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Oxidation Desulphurization of Heavy Naphtha Improved by Ultrasound Waves

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Abstract

The oxidation desulphurization assisted by ultrasound waves was applied to the desulphurization of heavy naphtha. Hydrogen peroxide and acetic acid were used as oxidants, ultrasound waves as phase dispersion, and activated carbon as solid adsorbent. When the oxidation desulphurization (ODS) process was followed by a solid adsorption step, the performance of overall Sulphur removal was 89% for heavy naphtha at the normal condition of pressure and temperature. The process of (ODS) converts the compounds of Sulphur to sulfoxides /sulfones, and these oxidizing compounds can be removed by activated carbon to produce fuel with low Sulphur content. The absence of any components (hydrogen peroxide, acetic acid, ultrasound waves and activated carbon) from the ODS process leading to reduce the performance of removal, hydrogen peroxide was the most crucial factor. The ultrasound waves increase the dispersion of carbon, water and oil phase, promotes the interfacial mass transfer, and this leads to accelerates the reaction. The ultrasound waves did not affect the chemical or physical properties of the fuel. The chemical analysis of treated fuel oil showed that <1% of the hydrocarbon fuel compounds were oxidized in the ODS process. In this work, desulphurization by oxidation is the main mechanism was tested with several parameters that effects desulphurization efficiency such as sonication time (5-40) min, activated carbon (0.01-0.5) gm, hydrogen peroxide (1-30) ml, and acetic acid (1-15) ml. It was found that the hydrogen peroxide amounts lead to increase oxidation rates of Sulphur compounds so, the desulphurization efficiency increases. The optimum amounts of oxidants are 10 ml hydrogen peroxide per 100 ml of heavy naphtha. Increasing the amount of acid catalyst lead to increase Sulphur removal, it was found that7.5 ml acid per 10 ml oxidant was the optimum amount. Activated carbon as a solid adsorbent and reaction enhancer with 0.1gm weight was found as the optimum amount for 100 ml heavy naphtha. Increasing sonication time lead to increase desulphurization rate, it was found that (10 min) is the optimum period. By applying the optimum parameters 89% of sulfur can be removed from heavy naphtha with 598.4 ppm Sulphur content.

Keywords: Ultra-low Sulphur fuel, Oxidative desulfurization, ultrasonic waves, hydrogen peroxide, acetic acid

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1- Introduction

Sulphur compounds in oil fractions are the main reason for many environmental pollution and equipment failure. The presence of Sulfur compounds with a high concentration in oil fraction lead with time to damage industrial equipment by causing corrosion effect [1].

Sulfur compounds are poison metals and catalysts used in industrial processes such as catalytic cracking and catalytic reforming by precipitation on the catalyst surface and close its pores [2].

Burning of oil fractions that contain a high concentration of Sulphur compounds lead to releases of Sulphur oxides gases (SOx) which cause smog and acid rains so that for environmental protection called for diminishing Sulphur compounds content to minimum concentration as much as probable by using suitable desulfurization processes [3].

Hydrodesulphurization (HDS) is the conventional desulphurization process, it is a familiar practice in the refinery for several years and has the dominance of pre-existent in the infrastructure of the refinery, but this process required high pressure and temperature [4].

Seek for preference way to sulphur component removal has been increased in the past years [5].

The selective oxidation of organic sulphur compounds at ambient pressure and room temperature in the process of oxidation desulphurization (ODS), permit the utilize of inexpensive adsorbents to get low sulphur content [6].

The challenge in oxidation desulphurization (ODS) is to recognize the conditions that perform ultra-deep desulphurization without using expensive catalysts or auxiliary chemicals and keep high fuel oils recovery [7]. Ultrasonic waves used to raise quick reactions by dissipating the multiphase admixtures of the oil phase and aqueous phase. The oxidation process modifies the physical properties of organic sulphur compounds so that these compounds can be removed by adsorption using inexpensive adsorbent [8].

