanced oxidative processes (AOPs) has presented successful results dealing with such refractory compounds and degradation of them in a greener method than the traditional ones [4], [8]. This method

presented a great background in various industries via treating different kinds of waste waters such as pharmaceutical, winery, paper mill, fuel desulfurization; leachate treatment and many others in the form of post-treatment, pre-treatment, or complementary with others [16]. Commonly the AOPs use oxidizing agents (ozone-based or non-ozone-based processes) in attendance of catalyst as an enhancement factor to produce a more excited hydroxyl radical which has an exaggerated powerful effect for oxidation than the other molecules [8], [17]. In the Fenton process, H_2O_2 plays a role as an oxidizing agent which converts to OH^\bullet in contact with Fe^{+2} as a catalyst and provides a more excited environment for treatment. In this practice, the Fenton process is applied as an enhancement method for the production of more excited reagents in order to get better results. Reactions in detail are summarized in Table 1. Concerning about this study, the main objective is the estimation of capability of the Fenton process as a treatment method. To assess the statistically important parameters and system optimization, an experimental factorial design methodology was applied. Furthermore, rate of the reaction and kinetics characteristics are estimated.

TABLE I
 STEPS IN FENTON PROCESS [18]

<i>Initiation step</i>	$Fe^{+2} + H_2O_2 \rightarrow 2Fe^{+3} + OH^- + OH^\bullet$
Hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals	
<i>Propagation step</i>	$2Fe^{+3} + OH^\bullet \rightarrow Fe^{+2} + OH^-$
Reduction of produced ferric species with hydroxyl radical and ferrous ion regeneration	$RS + OH^\bullet \rightarrow H_2O + RSO$
	$RSO + OH^\bullet \rightarrow H_2O + RSO_2$

II. EXPERIMENTS

A. Materials

Hydrogen peroxide (H_2O_2 , 34.5% by mass), Ferrous Sulfate Heptahydrate ($FeSO_4 \cdot 7H_2O$, 98-102%), DBT ($C_{12}H_8S$, 97%), Toluene (C_7H_8 , 96%), Methanol (CH_3OH , 96%) and Water, were obtained from Sumchun (Korea) and used without any purification.

B. Analytical Method for Sulfur Content Analysis

The treated fuel analyzed via analytical Jena EA3400 TS/TN Germany Analyzer for estimation of the remaining sulfur content in the fuel. This issue is conducted via approximately 100 μ l of the desulfurized fuel injected into the analyzer which combusted the fuel under temperature of 1050 $^\circ$ C in the two stages of combustion tube during 5 minutes and monitors the sulfur residual in the fuel.

C. Oxidation Experiments

In each experiment, 25 ml of toluene and special amount of DBT (900 ppm) introduced into a reactor equipped with the thermocouple and mechanical mixer. Then, $FeSO_4 \cdot 7H_2O$ feed and the mixture agitated continuously until the desired reaction temperature supplied in the water bath. Thereafter, hydrogen peroxide surcharged and oxidation reaction started during the recommended times. In the end, the reactor was removed from the water bath and cooled at the room temperature.

D. Extraction Experiments

Typically, solvent extraction was conducted as the complementary process followed by oxidation to remove the oxidized compounds more easily. Extractive solvents, water and methanol, with volume ratio of 1:1 were introduced into a separator funnel then shook manually for about 20 minutes and rested to appear two distinct phases. Finally, the upper layer was collected and neutralized for more analysis of sulfur content in the fuel.

III. TAGUCHI DESIGN OF EXPERIMENT

Taguchi works were based on the "quality engineering" science and developed a statistical engineering method which is an applicable tool in designing, optimization, and analyzing the experimental attempts and they were renewed as the design of experiment (DOE). This method is a suitable package of statistical, engineering, and economic considerations [19]. These calculations start by an orthogonal array (OA) which is a factorial based method involving a matrix that provides more accuracy, error reduction, incrementing efficiency, and reproducibility of experimental assays [20]. In this software, various types of "signal to noise" ratio applied as a criterion for estimation of differences between the target value and individuals. In this study, three different levels for three chosen parameters were considered, and OA L_9 (3×3) was applied. Corresponding levels are

presented in Table II. For the Taguchi design and analysis of results, Qualitek-4 software is employed with quality characteristic type (QC) of bigger is better.

