Ultrasound-Assisted Oxidative Desulfurization of Diesel

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ABSTRACT

Due to the dramatic environmental impact of sulfur emissions associated with the exhaust of diesel engines, last environmental regulations for ultra-low-sulfur diesel require a very deep desulfurization (up to 15 ppm), which cannot be met by the conventional hydrodesulfurization units alone. The proposed method involves a batch ultrasound-assisted oxidative desulfurization (UAODS) of a previously hydrotreated diesel (containing 480 ppm sulfur) so as to convert the residual sulfur-bearing compounds into their corresponding highly polar oxides, which can be eliminated easily by extraction with a certain highly polar solvent. The oxidizing system utilized was H_2O_2 as an oxidant, CH_3COOH as a promoter, with $FeSO_4$ as a catalyst; whereas acetonitrile was used as extractant. The major influential parameters related to UAODS process have been investigated, namely: ratio of oxidant/fuel, ratio of the promoter/oxidant, dose of catalyst, reaction temperature, and intensity of ultrasonic waves. Kinetics of the reaction has been also studied; it was observed that the UAODS of diesel fuels fitted pseudo-first-order kinetics under the best experimental conditions, whereas values of the apparent rate constant and activation energy were 0.373 min^{-1} and 24 KJ/mol, respectively. The oxidation treatment, in combination with ultrasonic irradiation, revealed a synergistic effect for diesel desulfurization. The experimental results showed that sulfur removal efficiency could amount to 98% at mild operating conditions (70 $^{\circ}$C and 1 bar). This indicates that the process is efficient and promising for the production of ultra-low-sulfur diesel fuels.

KEYWORDS: Ultra-low-sulfur diesel, Oxidative desulfurization, Ultrasound.

إزالة الكبريت من الديزل بإستخدام الأكسدة المعززة بالموجات الفوق الصوتية

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الخلاصة

نظرا لما تحويه المركبات الكبريتية المصاحبة للغاز العادم المنبعث من محركات الديزل من مخاطر كبيرة على الصحة والبيئة، يتجه العالم الى اصدار تشريعات صارمة لتحديد المحتوى الكبريتي في وقود الديزل بنسب قليلة جداً (تصل لحد 15 جزء من المليون) لا يمكن تحقيقها خلال وحدات الهدرجة التقليدية المتواجدة في المصافي. يتضمن البحث استخدام طريقة "الاكسدة المعززة بالموجات الفوق الصوتية" لدفعات من وقود الديزل المهدرج (يحوي على 450 جزء من المليون من الكبريت) وذلك لتحويل المركبات الكبريتية المتبقية الى نظائرها من الاكاسيد القطبية التي يمكن ازالتها بسهولة بواسطة مذيب قطبي معين. وقد شمل نظام الاكسدة مزيج من [بيروكسيد الهايدروجين/حامض الخليك/كبريتات الحديد]، بالاضافة الى الاسيتونتريل الذي تم توظيفه كمذيب قطبي. خلال البحث، تم دراسة المتغيرات المؤثرة على العملية ، والتي تشمل : نسبة بيروكسيد الهايدوجين الى الوقود، نسبة

حامض الخليك الى بيروكسيد الهايدروجين وكمية العامل المساعد و حرارة التفاعل وشدة الموجات الصوتية. ايضا تم دراسة حركية التفاعل تحت تاثير الموجات فوق الصوتية، ولوحظ انها تتبع تفاعلات "شبه المرتبة الاولى" تحت الظروف المثلى، وتم تحديد ثابت سرعة التفاعل وطاقة التنشيط الظاهرية للعملية تحت هذه الظروف. اثبتت عملية الاكسدة المعززة بالموجات فوق الصوتية جدارتها في ازالة المركبات الكبريتية في وقود الديزل، حيث اظهرت النتائج ان كفاءة العملية في ازالة الكبريت أمكنها الوصول الى 98% وتحت ظروف تشغيلية معتدلة (1 جو و 70 م°) . وبهذا يمكن اعتبار الطريقة مثمرة و واعدة في انتاج "وقود الديزل ذو المحتوى الكبريتي الفائق القلة".

الكلمات الرئيسية: ديزل ذو محتوى كبريتي فائق القلة، إزالة الكبيريت بالاكسدة، الموجات الفوق الصوتية.