The moderates condition used in the ODS process reduces the total energy required for sulphur removal in comparisons with the HDS process [9].

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Oxidation desulphurization considered an efficient process to remove Sulphur compounds that can't be removed by the HDS process such as benzothiophenes and dibenzothiophenes compounds [10].

This study is a first attempt to treat commercial heavy naphtha supplied from Al-Doura refinery to remove Sulphur content by the oxidation process improved by ultrasound waves. The effect of several variables on the process was studied, such as the effect of hydrogen peroxide, acetic acid, sonication time and activated carbon as adsorbent.

2- **Experimental Work**

2.1. Materials

Chemical materials utilized in this research are shown in table 1, the activated carbon used in this work is of 1184.9 m2/gm surface area. Heavy naphtha of 598.4 ppm sulphur content was derived from Al-Doura refinery with 60.7 API and a density of 0.7379 g/cm3.

Table 1. Chemical materials utilized in experiment work

chemical materials	function	molecular weight	Purity %	formula	company
Hydrogen peroxide	Oxygen source	34	50	H_2O_2	Hopkin and Williams, England
Acetic acid	Increase oxidation	60	99	$C_2O_2H_4$	Riedel-De Haen
Activated-carbon	Solid adsorbent	12.01	-----	C	Jacobi Carbons

2.2. Apparatus

The equipment used is as follows:

A-Q 500 Sonicator

Q 500 sonicator is the important apparatus employed in these experiments, **Fig. 1** ultrasound device. It is a strong device for ultrasound wave's processor displaying programmable action and numerical show of running parameters. Q500 sonicator is of 20 kHz and 500 W maximum amplitude of power ultrasound. The device is designed and produced by the company of Materials and Sonics, Inc. Model VX 500, Newton, United States).

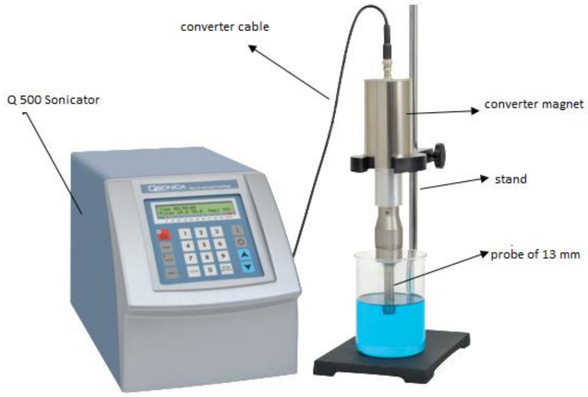


Fig. 1. Ultrasound device of Q 500 sonicator

B- Hot plate magnetics stirrer manufactured by PCE Americas Inc., USA.

2.3. Analysis

Sulphur content of heavy naphtha was obtained due to ASTM D-7093 by utilizing the Antek-Multitek device located in Al-Daura refinery, manufactured by (PAC LP, Houston, Texas, USA).

2.4. Procedure

100 ml of heavy naphtha with 598.4 ppm sulphur content put in a beaker, as oxidative agent amounts of hydrogen peroxide(H2O2) (1-30 ml) and as a catalyst amounts of acetic acid (1-15 ml) and activated-carbon (0.01-0.5 gm) as adsorbent, were added to this beaker. This beaker put in ultrasound effects for periods (5-40 min) of time with Amplitudes (20-60% Amp) of power ultrasound.

After the sonication process, the mixture put up in a magnetic stirrer for 1 hr. with 900 rpm to satisfy adsorption equilibrium [11], then the oil phase and aqueous phase separated and the oil phase went to analysis to know Sulphur content by the Antek-Multitek device.

3- **Results and Discussion**

3.1. Effects of hydrogen peroxide amount

The effects of changing hydrogen peroxide added amount on desulphurization of heavy naphtha are shown in Fig. 2.