TABLE II
EFFECTIVE PARAMETERS AND LEVELS

Factors	Levels		
Fe ²⁺ /H ₂ O ₂ (%mole)	0.05	0.07	0.09
Temperature (°C)	60	70	50
Reaction time (min)	20	30	40

IV. RESULT AND DISCUSSION

A. Analysis of Variance (ANOVA)

Optimization and factors effect for the fuel oxidation in the stirring tank reactor (STR) was assisted by DOE. By this method, relative roles of factor levels (L₂-L₁), also combined and individual effects are evaluated with the ultimate aim of process optimization. Table 3 summarized the results of analysis of variance (ANOVA) for the sulfur removal which includes the relative influences. Based on Taguchi, contribution percent (P%) is a suitable indicator which represents the most effective parameter contribution in proceeding the reaction. Considering P%, temperature is a key factor with the major effect on the sulfur removal efficiency as well as the great magnitude of (L₂-L₁), which is obvious from Table III. Furthermore, the degrees of influences of independent parameters on the performance statistics are represented via Fig. 1.

B. Interactions

Various parameters, apart from having an individual effect on the oxidative process, are interacted among them creating the possibility of comparison between different operating conditions and they are characterized via a parameter defined as severity index (SI) in the software. By the experimental results, significant interaction was observed between the temperature and the molar ratio (Table IV). High sensitivity of conversion rate and mass transfer conditions to the temperature as well as inherently oxidative property of this process are accounted for the majority although, in the individual effect, these two factors were not significant contributors in desulfurization of model fuel. As a consequence, evaluating the contribution of each factor by the ANOVA is a suitable tool for the operating condition controls which should be enforced on the process.

C. Molar Ratio Effect on Sulfur Removal Efficiency

In order to investigate the effect of Fenton reagents concentration on the removal rate, different Fe²⁺/H₂O₂ molar ratios are tested as shown in Table II. Additionally, chains of reactions proceeded during this process are summarized in Table I. Analysis of variance was calculated to investigate the significance of individual factors on the removal efficiency. In fact, increasing (Fe²⁺/H₂O₂) molar ratio can enhance the desulfurization efficiency considering reaction chains specially (R₁). Incrementing the availability of catalyst contributes to improving production of OH[•], but it showed an adverse effect at higher values, namely 0.09, because of decrementing of hydrogen peroxide portion. Moreover, the data of this study implied over 66% sulfur removal efficiency at 0.07 (Fe²⁺/H₂O₂) molar ratio (Fig. 2).

D. Reaction Time

The DOE data revealed that period of reaction time had the least effect contributing 3.62% on fuel desulfurization (Table III). On the basis of results presented by the Taguchi software, time contributes to 64.96% sulfur removal efficiency at bigger intervals as 40 minutes, which provide a suitable interfacial contact between reagents. In short, the average performance of reaction time provides 61.2% sulfur removal efficiency (Fig. 1).

E. Temperature Effect on Removal Efficiency

Considering the DOE results, temperature which is responsible for the physical and chemical properties variation in the solution indicated a significant role contributing 81.471% for all evaluated samples, as shown Table III. Increasing temperature increases the mass transfer rate and the reaction constant while reducing the solution viscosity and the interfacial tension. In the meanwhile, temperatures above 50 °C have adverse effect on account of hydrogen peroxide decomposition as stated by the literature [3]-[15] (Figs. 1 and 3). In spite of production of water as a nonhazardous interpretive byproduct of hydrogen peroxide decomposition, it results in decrementing of interfacial surface area between two phases, as shown in (1). So, better results are obtained at 73% removal efficiency at 50 °C.