1. INTRODUCTION

One of the major tasks of the current petroleum industry is the production of diesel fuel with ultra-low-sulfur content. Limits of sulfur content in diesel fuel are typically less than 50 parts per million (ppm) in most of the world’s developed countries, and often less than 15 ppm, while other countries across the globe are gradually transitioning towards these limits**, UN environment programme, 2014.**

Limitations for sulfur come from the fact that combustion of sulfur-bearing compounds in exhaust gas of diesel’s engines can lead for series of air pollution events, including formation of sulfur oxides (SO_X) and sulfate particulate matter (PM). Sulfur oxides can lead for the formation of sulfate aerosols which could be transported into the lungs causing serious health consequences. Furthermore, SO_X emissions can react with the surrounding moisture in the atmosphere forming sulfuric acid that lead to acidic rain fall which, in turn, increase pH of the soil preventing further growth, and can cause serious damage to the plants and crops, **Jonathan et al., 1979.** As for sulfate particulate matter (PM), it has been regarded as a serious carcinogenic material since it can be easily inhaled into the bronchioles of the lungs causing lung cancer and other respiration problems, **Norman et al, 2012**. Moreover, sulfur compounds can damage some types of catalysts, especially the noble metals used in the reforming units, even at small traces; they can also poison the catalyst in vehicles’ exhaust converts that are used to convert NO_X, CO and uncombusted hydrocarbons in the exhaust gas due to the high thermostability of sulfate that can permanently occupy the vacant sites of the catalyst causing reduction in the space available for the desired materials, **Dai et al., 2009**.

Existence of sulfur in diesel fuel is mainly being in the organic form. These organo-sulfur compounds are generally categorized into two groups: Refractory and Non refractory. Non refractory sulfur involves thiols (mercaptans), sulfides, and disulfides; while refractory sulfur involves thiophenes and their alkyl derivatives, such as benzothiophenes and dibenzothiophenes, **Frank et al., 2003**. The conventional hydrodesulfurization process (HDS) implemented by petroleum refineries can efficiently remove the non-refractory sulfur compounds, while negligible removal of the so-called refractory sulfur is being achieved, hence, this process experiences serious difficulties in the production of ultra-low-sulfur diesel (less than 15 ppm), and is only practical for production of diesel having total sulfur content of about 500 ppm, **Song et al., 2006**.

Since conventional HDS process fails to eliminate sulfur beyond 500 ppm, several complementary techniques have been introduced as possible methods for the production of ultra-low -sulfur diesel including: Extractive desulfurization (EDS), Adsorptive desulfurization (ADS), Oxidative desulfurization (ODS), and Biodesulfurization (BDS). Each technique has its own advantages/disadvantages over the other, and the ongoing studies are still attempting to promote them so as to find their ways in the refineries, **Music and Sertic, 2013**.

Oxidative desulfurization (ODS) is one of the promising techniques that can meet the global requirements of sulfur. In this process, the sulfur-containing compounds are initially oxidized to the respective sulfones and are later removed by extraction or adsorption using a suitable polar agent. However, despite of the advantages associated with ODS such as moderate operating conditions and higher selectivity for the refractory sulfur compounds ,ODS process faces several challenges to be competitive and ,therefore, several advances have been introduced to improve the efficiency of the process.

Oxidation process could be promoted using suitable organic acids, and better results could be achieved when using certain catalysts. **Die et al., 2008** and **Jiang et al., 2011**, show that using a combination of H_2O_2 and acetic acid is more powerful than using H_2O_2 alone. They also showed that the addition of fenton reagents (such as $FeSO_4$) has a good synergetic effect on the desulfurization efficiency of diesel fuel.

Jalil and Hasan, 2012, reported that sulfur content of gasoil can be significantly reduced from 0.954% to 0.310% when using activated carbon with ODS. **Niran and Saja, 2015**, also investigated the effect of activated carbon but on heavy gasoil and sulfur content was decreased from 3.9% to 2.7%.

Ehsan et al., 2014, tried to improve ODS of low density hydrocarbons (such as natural gas condensates) using microwave irradiation, they reported that sulfur content was severely reduced from 0.85% to 0.03% during process.

