# Desulfurization of Diesel Fuel by Oxidation and Solvent Extraction

**Dr. Wadood Taher Mohammed**
Assistant Professor
Department of Chemical Engineering
College of Engineering – University of Baghdad
Email: dr.wadood@yahoo.com

**Dr.Raghad Fareed Kassim Almilly**
Lecturer
Department of Chemical Engineering
College of Engineering – University of Baghdad
Email: rfkalm@yahoo.com

**Sheam Bahjat Abdulkareem Al-Ali**
Department of Chemical Engineering
College of Engineering – University of Baghdad
Email: sheam1982@yahoo.com

## ABSTRACT

This research presents a study in ultra-desulfurization of diesel fuel produced from conventional hydro desulfurization process, using oxidation and solvent extraction techniques. Dibenzothiophene (DBT) was the organosulfur compound that had been detected in sulfur removal. The oxidation process used hydrogen peroxide as an oxidant and acetic acid as homogeneous catalyst . The solvent extraction process used acetonitrile (ACN) and N-methyl – 2 - pyrrolidone (NMP) as extractants . Also the effect of five parameters (stirring speed :150 , 250 , 350 , and 450) rpm, temperature (30 , 40 , 45 , and 50) $^{o}$C, oxidant/simulated diesel fuel ratio (0.5 , 0.75 , 1 , and 1.5) , catalyst/oxidant ratio(0.125,0.25,0.5,and0.75) , and solvent/simulated diesel fuel ratio(0.5,0.6,0.75,and1) were examined as well as solvent type. The results exhibit that the highest removal of sulfur is 98.5% using NMP solvent while it is 95.8% for ACN solvent. The set of conditions that show the highest sulfur removal is: stirring speed of 350 rpm , temperature 50$^{o}$C , oxidant/simulated diesel fuel ratio 1 , catalyst/oxidant ratio 0.5 , solvent/simulated diesel fuel ratio 1. These best conditions were applied upon real diesel fuel (produced from Al-Dora refinery)with 1000 ppm sulfur content . It was found that sulfur removal was 64.4% using ACN solvent and 75% using NMP solvent.

**Key words**: ultra-desulfurization ,oxidation and extraction, simulated diesel fuel ,real diesel fuel.

# ازالة الكبريت لوقود الديزل بواسطة الاكسدة و الاستخلاص بالمذيب

**د. ودود طاهر محمد**
أستاذ مساعد
قسم الهندسة الكيمياوية
كلية الهندسة – جامعة بغداد

**د رغد فريد قاسم الملي**
مدرس
قسم الهندسة الكيمياوية
كلية الهندسة – جامعة بغداد

**شيم بهجت عبد الكريم العلي**
قسم الهندسة الكيمياوية
كلية الهندسة – جامعة بغداد

## الخلاصة

يقدم هذا البحث دراسة في الازالة فوق العادية للكبريت لوقود الديزل الناتج من عملية الازالة الهيدروجينية التقليدية للكبريت باستخدام تقنيات الاكسدة والاستخلاص بالمذيب .تم تتبع المركب العضوي الكبريتي البنزوثايوفين الثنائي في أزالة الكبريت . أجريت عملية الاكسدة باستخدام بيروكسيد الهيدروجين كعامل مؤكسد وحامض الخليك كعامل مساعد متجانس. تمت عملية الاستخلاص بالمذيب باستخدام الاسيتونايترايل و ن-مثيل-2-بايروليدون كعامل مستخلص . أيضا تم بحث تأثير خمسة عوامل

وهي :- سرعة الخلط (150,250,350, و 450) دورة\دقيقة ؛ درجة الحرارة (30,40,45,و50)$^{o}$م ؛نسبة العامل المؤكسد/مشبه وقود الديزل (0،5 , 0،75 , 1،1,5) ؛نسبة العامل المساعد/ العامل المؤكسد ( 0،125 ,0،25, 0،5, 0،75) ونسبة المذيب/مشبه وقود الديزل(0،5,0،6,0،75,و1) كما تم بحث نوع المذيب. أظهرت النتائج ان أعلى نسبة ازالة للكبريت هي 98،5% باستخدام مذيب ن- مثيل-2-بايروليدون بينما كانت 95،8% باستخدام مذيب الاسيتونابترايل . ان مجموعة الظروف التي أظهرت أعلى أزالة للكبريت هي: سرعة الخلط 350 دورة / دقيقة, درجة الحرارة 50 $^{o}$م ,نسبة العامل المؤكسد/مشبه وقود الديزل 1,نسبة العامل المساعد/العامل المؤكسد 0,5 ,نسبة المذيب/مشبه وقود الديزل 1. طبقت افضل الظروف على وقود الديزل الحقيقي(المنتج في مصفى الدورة) والحاوي على محتوى كبريتي 1000 جزء بالمليون . وجد ان نسبة ازالة الكبريت كانت 64،4% باستخدام مذيب الاسيتونايترايل و 75% باستخدام مذيب ن-مثيل-2-بايروليدون .

**الكلمات الرئيسية:** الازالة فوق العادية للكبريت, الاكسدة والاستخلاص , مشبه وقود الديزل, وقود الديزل الحقيقي .

## 1. INTRODUCTION

The problem of fuel desulfurization has been attracted the researchers' interesting since the early time of oil refinery . This was because sulfur compounds have the most damaging effects on the equipment using fuel containing such compounds. The phenomenon of acid rain was first studied by Likens etal.,**Likens,et al.,1972**. Over the last decade many limitations were cited to reduce sulfur emissions from transportation means,**European Directive,2002**. Since then the main task of the refineries was to produce large yields of valuable products of the least sulfur content. This was achieved by hydro desulfurization (HDS) process , **Mochida,and Choi,2004** . Because sulfur–containing compounds have different reactivities and chemistries , HDS was of limited results in reducing sulfur content . Under this context , many researchers have developed alternative methods to meet the challenging requirements . This was done through many techniques such as: Desulfurization by adsorption , **Xiaoliang Ma, et al., 2003** , and **Al Zubaidy, et al. , 2013** ; Desulfurization by precipitation **, Milenkovic, et al., 1999** , and **Shiraishi, et al. , 2002**; Desulfurization via extraction **, Ali, et al., 2009** , and **Fa-tang , et al. , 2012** ; Desulfurization by alkylation , **Song, et al., 2002** , and **Arias, et al. , 2008** ; Desulfurization by selective oxidation (ODS) , **Campos-Martin, et al., 2010** , and **Ismagilov, et al., 2011** .