TABLE III
ANALYSIS OF VARIANCE (ANOVA) FOR SULFUR REMOVAL AND MAIN EFFECTS

Factors	DOF (f)	Sum of squares	Variance (V)	F-Ratio (F)	Pure sum (S')	Percent P (%)	(L ₂ -L ₁)
Fe ²⁺ /H ₂ O ₂ (molar ratio)	2	62.626	31.313	2.096	32.749	3.206	6.344
Temperature (°C)	2	861.903	430.951	28.848	832.026	81.471	-11.811
Time (min)	2	66.846	33.423	2.237	36.969	3.62	0.844
Other error		29.876	14.938			11.703	

F. Optimization

Taguchi DOE methodology also allows the optimization for any given set of variables defined over specific region of levels to organize the individual performance of the

parameters. The optimized levels rely on the quality characteristics defined for the factors under the analysis. By the levels recommended in Table V, the predictive system performance is estimated. In this process, the maximum

performance anticipated is 80.53% efficiency for the removal. The confirmation test is conducted for this prediction and 77.43% sulfur removal efficiency is observed. It represents a great approval for the accuracy of the experiments.

TABLE IV
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]

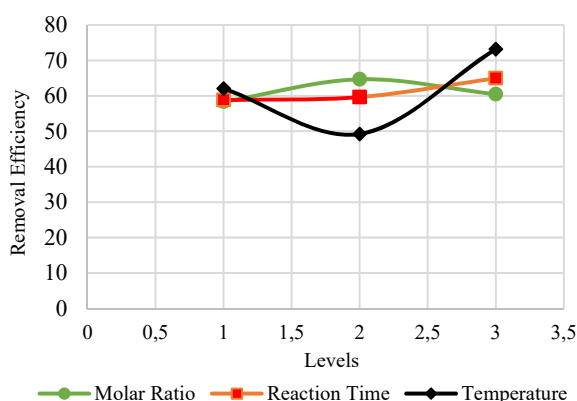


Fig. 1 Individual factors performance at different levels (QC type: Bigger is better)

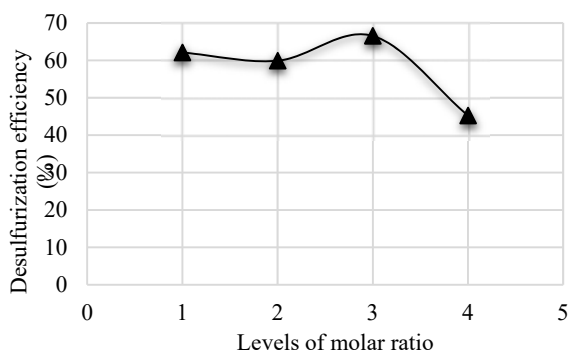


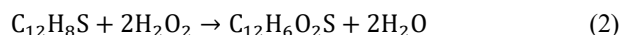
Fig. 2 Effect of Fe²⁺/H₂O₂ molar ratio on the sulfur removal (Test condition: T: 70 °C, time: 30 min)

G. Fuel Properties

Selectivity, inherently safety, and less intermediary effects are the main performance indicators for any treatment method to be analyzed. Appropriate oxidative technique should not have any negative influence on the fuel properties, namely cetane number, density, viscosity, lubricating properties, and any individual characteristics of the fuel. In Fig. 4, GC chromatogram shows the desulfurized fuel identity. This graph suggests that the Fenton technology yields no negative effect on the fuel and can be authentic for the industrial applications.

H. Study on Apparent Kinetics of the Reaction

Several researchers reported that the reaction mechanisms of oxidation of OSC in a biphasic system are similar to single phases although they are very complex [21]. Rate constant as a consequence of kinetics study is a suitable criterion for comparing different techniques and identifying the reaction progress. The oxidation proceeding evaluated at different time intervals governs the optimum conditions estimated via DOE. The oxidation reaction of DBT in the Fenton process is described in (2):



Three kinds of kinetic modeling are the most common: zero, first, and second-pseudo order. The pseudo-first order model has been widely used for the oxidative systems due to its good representation of the experimental data for most of the systems and can be written via (3):

$$\frac{d[\text{C}_{\text{DBT}}]}{dt} = k'[\text{C}_{\text{DBT}}][\text{OH}^\circ] \quad (3)$$