Najafi et al., 2011, tested the effect of sonic irradiation on ODS, they showed that sulfur removal efficiency of the process can be increased by 20% when assisted by ultrasonic waves.

The current study proposes to evaluate the effect of ultrasonic irradiation for enhancing the oxidation of a previously hydrotreated diesel using [H_2O_2 - CH_3COOH - $FeSO_4$] oxidative system. Ultrasound was employed to overcome the hindered mixing challenge between the organic layer (diesel) and the inorganic layer (oxidative system) so as by enhancing total mass transfer of the process, as **Suslick et al., 2008,** referred.

2. EXPERIMENTAL

2.1 Materials and Apparatus

Light hydrotreated (480 ppm) commercial diesel fuel supplied by Al-Quds power station was used as a feedstock. The following chemicals were also utilized in this study: 50 wt% H_2O_2 (GmbH Chem.), CH_3COOH (GCC Chem.), $FeSO_4.7H_2O$ (EDUTEK Chem.), and Acetonitrile (BiSolve Chem.). All chemicals reported were commercial Lab. grade, purchased from local markets, used as received without any pretreatment or purification, unless otherwise indicated.

Oxidation of sulfur compounds was conducted using an ultrasonic processor manufactured by Sonics and Materials, Inc. (Model VCX-750, 20 kHz and 750W of nominal power, USA) provided with a built-in convertor (Model CV33, 220V operational input voltage @ 50/60 Hz); for all experiments, an ultrasonic probe (½ in., full wave titanium probe solid, 254 mm long) was dipped directly into the oil/oxidation system mixture. While extraction of the oxidized sulfur compounds was performed using a high-shear rotor-stator type mixer manufactured by Heidolph Instruments, Inc., Stuttgart, Germany (Model SilentCrusher M), equipped with an external generator (type 6F).Total sulfur content of the treated diesels was analyzed by RX-620SA sulfur meter made by Tanaka Scientific Limited, Japan; the RX-620SA determines the total sulfur amount in petroleum products using an energy dispersive X-ray fluorescence (EDXRF) method, which is an accurate, non-destructive, and quick method prescribed in ISO 8754 and ASTM D4294-03.

2.2 Procedure

Parameters: This study involves the investigation of the influential parameters on ODS process including: concentration of the oxidant, ratio of the promoter, dose of catalyst, reaction temperature, and intensity of ultrasonic waves, in addition for the process kinetics. These parameters were carried out under the following ranges: O/S mol ratio = (2 – 10); CH_3COOH/H_2O_2 vol. ratio = (0.25 – 1); $FeSO_4/H_2O_2$ wt. ratio = (0.1- 0.4); Temp. $^{\circ}C$ = (30 – 90); Ultrasonic amplitude % = (30 – 60).

Oxidation Experiments: In each oxidation run, 15 mL of 480 ppm sulfur content feedstock was introduced into a 100 mL standard Griffin beaker. Oxidation system is previously prepared by mixing acetic acid with ferrous sulfate powder, and then hydrogen peroxide is gradually added with continuous shaking. The oxidation system is then mixed with the feedstock in the beaker which is pre-equipped with a temperature probe attached to the ultrasonic processor, as shown in **Fig.1**, so as to control reaction temperature. Subsequently, the ultrasonic probe was dipped in the reaction mixture, and the reaction proceeded under ultrasonic irradiations for a preset period of time. Afterward, ultrasonication is stopped, and the aqueous and hydrocarbon phases were decanted in a separation funnel.

Extraction Experiments: In each extraction experiment, 10 mL of the previously oxidized diesel fuel was charged to a 100 mL standard Griffin beaker with an appropriate amount of acetonitrile, which is 1:1 solvent/diesel (v/v). This mixture is then placed under vigorous stirring for 10 min using high-shear rotor type mixer. The extraction blend is then allowed to separate into two distinct phases (aqueous and hydrocarbon phases) in a separation funnel.

Sulfur Content Analysis: The treated diesel is then taken for analysis of total sulfur content using RX-620SA sulfur meter which is a 12-sample carousel model. Once a sample is set, the total sulfur is determined automatically in 300 seconds (typical).