This research presents a study of deep desulfurization of diesel fuel by oxidation and solvent extraction technique. A detailed parametric study was performed with simulated diesel fuel doped with DBT to select the best set of conditions and then on real one. Hydrogen peroxide was selected as an oxidant, acetic acid as a homogeneous catalyst .Acetonitrile (ACN) and N-methyl -2 -pyrrolidone (NMP) were chosen as solvents. The oxidation and extraction steps were conducted once consecutively and other simultaneously.

## 2. EXPERIMENTAL WORK

### 2.1 Materials

N-heptane 99.5% purity (Gainland Chemical Company GCC) ; toluene 99% purity (Sigma US); hydrogen peroxide 50% (Sigma-Aldrich) ; acetic acid 95% purity (Tetenal UK) ; dibenzothiophene 99% (Himedia) ; acetonitrile 98% (Ptromchem.) ; N-methyl – 2 – pyrrolidone 99% (Himedia). Simulated diesel 200B n-heptane 80%wt , toluene 20%wt, doped with 1.7242 g of DBT for each liter to get a sulfur content of 355 ppm. Real diesel fuel with sulfur content of 1000 ppm was supplied by Al-Dora refinery .

## 2.2 Equipment

The experimental apparatus used in this study consisted of a 500-ml glass beaker immersed in a water bath (GFL) ; a thermometer (Eintauchtiefe 45 mm) which is inserted into the beaker to measure the temperature of the mixture ; mixer (Hiedolph RZR 2021) for stirring the mixture . The apparatus is shown in **Fig. 1**.The following parameters were studied .

## 2.3 Procedure

I-Simultaneous Technique: the oxidation and extraction were performed in one single step where the oxidation reaction occurred in the presence of a solvent (ACN once and NMP other time) . The model fuel , catalyst (acetic acid ) and solvent were added at the required ratios. After the mixture had reached the desired temperature, hydrogen peroxide was added . The mixer stirring speed was set at the desired value . After 2 h it was stopped .The mixture was left 24 h in a 250-ml separating funnel to ensure settling and phase separation . The upper layer (simulated fuel ) was then withdrawn and analyzed .

II-Consecutive Technique : In this technique , the oxidation was performed first and then immediately followed by extraction as follows:

1-The prepared amount of simulated diesel fuel was transferred to the reactor together with the desired amount of acetic acid (catalyst ).

2-Waiting until the mixture reached the desired temperature .

3-Hydrogen peroxide (oxidant) added to the mixture .

4-The mixer stirring speed was set on the required value . After 2 h , it was stopped .

5-The mixture was transferred to a 250-ml separating funnel to allow the separation of phases .

6-The upper layer (oxidized simulated diesel fuel ) was separated and mixed with certain amount of solvent (ACN or NMP) for another 2 h under proper stirring speed .

7- After the stirring was stopped , the phases were allowed to settle and separate in 24 h. The upper layer was withdrawn and analyzed .

The experiments were conducted according to $2^k$ factorial design. There are four factors that can be varied during a single experiment, keeping the others constant according to preliminary studying (temperature $50^oC$ , stirring speed 350 rpm). These are:

Solvent type (ACN , NMP )

Solvent/model fuel ratio ( 0.5,0.6,0.75, and 1)

Oxidant/model fuel ratio (0.5,0.75,1, and 1.5 )

Catalyst/oxidant ratio (0.125,0.25,0.5, and 0.75)

## 2.4 Test Methods

1-Pyro-Fluorescence:This analysis was done in Al-Dora refinery using ANTEK 9000 N/S analyzer to give sulfur content in the simulated diesel fuel .

2-X-ray Fluorescence: This analysis was done in the oil training institute using Horiba sulfur –in-oil analyzer (SLFA-2100) to give sulfur content in real diesel fuel.

## 3. RESULTS and DISCUSSION

The experimental runs were carried out in two – stage testing, preliminary and main study. The first one includes selection of best technique, simultaneous or consecutive and effect of stirring speed. The other included detailed study for the best operational conditions to remove dibenzothiophene (DBT) from simulated diesel fuel and the real one. This study included effect of the temperature, solvent/simulated diesel fuel ratio, $H_2O_2$/simulated diesel fuel ratio and acetic acid/$H_2O_2$ ratio.

### 3.1 Preliminary Study

- Technique selection

This study included three experiments with different conditions elected from literature and preliminary experiments . The results are illustrated in **Fig. 2**, showing that the outcomes of consecutive versus simultaneous oxidation and extraction procedures are almost the same. However; simultaneous technique was more attractive to applied.

- Effect of stirring speed

The results obtained showing that using stirring speed of 350 rpm gave the highest sulfur removal keeping other variables constant (temperature 50 °C, solvent/simulated diesel fuel ratio (either acetonitrile or N-methyl-2-pyrrolidone) 1:1, Oxidant / simulated diesel fuel ratio 1:1 and catalyst/oxidant ratio 0.5:1). **Fig. 3** indicates that the percentage removal of DBT is increased by increasing the stirring speed up to 350 rpm. At this stirring speed, it reached to 95.8% sulfur removal using ACN and 98.5% using NMP .Then the percentage removal became quickly impressive and mass transfer limitations were found to be insignificant at higher speeds. Therefore; the stirring speed was kept at that value for all next experiments.

The contact and mixing conditions between the two phases have a great influence on the interface transfer and emulsion droplet. At lower mixing speed, there are fewer droplets in the emulsion; hence, the reaction rate is low with less contact surface area. Increasing the mixing speed leads to the formation of more droplets, more uniform shape resulted in larger surface area. Therefore; high mass transfer will be gained and the reaction will be accelerated. However, if the mixing speed is too high, whirlpools will be formed in the system, and, in this situation mass transfer will be decreased and the reaction will be slowed. These results were in agreement with that of Hang et al**., Hang, et al., 2006** .

### 3.2 Main Study

- Effect of temperature

The effect of temperature studied at a range from 30 to 50 °C keeping other variables constant at two different conditions according to the experimental design proposed. The first one done at (0.5:1 solvent/simulated diesel fuel, 0.5:1 $H_2O_2$/simulated diesel ratio and 0.125:1 acetic acid/$H_2O_2$ ratio) and the other at (1:1 solvent/simulated diesel fuel ratio, 1:1 $H_2O_2$/simulated diesel fuel ratio and 0.5:1 acetic acid/$H_2O_2$ ratio) for 2 h of reaction time.The results of this set are illustrated in **Figs. 4 and 5**.