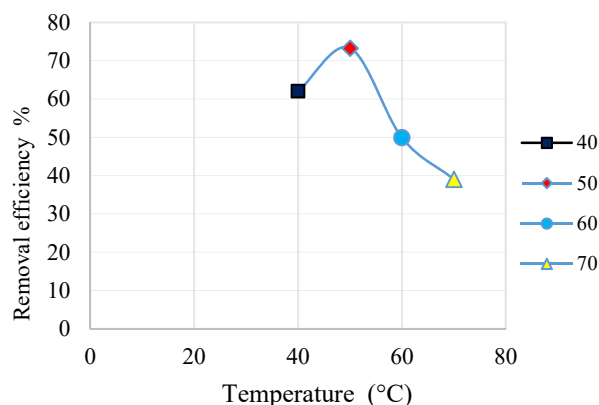


Fig. 3 Effect of temperature on the sulfur removal (test condition: molar ratio: 0.05, time: 30 min)

TABLE V
OPTIMUM CONDITION

Factor	Level description	Level	Contribution percent (P %)
Fe ²⁺ /H ₂ O ₂ (molar ratio)	0.07	2	3.526
Temperature (°C)	50	3	12.043
Time (min)	40	3	3.823

For the simplification considering that the amount of H₂O₂ is in excess, the change in concentration of H₂O₂ compared to DBT is negligible. Consequently (3) can be written as:

$$\frac{d[\text{C}_{\text{DBT}}]}{dt} = k[\text{C}_{\text{DBT}}] \quad (4)$$

As depicted in Fig. 5, the calculated reaction constant is 0.0313 min⁻¹, which is in a good agreement with the literature [8].