Kinetics: In order to explore the kinetics of the ultrasonic-assisted oxidative reaction of sulfur, a set of experiments under various periods of time (at the best process conditions) was carried out. A pseudo-first order reaction (with respect to overall sulfur content) was pre-assumed to fit the reaction kinetics; two reactants are mainly involved which is the oxidant and organo-sulfur, since acetic acid (which acts as a promoter) and iron salts (which act as a catalyst) are not involved in the overall reaction. Moreover, the amount of H_2O_2 was taken in excess and concentration of oxidant, as compared to sulfur, remains essentially constant throughout the reaction; hence, the rate equation could be formulated as in Eq. (1). The validity of first order assumption was then confirmed by plotting the logarithmic value of sulfur concentration against time and see how far was correlation coefficient (R^2) from unity. Once pseudo-first order assumption is confirmed, the rate constant (k) can be obtained from the slop of linearization plot, and activation energy can be calculated by plotting Arrhenius correlation using an additional set of experiments at same operating conditions but at different temperature.

$$\frac{d[S]}{dt} = -k\,[S] \tag{1}$$

3. RESULTS AND DISSCUSION

3.1 Ratio of oxidant / diesel (O/S ratio)

In order to investigate the effect of H_2O_2 dosage on ODS process, oxidation of sulfur compounds was carried out under various O/S molar ratios, at a temperature of 70 ºC and 10 minutes of sonication operating at 40% amplitude; as shown in **Fig.2**, sulfur removal efficiency was improved when increasing O/S ratio. Diesel oil is a complex mixture of hydrocarbons, including organic compounds of sulfur, oxygen, and nitrogen, which could have a tendency for competitive oxidation in the presence of the oxidant, **Shiraishi et al., 2002**. Hence, an excess H_2O_2 is required to ensure a full oxidization of the sulfur. It is worthy to note that further increase in O/S ratio, beyond 6:1, will only slightly improve the ODS efficiency. So, the value of O/S=6 was chosen as the best ratio, at which sulfur removal efficiency was about 67%.

3.2 Ratio of promoter/oxidant (CH_3COOH / H_2O_2 ratio)

Oxidation of sulfur compounds was carried out under various CH_3COOH/H_2O_2 vol. ratios at the best operating conditions obtained from utilizing H_2O_2 alone (t=10 min; Amp=40%; T=70 ºC; and O/S=6). As shown in **Fig.3**, sulfur removal efficiency was increased when increasing CH_3COOH/H_2O_2 ratio, reaching 85% when the ratio was 0.5. The reaction of acetic acid with H_2O_2 yields peracetic acid, a form of peroxycarboxylic acids, which can be decomposed to form hydroperoxyl radicals ($^{\bullet}OOH$) that are more efficient than hydroxyl radicals ($^{\bullet}OH$) produced from the decomposition of H_2O_2, **Lv et al., 2001**. However, when CH_3COOH/H_2O_2 ratio was beyond 0.5, sulfur removal efficiency is reversely affected and this could be attributed to the instability of peracetic acid when exceeding certain concentration, hence, counteracting the decomposition of the peroxycarboxylic acid and lowering the sulfur removal efficiency, **Dai et al., 2008**.

3.3 Effect of catalyst dose

To understand the role of ferrous sulfate ($FeSO_4$) in enhancing the sulfur removal efficiency, oxidation of sulfur compounds was carried out under various mass ratios of $FeSO_4/H_2O_2$ at the best conditions (t=10 min; Amp=40%; T=70 ºC; O/S=6; and CH_3COOH/H_2O_2=0.5). As shown in **Fig.4**, sulfur removal efficiency was significantly improved when increasing $FeSO_4/H_2O_2$ ratio to 0.2, reaching a value of 97.5%. Iron has a strong catalytic power to generate highly reactive hydroxyl radicals in a rapid redox reaction; iron (II) is oxidized by hydrogen peroxide to iron (III), forming a hydroxyl radical $^{\bullet}OH$. Iron (III) is then reduced back to iron (II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical •OOH. The net effect is a disproportionation of hydrogen peroxide to create two different oxygen-radical species in which they engaged in secondary oxidation reactions, **Jaykumar et al., 2013**. It should be noticed that any increment in the ratio of ferrous sulfate beyond 0.2 leads for a dramatic decrease in the sulfur removal efficiency. This could be attributed to the deviation of redox potential from its optimal range, which lies between (0.682 ~ 1.77) Volt, preferably 0.77 Volt, for (Fe^{+2}/Fe^{+3}) reaction, **Edwards and Ruggero, 1992**. Hence, the best dose of $FeSO_4/H_2O_2$ in this experiment is 0.2.