When the temperature is increased from 30 °C to 50 °C in the first set of conditions mentioned above, sulfur removal is increased from 25.6% to 32.5% for ACN and from 41% to 46.8% for NMP. While for the second set of conditions, increasing temperature from 30°C to 50 °C led to increase sulfur removal from 87.9% to 95.8 % for ACN and from 94.1% to 98.5% for NMP.

The factors that influence the removal of DBT were also related to the solubility of $DBTO_2$ in the solvent. Sulfur compounds are oxidized to sulfoxides or sulfones. These are highly polar compounds, which have high solubility in polar extractants. The results suggested that the solubility of $DBTO_2$ in the polar solvent increased with increasing temperature. Beside that increasing temperature decreased the solvent viscosity which played a positive role in sulfur removal due to the great effect on their extraction ability. Namely it facilitated mass transfer of S-compounds from the oil to the solvents.

It had been noticed that at higher temperatures (above 50 °C), a solvent miscibility in the model fuel phases occurred. This caused losing of solvent. It also caused thermal decomposition of $H_2O_2$. Therefore, increasing temperature above 50 °C was avoided.

These results were in agreement with that of Hang et al., **Hang, et al., 2006** , **Ali et al., Ali, et al., 2009** , and Fa-tang Li et al., **Fa-tang , et al., 2012** .

- Effect of oxidant ($H_2O_2$)/simulated diesel fuel ratio

The effect of the ratio of hydrogen peroxide/simulated diesel feul on the sulfur removal was found to be a very important parameter due to its effect on the conversion of DBT to $DBTO_2$. The results are illustrated in **Figs. 6-9** .These results indicate that increasing the ratio of ($H_2O_2$)/simulated diesel fuel leads to increase sulfur removal.

The experiments showed that increase the $H_2O_2$/simulated diesel fuel ratio from 0.5:1 to 1:1 leads to increase the sulfur removal from 32.5% to 43.7% for ACN and from 46.8% to 71.3% for NMP at operational conditions of 50 °C, solvent/ simulated diesel fuel 0.5:1 and acetic acid/$H_2O_2$ 0.125:1. While reducing temperature to 30 °C and keeping the other parameters constant, the sulfur removal was increased from 25.6% to 33.5% for ACN and from 41% to 48.1% for NMP.

This effect was investigated at other conditions: 50 °C, solvent/ simulated diesel fuel 1:1 and acetic acid/$H_2O_2$ 0.5:1, while $H_2O_2$/simulated diesel fuel 1:1, sulfur removal was increased from 87.8% to 95.8% for ACN and from 91.5% to 98.5% for NMP. While reducing temperature to 30 °C with the same other conditions, sulfur removal was increased from 75.2% to 87.9% for ACN and from 90% to 96.3% for NMP.

It had been noticed that the sulfur removal reached the highest value at $H_2O_2$/simulated diesel fuel ratio of 1:1. After that it almost stayed constant, which indicates that this ratio is the best one to achieve almost complete DBT conversion into $DBTO_2$ within a reasonable period of time (2h).

In fact, the oxidation efficiency of $H_2O_2$ can be affected by several factors, including temperature, degree of hindrance of sulfur-containing compounds and catalyst (acetic acid)/$H_2O_2$ ratio.

Temperature is the most significant factor which suggested an important interaction between temperature and $H_2O_2$/simulated diesel fuel ratio. At high temperatures (above 50 °C), more excess oxidant would be necessary because of the loss of $H_2O_2$ due to thermal decomposition. In contrast, the water hindrance of $H_2O_2$ aqueous solution in desulfurization progress would be more significant at temperatures about 50 °C.

- Effect of acetic acid/$H_2O_2$ ratio

The effect of catalyst (acetic acid) to the oxidizing agent (hydrogen peroxide) was found to be one of the important parameters due to its multiple effects on both the conversion of DBT to $DBTO_2$ and removal of sulfur content from diesel fuel.

The results are plotted in **Figs. 10-13**. These results indicate that increasing the ratio of acetic acid/$H_2O_2$ from 0.125:1 to 0.5:1 leads to increase sulfur removal from 32.5% to 86.6% for ACN and from 46% to 94.9% for NMP at operating conditions of 50 °C, solvent/ simulated diesel fuel 0.5:1, and $H_2O_2$/simulated diesel fuel 0.5:1. Further increase of acetic acid/ $H_2O_2$ ratio to 0.75:1 leads to decrease in sulfur removal to 79.3% and 85% for ACN and NMP, respectively. Decreasing the temperature to the value above 30◦C and keeping other conditions constant lead to increase in sulfur removal from 25.6% to 52.2% for ACN and from 41% to 60.8% for NMP. Then at acetic acid/ $H_2O_2$ ratio of 0.75:1, sulfur removal decrease to 47.2% for ACN and to 55.2% for NMP.

The subject has been investigated in other conditions, 50 °C, solvent/ simulated diesel fuel ratio 1:1, and $H_2O_2$/simulated diesel fuel ratio 1:1. The results showed that the sulfur removal increases from 35% to 95.8% for ACN and from 65.8% to 98.5% for NMP as acetic acid/$H_2O_2$ ratio increases from 0.125: to 0.5:1. Then sulfur removal decreased to 85.6% for ACN and 89% for NMP when the ratio of acetic acid/$H_2O_2$ increased further to 0.75:1.

Again sulfur removal investigated at temperature 30°C, solvent/simulated diesel fuel ratio 1:1, $H_2O_2$/simulated diesel fuel ratio 1:1. The results of NMP solvent showed that the sulfur removal increases from 74.2% to 94.1% then decreases to 86.8% at acetic acid/ $H_2O_2$ ratio of 0.75:1, while for ACN, it increases from 31.3% to 87.9% then decreases to 80.1%.

It was concluded from the set of experiments that the optimal ratio of acetic acid/$H_2O_2$ is 0.5:1; it is not efficient to increase this ratio further more because a decline in DBT conversion would be noticed due to a decline in acetic acid dissociation, which is necessary as a catalyst for the sulfur oxidation reaction.

The decline in organic acid dissociation is a result of acid self – dimerization and / or association with water. Another factor contributing to this observation is the decline in the availability of the proton necessary for peroxide dissociation to yield oxygen which is necessary for sulfur oxidation. This decline in proton availability is due to the decreasing in water concentration upon adding more organic acid.

According to our experimental results, the reversible reaction of acetic acid with hydrogen peroxide produces peroxyacetic acid as a high active oxidant which can efficiently oxidize DBT to respective sulfoxide (DBTO) and then to respective sulfone ($DBTO_2$). That illustrates the effect of acetic acid as a catalyst on the oxidation process by increasing the efficiency of hydrogen peroxide. With the increase of $H_2O_2$ and $CH_3COOH$ (to a certain limit), the oxidant have more opportunities to react with DBT, and as a result, the sulfur removal increases.