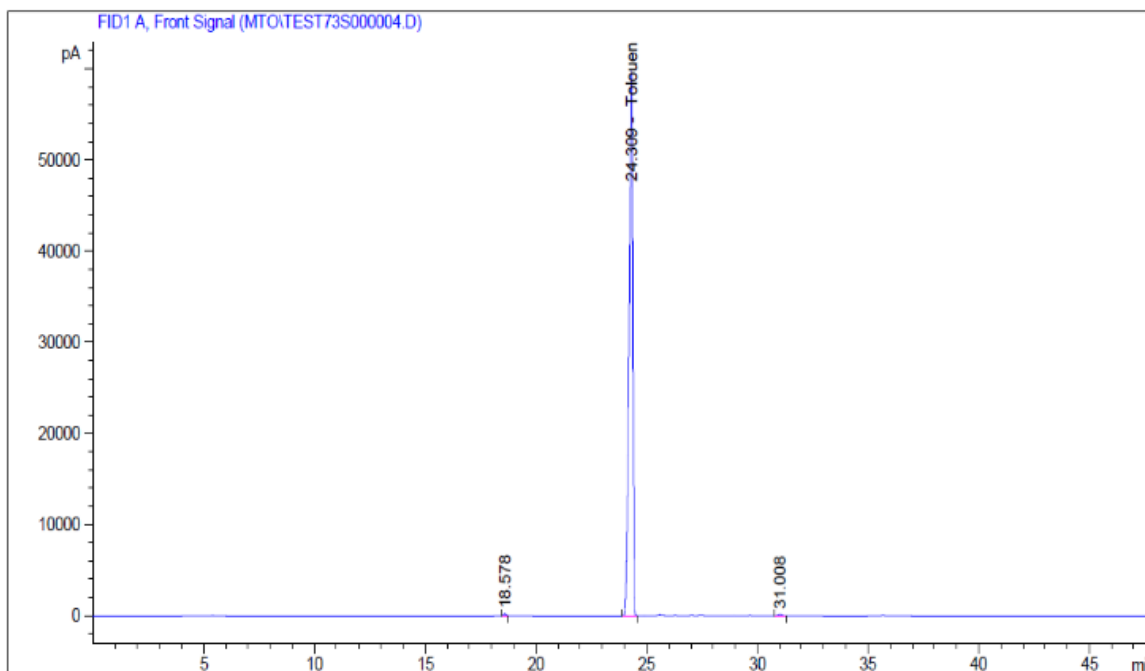


Fig. 4 Effect of Fenton process on the model fuel properties

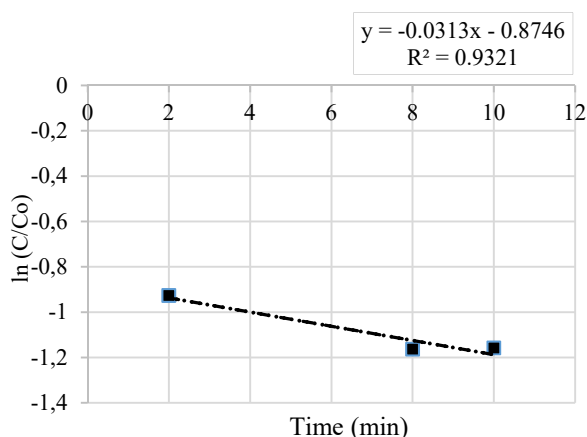


Fig. 5 The pseudo-first order mechanism ($\text{Fe}^{+2}/\text{H}_2\text{O}_2$: 0.05, T: 50°C, time: 40 min)

V. CONCLUSION

The ODS process had received much more attention for the deep desulfurization of middle distillates thanks to its mild operational conditions and high reactivity toward oxidation of most refractory sulfur compounds. In this research, the ODS of liquid hydrocarbon fuel was enhanced through the Fenton reagents. Toluene was fed with DBT as the model fuel and performance of three important parameters were investigated through the Taguchi experimental design. It was found that under the optimum conditions designed on the Fenton process, over 77% removal efficiency was attained. Good accuracy of correlative coefficient R of the reaction rate constant leads to a pseudo-first order kinetics for this system. By the Fenton technology and using $\text{Fe}^{+2}/\text{H}_2\text{O}_2=0.05$ molar ratio under oxidation period of 40 minutes, the sulfur content is reduced

from 900 ppm to 203 ppm at temperature of 50 °C. It should be mentioned that integrating of this capable economic technique with a simple chemical or physical post-treatment process can satisfy the environmental regulations. Furthermore, it can be a suitable process in combination of traditional HDS technique which is used commonly.

REFERENCES

- [1] M. K. Bolla, H. A. Choudhury, and V. S. Moholkar, "Mechanistic features of ultrasound-assisted oxidative desulfurization of liquid fuels," *Ind. Eng. Chem. Res.*, vol. 51, p. 9705–9712, May 2012.
- [2] S. S. Cheng, "Ultra clean fuels via modified UAOD process with room temperature ionic liquid (RTIL) & solid catalyst polishing," Ph.D. Thesis, University of Southern California 256p, May 2008.
- [3] A. M. Dehkordi, M. A. Sobati, and M. A. Nazem, "Oxidative desulfurization of non-hydrotreated Kerosene using Hydrogen Peroxide and Acetic Acid," *Chinese J. Chem. Eng.*, vol. 17, no. 5, pp. 869–874, August 2009.
- [4] Y. Dai, D. Zhao, and Y. Qi, "Sono-desulfurization oxidation reactivities of FCC diesel fuel in metal ion/ H_2O_2 systems," *Ultrason. Sonochem.*, vol. 18, no. 1, pp. 264–268, June 2011.
- [5] A. Deshpande, A. Bassi, and A. Prakash, "Ultrasound-assisted, base-catalyzed oxidation of 4,6-dimethyldibenzothiophene in a biphasic diesel-acetonitrile system," *Energy and Fuels*, vol. 19, no. 1, pp. 28–34, October 2005.
- [6] F. A. Duarte, P. de A. Mello, C. A. Bizzi, M. A. G. Nunes, E. M. Moreira, M. S. Alencar, H. N. Motta, V. L. Dressler, and É. M. M. Flores, "Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process," *Fuel*, vol. 90, no. 6, pp. 2158–2164, January 2011.
- [7] J. B. Bhasarkar, S. Chakma, and V. S. Moholkar, "Mechanistic features of oxidative desulfurization using sono Fenton-Peracetic Acid (Ultrasound/ $\text{Fe}^{2+}-\text{CH}_3\text{COOH}-\text{H}_2\text{O}_2$) system," *Ind. Eng. Chem. Res.*, vol. 52, pp. 9038–9047, June 2013.
- [8] Y. Dai, Y. Qi, D. Zhao, and H. Zhang, "An oxidative desulfurization method using ultrasound/Fenton's reagent for obtaining low and/or ultra-low sulfur diesel fuel," *Fuel Process. Technol.*, vol. 89, no. 10, pp. 927–932, March 2008.
- [9] H. Mei, B. W. Mei, and T. F. Yen, "A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization," *Fuel*, vol. 82, no. 4, pp. 405–414, September 2003.