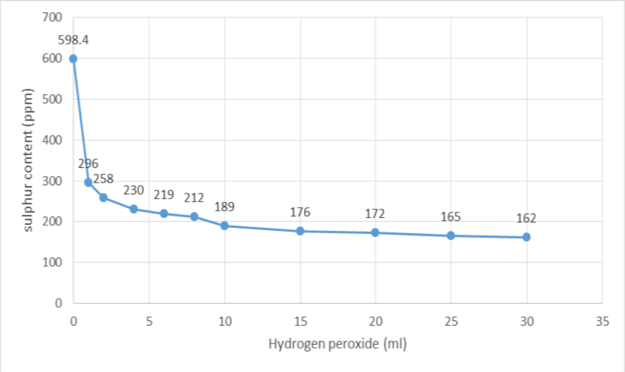


Fig. 2. effects amounts of oxidant on Sulphur content for 100 ml of heavy naphtha, 10 min sonication time, 20% Amp ultrasound power, 0.1 gm activated carbon and 1ml acid.
Note: Amp means amplitude

As shown in Fig. 2, the desulphurization efficiency increases with increasing amounts of oxidant hydrogen peroxide, this is because of increasing the free radicals in the mixture which leads to increase oxidation of Sulphur compounds, this behavior was also pointed out by Hosseini, 2012, [12].

The optimum volume of hydrogen peroxide is 10 ml, for this reason, all subsequent experiments are selected at hydrogen peroxide volume 10 ml hydrogen peroxide per 100 ml of naphtha.

3.2. Effects of Acetic Acid Amount

The effects of changing the amounts of acetic acid on desulphurization process are shown in Fig. **3**.

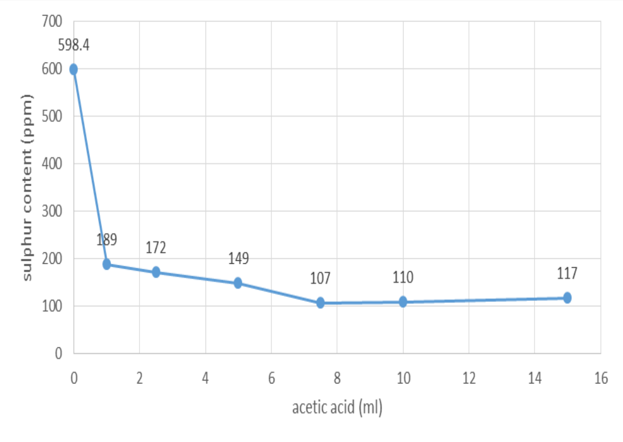
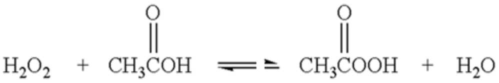


Fig. 3. Effects amount of acid on Sulphur content for 100 ml heavy naphtha, 10 ml hydrogen peroxide, 10 min sonication time, 20% Amp power ultrasound and 0.1 gm activated carbon

As shown in Fig. **3**, increasing the amounts of acid catalyst lead to increase the removal of Sulphur until 7.5 ml of acid that is because beyond this amounts adverse reaction occurs, this behavior was due to the reaction between oxidant and acid.



$$H_2O_2 + CH_3\overset{\overset{O}{\|}}{C}OH \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}OOH + H_2O \qquad \dots (1)$$

The reaction of hydrogen peroxide and acetic acid produces peracetic acid. this acid is a form of proxy-carboxylic acids, that can decompose to produce hydro-proxy radicals (.OOH), these radicals are more effective than hydroxyl radicals (.OH) formed from hydrogen peroxide decomposition, so oxidation process increases.

it was found that the best Sulphur removal when utilized 7.5 ml acetic acid per 10 ml hydrogen peroxide. The optimum ratio of acid to oxidant is 0.75, for this reason, all subsequent experiments are selected at acid to oxidant ratio of 0.75.