These results were in agreement with that of Ali et al., **Ali, et al., 2009** , and **Fa-tang Li et al., Fa-tang , etal., 2012**.

*Effect of solvent/simulated diesel fuel ratio

Although DBT had been converted to DBTDO by oxidation process, the sulfur would not completely be removed from the simulated diesel fuel. The basis of using acetonitrile or N-methyl-2-pyrrolidone as an extraction solvent is that the solubility of $DBTO_2$ in such solvent is one order of magnitude higher than that in the simulated diesel fuel. This supports the need of adding acetonitrile, N-methyl-2-pyrrolidone or any other suitable solvent.

The results are illustrated in **Figs. 14-17** .These results indicate that increasing the ratio of solvent (either ACN or NMP)/simulated diesel fuel leads to increase in sulfur removal. The experiments showed that increase the solvent/simulated diesel fuel ratio from 0.5:1 to 1:1 leads to increase the sulfur removal from 32.5% to 71.2% for ACN and from 46.8% to 91% for NMP at operational conditions of 50 °C, $H_2O_2$/simulated diesel fuel ratio of 0.5:1 and acetic acid/ $H_2O_2$ ratio of 0.125:1. While reducing the temperature to 30 °C and keeping the other factors constant lead to increase in sulfur removal from 25.6% to 67% for ACN and from 41% to 72% for NMP.

This effect was investigated at other conditions: 50 °C, $H_2O_2$/simulated diesel fuel ratio of 1:1 and acetic acid/ $H_2O_2$ ratio of 0.5:1. Results showed that increasing the ratio of solvent/simulated diesel fuel ratio from 0.5:1 to 1:1 leads to increase in sulfur removal from 89.3% to 95.8% for ACN and from 95% to 98.5% for NMP. While reducing the temperature to 30 °C showed that the percent removal changed from 84.5% 87.9% for ACN and from 88.1% to 94.1% for NMP.

From all above, when DBT was converted to its corresponding polar compound ($DBTO_2$) by means of oxidation, the capabilities of the tested solvents for sulfur removal enhanced significantly.

NMP exhibits a notable sulfur removal of 98.5% for DBT because of the similarity – intermisicibility theory based on the fact that NMP and DBT contain five-membered ring.

ACN was appropriate solvent because it is able to extract and dissolve the reaction products and exhibits a low surface tension, which facilitate the transfer of products and reagents at the polar-polar interphase, increasing notably the mass transfer along the interphase. However, ACN is partially dissolved in the (polar) fuel phase, then ACN molecules are present in the fuel phase, in consequence the final nitrogen concentration in the fuel will increase. To avoid this, a later separation unit is mandatory to remove the fraction of ACN transferred to the fuel phase.

During oxidation/extraction process, DBT was oxidized to its corresponding sulfone (DBTDO) by per acetic acid ($CH_3COOOH$) obtained from $H_2O_2$ and $CH_3COOH$ and then extracted from the oil phase into the solvent phase. The decrease in DBT concentration in the solvent promoted the extraction process, and the sulfur content in oil phase decreased continuously. Increasing of sulfone (polar compound) leads to increase extraction ability of the solvents (due to similar polarity). This illustrates the effect of oxidation process on the efficiency of extraction process. It was clear that the solvent efficiency was affected by the ratios of oxidant and catalyst. If no oxidant was added, sulfur removal would significantly decrease by extraction step only. With increasing in oxidant and catalyst, the oxidant had more opportunities to react with DBT, and thus the sulfur removal increased.

The results were in agreement with those of Ali et al**., Ali, et al., 2009 ,** Capel-Sanchez et al., **Capel-Sanchez, et al., 2010** , **and Fa-tang Li et al**., **Fa-tang , et al., 2012** .

## 3.3 Desulfurization of Real Diesel Fuel

The removal of sulfur content from the real diesel fuel was more difficult than that from the simulated diesel fuel because many nitrogen, oxygen, and aromatic compounds exist in actual oil.

Two experiments with best conditions that had been concluded from the set of experiments applied on simulated diesel fuel [temperature of 50 ˚C, solvent/real diesel fuel ratio of 1:1, $H_2O_2$/real diesel fuel of 1:1, acetic acid/ $H_2O_2$ of 0.5:1 and stirring speed of 350 rpm] were applied. Results are plotted in **Fig. 18** showing that sulfur removal reached to 62.5% and 75% for acetonitrile and N-methyl-2-pyrrolidone respectively.

Another experiments with more severe conditions were conducted to study the behavior of the real diesel fuel ( i.e. temperature of 70 ˚C, stirring speed of 500 rpm, solvent/real diesel fuel of 2:1, $H_2O_2$/real diesel fuel of 2:1 and acetic acid/ $H_2O_2$ of 0.5:1). Sulfur removal was almost the same for ACN and NMP as shown previously. It is suggested that the reason of remaining sulfur removal constant despite of varying the conditions, is due to the presence of nitrogen compounds in real diesel fuel beside other types of sulfur compounds that do not react in our process technique.

These results were in agreement with that of Rao et al. , **Rao, et al., 2007** , and **Fa-tang Li et al.** , **Fa-tang Li, et al., 2011**.

## 4. CONCLUSIONS

- The techniques of consecutive versus simultaneous (oxidation , extraction ) processes are almost the same .
- Simultaneous oxidation / extraction process had the ability to remove almost all the DBT from the simulated diesel fuel.
- The time 2 h was sufficient for converting DBT to DBTDO by oxidation step .
- The solvent NMP was found to be better for the removal of sulfur than ACN .

- The optimum conditions to operate the simultaneous oxidation / extraction are [ stirring speed 350 rpm , temperature 50 $^{o}$ C , solvent / simulated diesel fuel 1:1 , $H_2O_2$/ simulated diesel fuel 1:1 , acetic acid / oxidant 0.5:1 ] for both NMP and ACN .

- It is impossible to obtain ultra- desulfurization using extraction process only , nevertheless ; using NMP or ACN .