3.4 Effect of temperature

To investigate the influence of temperature on the oxidation of sulfur compounds in diesel fuel, several experiments were carried out under various temperatures ranging from 40 ºC to 90 ºC (the upper limit was determined by the boiling point of the more volatile component in the mixture) at the following conditions: [t=10 min; Amp= 40%; O/S=6; CH_3COOH/H_2O_2=0.5; $FeSO_4/H_2O_2$

=0.2]. **Fig.5** shows that sulfur removal efficiency reaching its highest value when temperature became 70 ºC giving a maximum sulfur removal efficiency of 98%, corresponding for sulfur content of 12 ppm. Any elevation in temperature accelerates reaction rate, lowers the reaction activation energy, and promotes the formation of peroxycarboxylic acid, **Joskić et al., 2014**, which, in turn, generates highly reactive radicals ($^{\bullet}OH$) that motivates oxidation and increases the sulfur removal rate. However, when the temperature exceeded 70ºC, sulfur removal efficiency decreased; because of the thermodynamics instability of H_2O_2 at higher temperature, it will undergoe a decomposition reaction to produce H_2O and O_2 molecules rather than $^{\bullet}OH$ radical which inversely affect oxidation step, **Manatt and Margaret, 2004**. In addition for that, high temperature causes mal functioning of ultrasonication due to the decrease in mixture viscosity, **Gronroos et al., 2008**.

3.5 Effect of ultrasonication intensity

Since wave amplitude is considered as a function of ultrasound intensity, oxidation reaction was tested at different amplitudes (30, 40, 50, and 60%) at t=10 min; temp= 70º C; O/S=6; CH_3COOH/H_2O_2=0.5; and $FeSO_4/H_2O_2$ = 0.2. **Fig.6** shows that sulfur removal efficiency was slightly improved from 95% to 98% when increasing the amplitude value from 30% to 40%. Any increment in the ultrasonic intensity boost cavitation, produce more free radical, activate the state oxygen atoms, strengthen the oxidative capability, and subsequently improve the efficiency of the sulfur removal, **Mello et al., 2009**. However, it was observed that a slight decrease in desulfurization efficiency occurred when using amplitudes higher than 40%. Since ultrasonic intensity is a measure of particle displacement, excessive intensity could hinder the vibration of bubbles in the acoustic period which consequently inhibit the cavitational effect, **Najafi et al., 2011**.

3.6 Kinetics

In order to get the rate constant for the process, a pseudo-first order reaction model was assumed to fit the reaction kinetics, then a set of experiments for sulfur content determination was done at different periods of time, as shown in **Fig.7**, under best operating conditions (temp= 70º C; O/S=6; CH_3COOH/H_2O_2=0.5; and $FeSO_4/H_2O_2$ =0.2), which is subsequently linearized, as in **Fig.8**, by taking the logarithmic values of sulfur content axis and re-plotting against time. The value of correlation coefficient (R^2) for the linearization plot was 0.98 which strongly supports the assumption of first order kinetics. The rate constant (k) was then calculated from the slop of **Fig.8** with a value of 0.373 min^{-1} , which is higher than its value with the conventional ODS (without ultrasonication), as reported in previous literature, **Dai et al., 2009**. The same procedure was repeated at 40 ºC and the rate constant was obtained with a value of 0.230 min^{-1}; there with k value at 70 ºC, Arrhenius relation was plotted as in **Fig.9**. The activation energy was then obtained from the slop of Arrhenius plot with a value of 24 kJ/mol at 70 ºC. **Wan et al., 2012** pointed that the activation energy for DBT oxidation without ultrasound was 45 kJ/mol, hence, activation energy for the reaction was obviously decreased with the utilization of ultrasound which is definitely enhanced the process, made reaction faster and with milder conditions.