- [10] P. D. a Mello, F. a. Duarte, M. a G. Nunes, M. S. Alencar, E. M. Moreira, M. Korn, V. L. Dressler, and E. M. M. Flores, "Ultrasound-assisted oxidative process for sulfur removal from petroleum product feedstock," *Ultrason. Sonochem.*, vol. 16, no. 6, pp. 732–736, March 2009.
- [11] Z. Shayegan, M. Razzaghi, A. Niazi, D. Salari, M. T. S. Tabar, and A. N. Akbari, "Sulfur removal of gas oil using ultrasound-assisted catalytic oxidative process and study of its optimum conditions," *Korean J. Chem. Eng.*, vol. 30, no. 9, pp. 1751–1759, May 2013.
- [12] M.-W. Wan, L. C. C. Biel, M.-C. Lu, R. de Leon, and S. Arco, "Ultrasound-assisted oxidative desulfurization (UAOD) using phosphotungstic acid: effect of process parameters on sulfur removal," *Desalin. Water Treat.*, vol. 47, no. 1–3, pp. 96–104, March 2012.
- [13] M. A. Sobati, A. M. Dehkordi, and M. Shahrokhi, "Extraction of oxidized sulfur-containing compounds of non-hydrotreated gas oil," *Chem. Eng. Technol.*, vol. 33, no. 9, pp. 1515–1524, May 2010.
- [14] M. a. Kelkar, P. R. Gogate, and A. B. Pandit, "Process intensification using cavitation: Optimization of oxidation conditions for synthesis of sulfone," *Ultrason. Sonochem.*, vol. 13, no. 6, pp. 523–528, October 2006.
- [15] Z. Wu and B. Ondruschka, "Ultrasound-assisted oxidative desulfurization of liquid fuels and its industrial application," *Ultrason. Sonochem.*, vol. 17, no. 6, pp. 1027–1032, November 2010.
- [16] I. Saraiva, J. P. Vilar, F. C. V. Silva, and R. A. R. Boaventura, "Biodegradability enhancement of a leachate after biological lagooning using a solar driven Photo-Fenton reaction, and further combination with an activated sludge biological process, at pre-industrial scale," vol. 7, April 2013.
- [17] S. Sanchis, A. M. Polo, M. Tobajas, J. J. Rodriguez, and A. F. Mohedano, "Coupling Fenton and biological oxidation for the removal of nitrochlorinated herbicides from water," *Water Res.*, vol. 49, pp. 197–206, November 2013.
- [18] R. Omrani Manesh, "Investigation of physico-chemical treatment of Shiraz landfill leachate," MSc. thesis, Civil Environmental Engineering University, Shiraz, 134p, June 2008.
- [19] A. B. Engin, O. Ozdemir, M. Turan, and A. Z. Turan, "Color removal from textile dyebath effluents in a zeolite fixed bed reactor: determination of optimum process conditions using Taguchi method," *J. Hazard. Mater.*, vol. 159, no. 2–3, pp. 348–53, February 2008.
- [20] S. V. Mohan, B. P. Reddy, and P. N. Sarma, "Bioresource technology Ex situ slurry phase bioremediation of chrysene contaminated soil with the function of metabolic function: Process evaluation by data enveloping analysis (DEA) and Taguchi design of experimental methodology (DOE)," *Bioresource Technology*, vol. 100, pp. 164–172, June 2009.
- [21] M.-C. Lu, L. C. C. Biel, M.-W. Wan, R. de Leon, and S. Arco, "The Oxidative Desulfurization of Fuels with a Transition Metal Catalyst: A Comparative Assessment of Different Mixing Techniques," *Int. J. Green Energy*, vol. 11, no. 8, pp. 833–848, September 2014.