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## ABBREVIATIONS

| | |
|---|---|
| ACN | acetonitrile |
| DBT | dibenzothiophene |
| DBTDO , $DBTO_2$ | dibenzothiophene dioxide |
| DBTO | dibenzothiophene oxide |
| HDS | hydro desulfurization |
| NMP | N-methyl-2-pyrrolidone |
| ODS | desulfurization by selective oxidation |

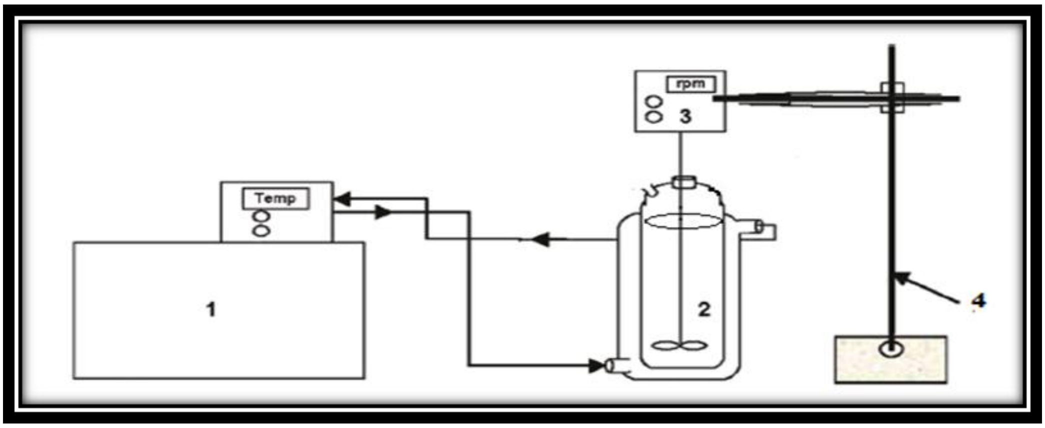

**Figure 1.** Schematic diagram of the experimental apparatus.

1- water bath; 2- glass beaker; 3- mixer; 4- stand.

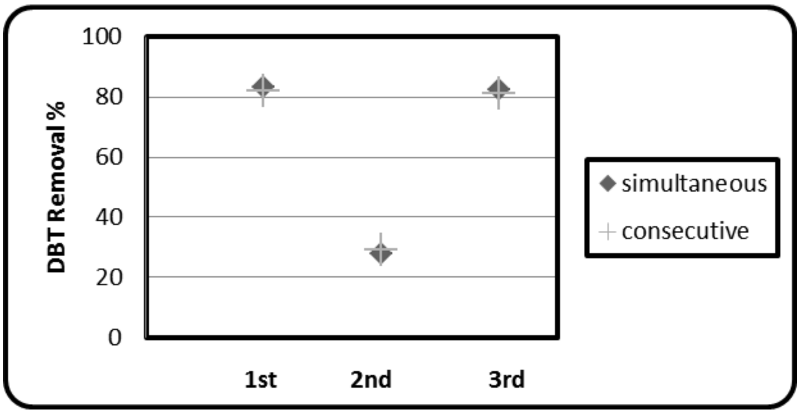

**Figure 2.** Simultaneous vs. consecutive oxidation/extraction using NMP as extractant.

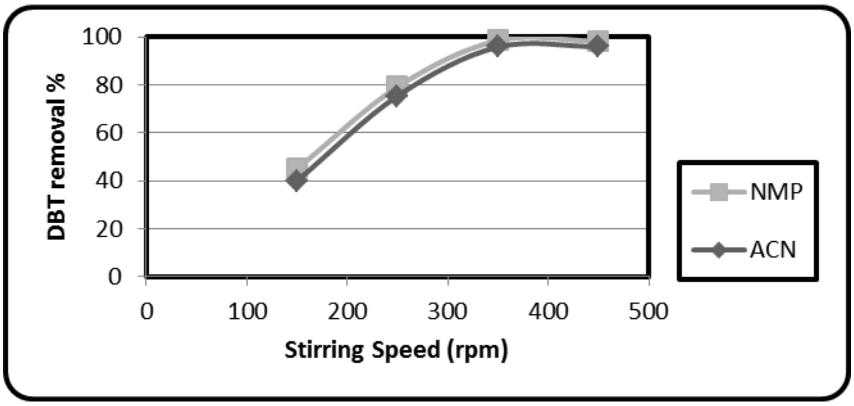

**Figure 3.** Sulfur removal versus stirring speed.

(Operating conditions: 50 ˚C, 1:1 solvent/simulated diesel fuel ratio, 1:1 $H_2O_2$/simulated diesel fuel ratio and 0.5:1 acetic acid/$H_2O_2$ ratio for 2 h reaction time).

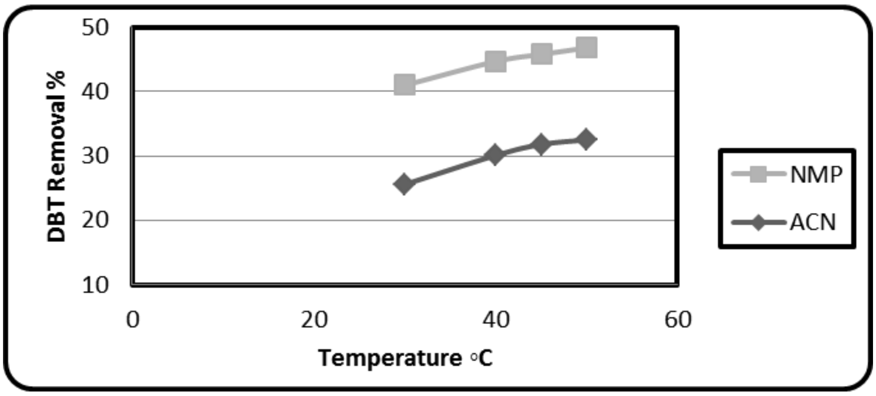

**Figure 4.** Effect of temperature on DBT removal.

(Operating conditions: 0.5:1 solvent/simulated diesel fuel ratio, 0.5:1 $H_2O_2$/simulated diesel fuel ratio and 0.125:1 acetic acid/$H_2O_2$ ratio for 2h reaction time) .

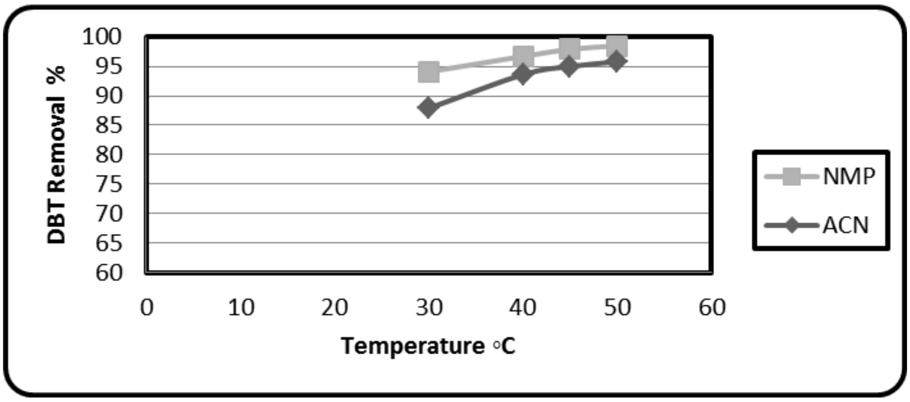

**Figure 5.** Effect of temperature on DBT removal.

(Operating conditions: 1:1 solvent/simulated diesel fuel ratio, 1:1 $H_2O_2$/simulated diesel fuel ratio and 0. 5:1 acetic acid/$H_2O_2$ ratio for 2h reaction time) .