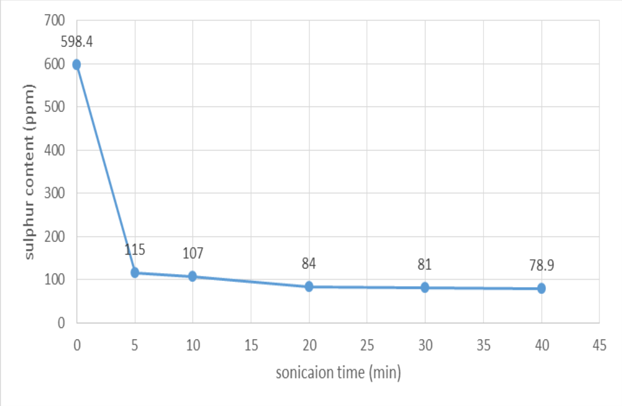


Fig. 4. The relation between Sulphur content and sonication time for 100 ml naphtha, 10 ml hydrogen peroxide, 7.5 ml acetic acid, 20% Amp of ultrasound power and 0.1 gm activated carbon

As shown in Fig. **4**, increasing the sonication time leads to an increase in the oxidation of Sulphur compounds due to increasing exposure periods of these compounds to the oxidants, then increasing desulphurization rate.

These longer times of reaction under the energy of ultrasound lead to strong cavitation formation that leads to fine emulsions formation for the oxidation reaction, this fine emulsion increase contacts and exposure of the oxidative system to organic Sulphur compounds, so increase desulphurization efficiency. These results are in good agreement with that of Teng-Chien Chen., et al 2010, [13]. The optimum period of sonication time is 10 min, for this reason, all experiments are selected at 10 min sonication time.

3.4. Effects of Activated Carbon Amounts

The results related to satisfying these effects are shown in Fig. **5**

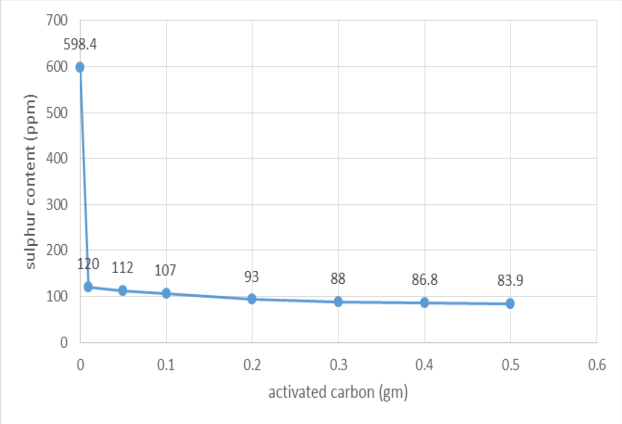


Fig. 5. Sulphur content with different amounts of activated carbon for 100 ml heavy naphtha, 10 min sonication time, 20% Amp ultrasound power, 10 ml hydrogen peroxide and 7.5 ml acetic acid

As shown in figure 5, the increase of activated carbon amounts leads to increase desulphurization efficiency due to increased oxidation rates by increase attractions the organic Sulphur compounds to the aqueous phase where oxidation occurs, this behavior was also pointed out by Gonzalez., et al 2012, [8]. The optimum amount of activated carbon is 0.1 gm so that all experiments are selected at 0.1 gm activated carbon.

4- Conclusion

Based on the results obtained, the conclusions can be demonstrated as follows:

It was found that increasing hydrogen peroxide amounts lead to an increased oxidation rate, so desulphurization efficiency increases.

The ultrasound-assisted oxidative desulphurization process with adsorption by active carbon has high effects on desulphurization of crude oil fractions up to 89 % for heavy naphtha.

The amounts of acetic acid used in this process have an optimum value, if more than the optimum value, the adverse reaction will occur leading to decrease the efficiency of desulphurization, 7.5 ml acetic acid per 10 ml of hydrogen peroxide is the optimum value of acetic acid in this work.

Increasing the time of sonication lead to increase Sulphur removal, but using too much time leads to increase in the cost of operation, it was found that the optimum sonication time for heavy naphtha is 10 min.