3.7 Effect of UAODS on the properties of diesel

As shown in **Table 1**, the UAODS process has not altered the properties and characteristic of diesel significantly. The density and the API gravity almost remained unchanged before and after treatment; the small variation could be attributed to the separation of some aromatic hydrocarbons during the extraction stage. Density fixation could be also a good indication that there is no increase in water content during treatment. There was no negative effect on the characterization of distillation curve, and distillation points were almost the same. Regarding Cetane number, a little improvement was occurred, which could be due the removal of cyclic sulfur compounds. However, a reduction in viscosity was occurred which could be attributed to the fact that some of the long-chain molecules have been subjected to cracking during the exposure for the ultrasound waves, **Madras and Vijayalakshmi, 2005**. PNA content (an indication of soot formation) was decreased from 3.37% to 1.35% which reduces the impact on the environment.

CONCLUSIONS

Based on the present experimental work and the results obtained from utilization of UAODS technique for treating a previously hydrotreated diesel fuel, the following points can be concluded: UAODS is a promising technique for producing ultra-low-sulfur diesel (<15 ppm), since 98% of the initial sulfur can be removed, corresponding to12 ppm sulfur content, when using the best operating conditions. The best operating conditions for the process are: (time=10 min; Amp=40%; temp=70ºC; O/S=6; CH_3COOH/H_2O_2=0.5; $FeSO_4/H_2O_2$=0.2). The UAODS of previously hydrotreated diesel fuels fitted a pseudo-first-order kinetics under the best experimental conditions, and values of the apparent rate constant and activation energy were 0.373 min^{-1} and 24 kJ/mol, respectively. There was no significant change in the main properties of diesel during UAODS treatment; however, a small improvement in Cetane No. (About 1.1%) was noticed. The researchers believe that the results of this study should provide important inputs for further research in UAODS field.

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NOMENCLATURE

ADS = adsorptive desulfurization.
Amp = amplitude, %.
BDS = biodesulfurization.
C = residual sulfur concentration, ppm.
C_o = initial sulfur concentration, ppm.
EDT = extractive desulfurization
HDS = hydrodesulfurization.
k = first order rate constant, min^{-1}.
ODS = oxidative desulfurization.
O/S = oxidant to sulfur molar ratio.
PM = particulate matter.
PNA = poly nuclear atomic.
R^2 = correlation coefficient.
SR% = sulfur removal efficiency
SO_X = sulfur oxides.

T = temperature.
t = time.
UAODS = ultrasound-assisted ODS

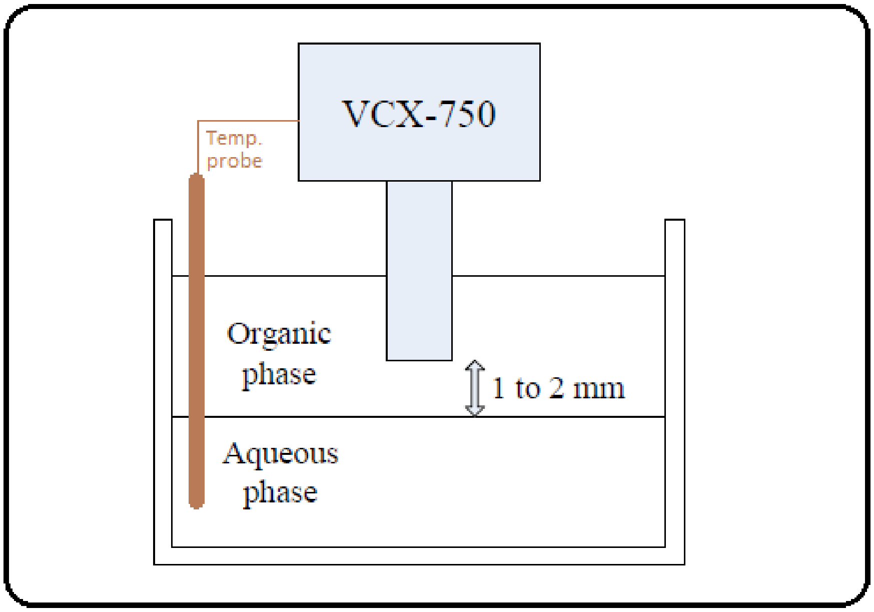

Figure 1. Schematic diagram of UAODS setup.