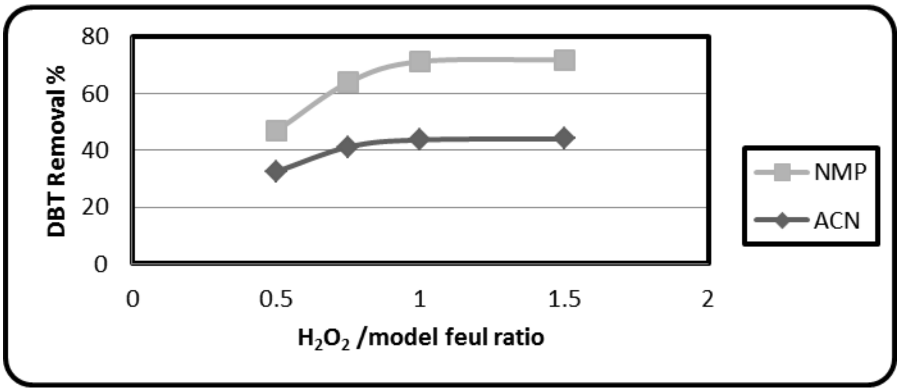

**Figure 6.** Effect of $H_2O_2$/simulated diesel fuel ratio on DBT removal.

(Operating conditions: 50 ˚C, 0.5:1 solvent/simulated diesel fuel ratio and 0.125:1 acetic acid/$H_2O_2$ ratio for 2h reaction time).

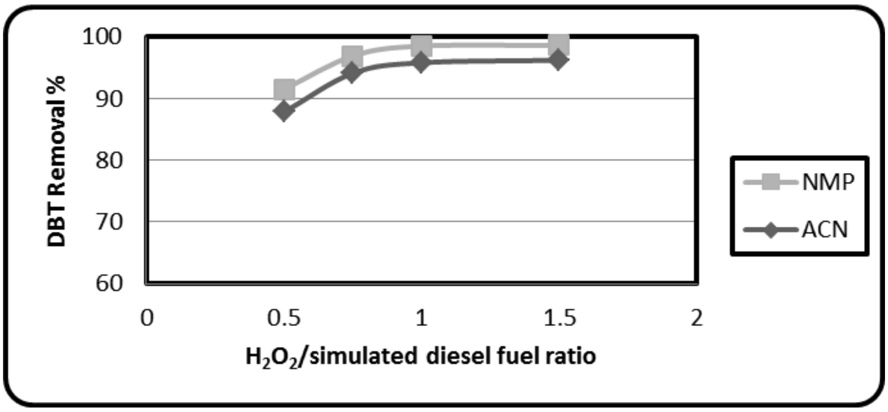

**Figure 7.** Effect of $H_2O_2$/simulated fuel ratio on DBT removal.

(Operating conditions: 50 ˚C, 1:1 solvent/simulated diesel fuel and 0.5:1 acetic acid/$H_2O_2$ ratio for 2h reaction time).

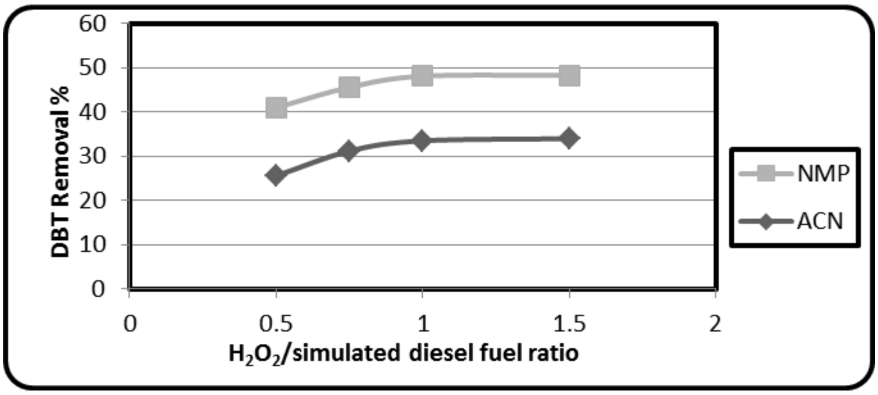

**Figure 8.** Effect of $H_2O_2$/simulated diesel fuel ratio on DBT removal .

(Operating conditions: 30 ˚C, 0.5:1 solvent/simulated diesel fuel ratio and 0.125:1 acetic acid/$H_2O_2$ ratio for 2h reaction time).

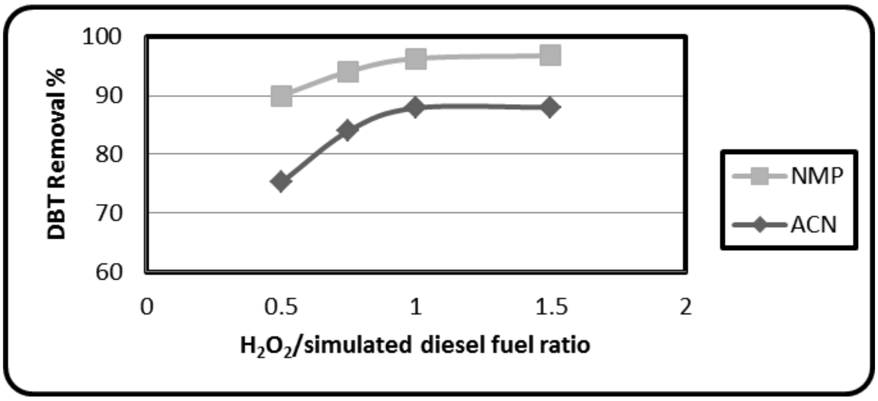

**Figure 9.** Effect of $H_2O_2$/simulated diesel fuel ratio on DBT removal.

(Operating conditions: 30 ˚C, 1:1 solvent/simulated diesel fuel ratio and 0.5:1 acetic acid/$H_2O_2$ ratio for 2h reaction time).

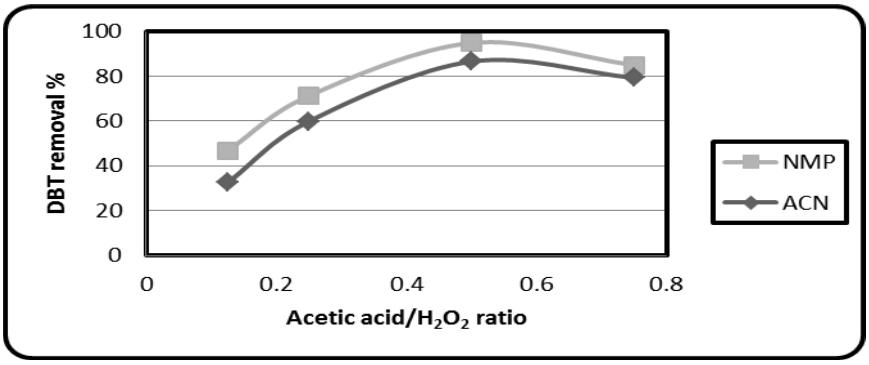

**Figure 10.** Effect of acetic acid/$H_2O_2$ ratio on DBT removal.

(Operating conditions: 50 ˚C, 0.5:1 solvent/simulated diesel fuel and 0.5:1 $H_2O_2$/simulated diesel fuel for 2h reaction time) .

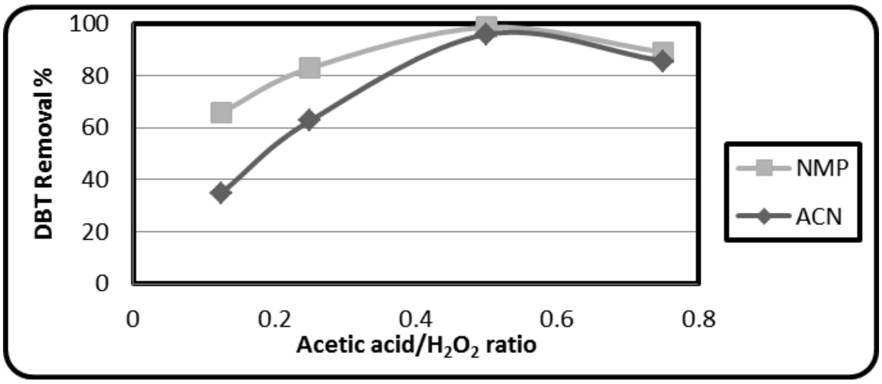

**Figure 11.** Effect of acetic acid/$H_2O_2$ ratio on DBT removal.

(Operating conditions: 50 ˚C, 1:1 solvent/simulated diesel fuel and 1:1 $H_2O_2$/simulated diesel fuel for 2h reaction time).

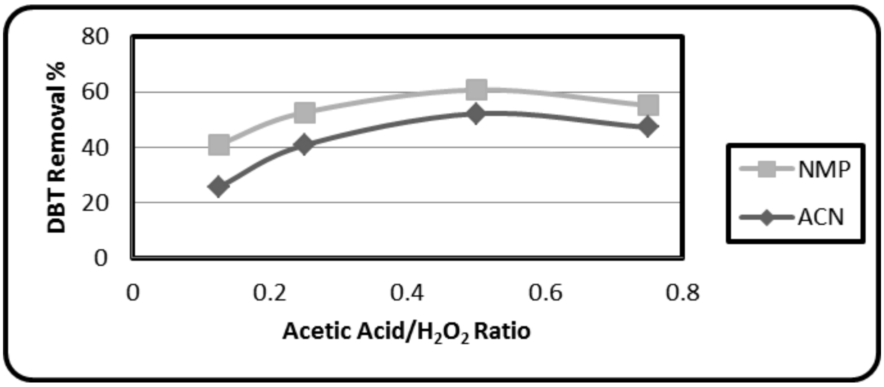

**Figure 12.** Effect of acetic acid/$H_2O_2$ ratio on DBT removal .

(Operating conditions: 30 ˚C, 0.5:1 solvent/simulated diesel fuel and 0.5:1 $H_2O_2$/simulated diesel fuel).

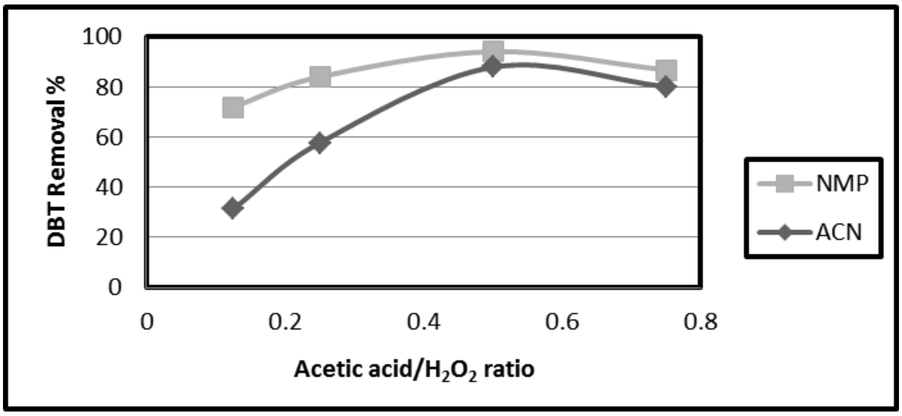

**Figure 13.** Effect of acetic acid/$H_2O_2$ ratio on DBT removal .

(Operating conditions: 30˚C, 1:1 solvent/simulated diesel fuel and 1:1 $H_2O_2$/simulated diesel fuel).

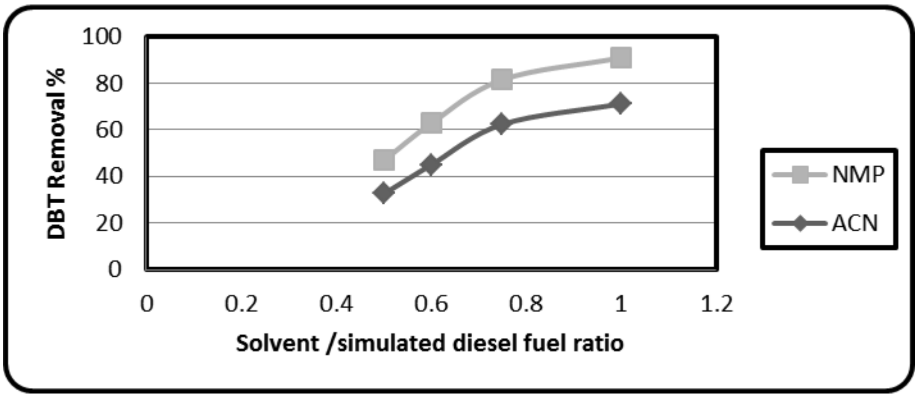

**Figure 14.** Effect of solvent/simulated diesel fuel ratio on DBT removal.

(Operating conditions: 50˚C, 0.5:1 $H_2O_2$/simulated diesel fuel ratio 0.125:1 and acetic acid/ $H_2O_2$) .