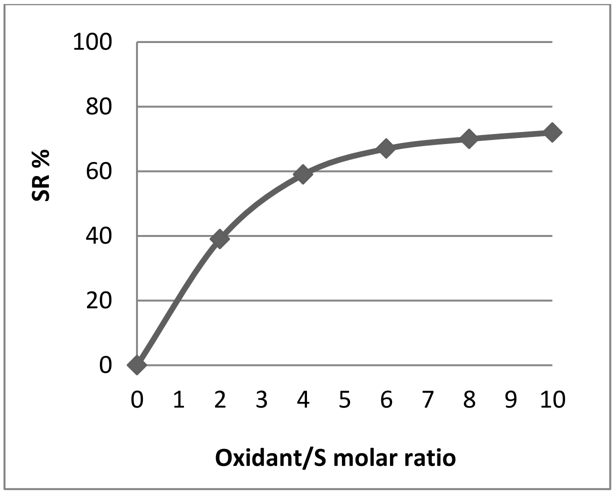

Figure 2. Effect of O/S ratio on sulfur removal efficiency (t=10 min; Amp=40%; T=70 ºC).

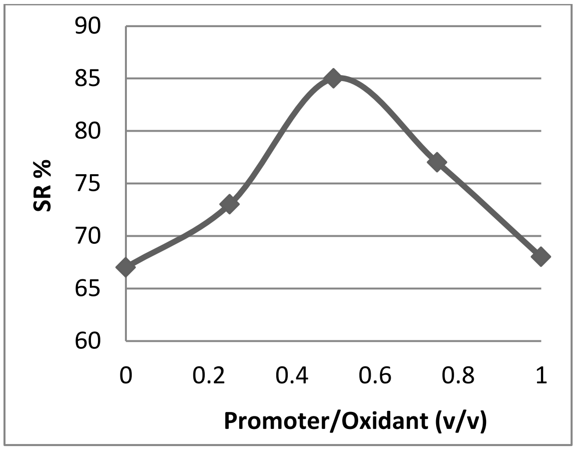

Figure 3. Effect of promoter/oxidant ratio on sulfur removal efficiency (t=10 min; Amp=40%; T=70 ºC; O/S=6).

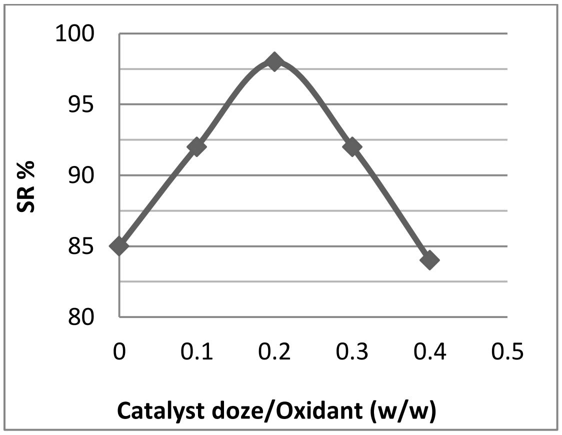

Figure 4. Effect of catalyst dose on sulfur removal efficiency (t=10 min; Amp=40%; T=70 ºC; O/S=6; $CH_3COOH/H_2O_2=0.5$).

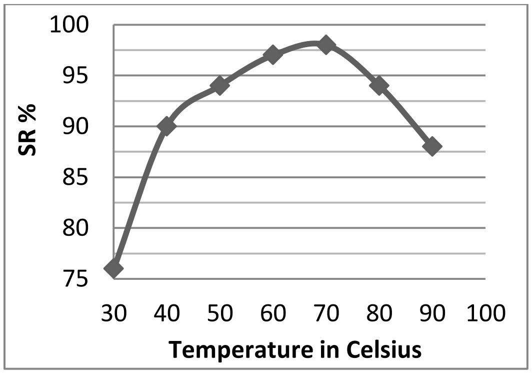

Figure 5. Effect of temperature o sulfur removal efficiency (10 min; 40% Amp; O/S=6; $CH_3COOH/H_2O_2=0.5$; $FeSO_4/H_2O_2=0.2$).