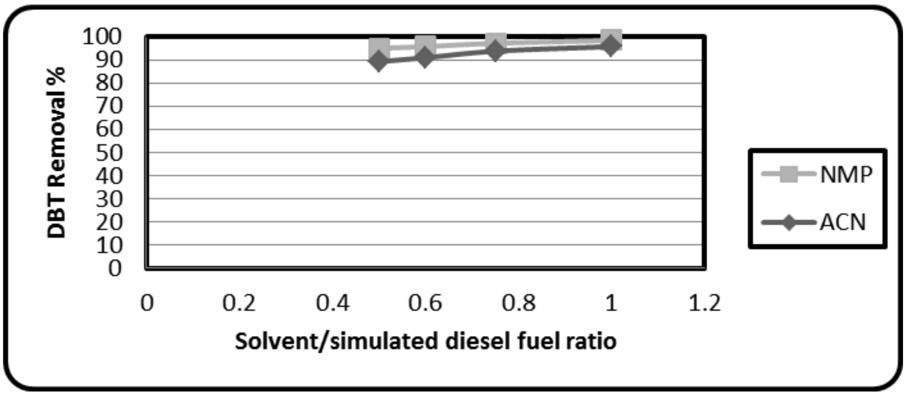

**Figure 15.** Effect of solvent/simulated diesel fuel ratio on DBT removal.

(Operating conditions: 50˚C, 1:1 $H_2O_2$/simulated diesel fuel ratio and 0.5:1 acetic acid/ $H_2O_2$ ratio).

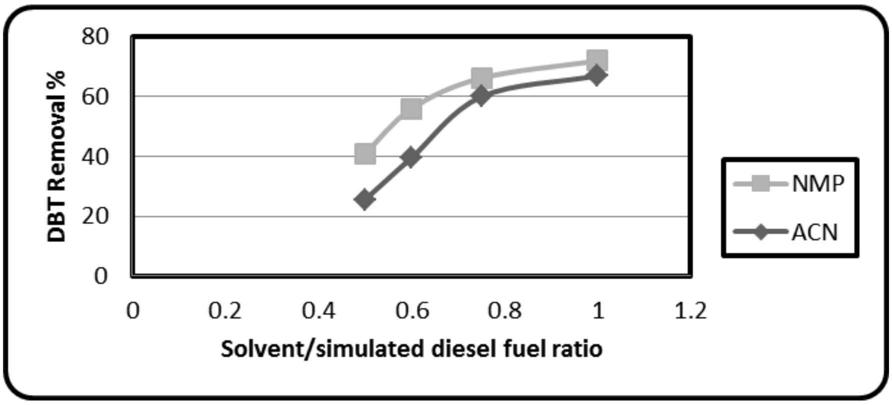

**Figure 16.** Effect of solvent/simulated diesel fuel ratio on DBT removal.

(Operating conditions: 30°C, 0.5:1 $H_2O_2$/simulated diesel fuel ratio and 0.125:1 acetic acid/$H_2O_2$).

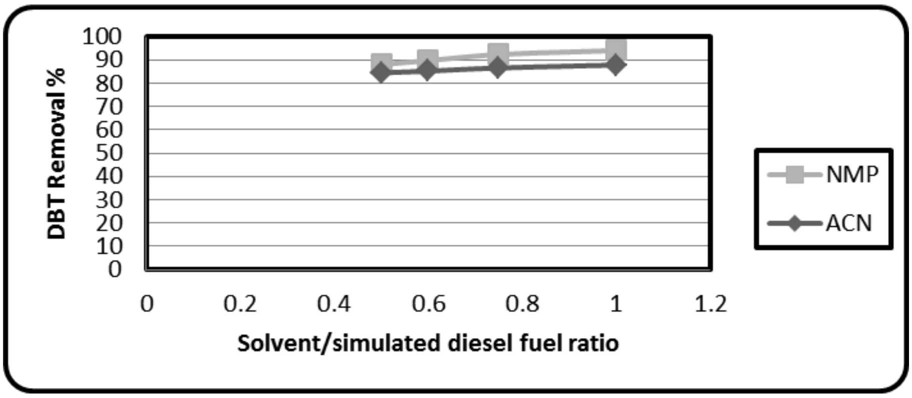

**Figure 17.** Effect of solvent/simulated diesel fuel ratio on DBT removal.

(Operating conditions: 30 °C, 1:1 $H_2O_2$/simulated diesel fuel ratio and 0.5:1 acetic acid/ $H_2O_2$).

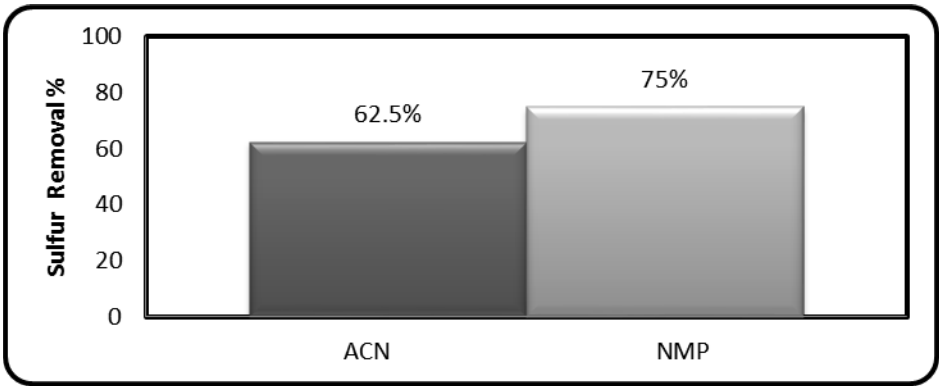

**Figure 18.** sulfur removal from real diesel fuel.

(Operating conditions: 50 °C, stirring speed 350 rpm, 1:1 solvent/real diesel fuel ratio, 1:1 $H_2O_2$/real diesel fuel ratio and 0.5:1 acetic acid/$H_2O_2$ ratio for 2h reaction time).