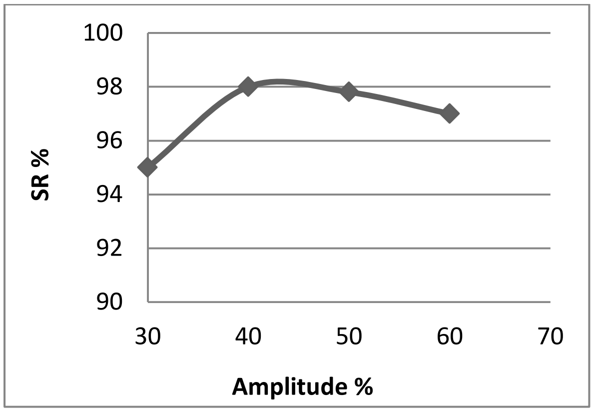

Figure 6. Effect of wave amplitude on sulfur removal efficiency
(10 min; Temp=70ºC; O/S=6; CH_3COOH/H_2O_2=0.5; $FeSO_4/H_2O_2$=0.2).

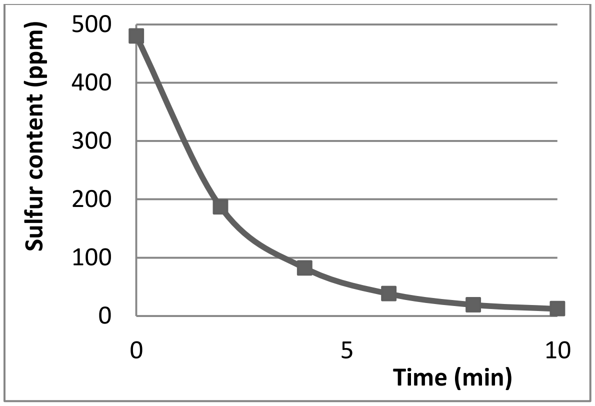

Figure 7. Sulfur content VS Time.

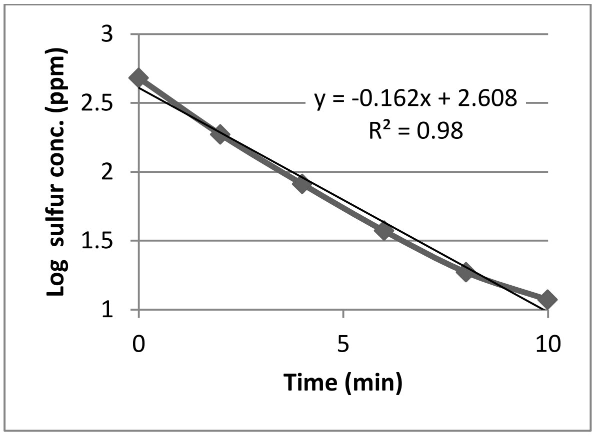

Figure 8. Linearization of first order model.

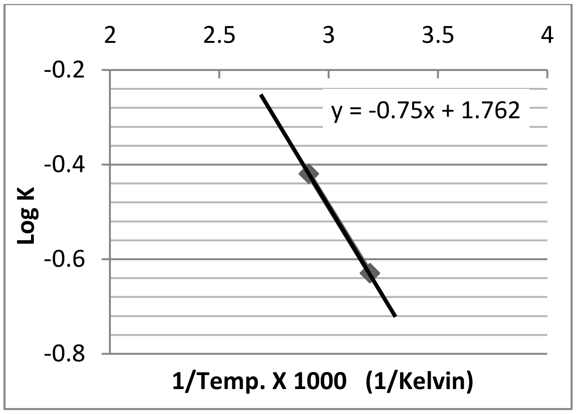

Figure 9. Arrhenius plot.

Table 1. Properties of diesel before and after treatment

Property	Value before treatment	Value after treatment	Unit
Density@ 20 °C	831.78	828	kg/m^3
°API GR. @ 20/20 °C	38.4	39.2	---
Kinematic viscosity @20 °C	5.5	5	CST
Sulfur content	480	12	ppm
Cetane No.	43.9	45	---
PNA	3.37	1.53	wt%
Distillation points:			
IBP	177	169	°C
T10	217	213	°C
T90	351	352	°C
FBP	363	363	°C