Increasing amounts of active carbon lead to increase adsorption rate but at 0.5 gm ≥ the amount becomes too much, so the favorite amount for 100 ml heavy naphtha is 0.1 gm. The process is done without any effects in the chemical or physical properties of the fuel.

References

[1] Rawnaq B. Jimaa, Zaid H. Mahmoud, Farah K. Ali., 2018. Evaluation the Efficiency of CuFe2O4 Prepared Photolysis by OSD and Photo degradation., Entomol. Appl. Sci. Lett., 2018, 5 (2) pp.91-100.

[2] A. Shamseddini, F. Esmaeilzadeh and D. Mowla., 2017. Diesel Oil Upgradation by Ultrasound Irradiation: A Study on the Effects of Main Operational Parameters. Phys. Chem. Res., Vol. 5, No. 4, 691-707, December 2017.

[3] Zhu W., Zhu G., Li H., Chao Y., Chang Y., Chen G. & Han C., 2011. Oxidative desulfurization of fuel catalyzed by metal-based surfactant-type ionic liquids. “Journal of Molecular Catalysis. A, Chemical”, 347, pp.8–14.

[4] Abdul-Halim A. Mohammed and Zeinab K. Nassrullah, 2013. Preparation and Formation of Zeolite 5A from Local Kaolin Clay for Drying and Desuphurization of Liquefied Petroleum Gas. " Iraqi Journal of Chemical and Petroleum Engineering", Vol.14 No.1 (March 2013) 1- 13.

[5] Campos-Martin J.M., Capel-Sanchez M. C., Perez-Presas P., Fierro J. L. G., 2010. Oxidative processes of desulfurization of liquid fuels. Journal of Chemical Technology and Biotechnology, 85(7), pp.879–890.

[6] Iman Najafi, Mohammad Amin Makarem, Mahmood Amani., 2011., Application of Ultrasound Waves to Increase the Efficiency of Oxidative Desulfurization Process., Advances in Petroleum Exploration and Development, 2(2), 63-69.

[7] Mello P.A., Duarte F.A., and Nunes M. G., 2009, Ultrasound-Assisted Oxidative Process for Sulfur Removal from Petroleum Product Feedstock, Ultra son. Sonochem Journal. Vol.16, pp. 732-736.

[8] Lino A. Gonzalez, Peter Kracke, William H. Green, Jefferson W. Tester, Linda M. Shafer, and Michael T. Timko., 2012. Oxidative Desulfurization of Middle-Distillate Fuels Using Activated Carbon and Power Ultrasound. Cambridge, Massachusetts 02139, United States. Energy Fuels 2012, 26, 5164−5176.

[9] Nada Sadoon Ahmedzeki and Arowa Salah Alddin Mahdi, 2014. Research Octane Number Improvement of Iraqi Gasoline by Adsorption of n-Paraffins Using Zeolite Molecular Sieves, "Iraqi Journal of Chemical and Petroleum Engineering", Vol.15 No.2 (June 2014) 27- 37.

[10] Safa Nabeel Abdulqahar, Majid I. Abdulwahab and Khalid K. Hummadi., 2019. Reuse of Spent Hydrotreating Catalyst of the Middle Petroleum Fraction. "Iraqi Journal of Chemical and Petroleum Engineering", Vol.20 No.1 (March 2019) 15 – 22.

[11] Kinya Sakanishi, Hamdy Farag, Shinya Sato, Akimitsu Matsumura, and Ikuo Saito., 2003., Adsorptive removal of sulfur compounds from naphtha fractions by using carbon adsorbents, "National Institute of Advanced Industrial Science and Technology".

[12] H. Hosseini., 2012. Novel Methods for Desulfurization of Fuel Oils., Department of Chemical Engineering, Abadan Branch, Islamic Azad University, Abadan, Iran., World Academy of Science, Engineering and Technology, Vol:6, No:11, 2012.

[13] Teng-Chien Chen, Yun-Hwei Shen, Wen-Jhy Lee, Chih-Chung Lin, Meng-Wei Wan., The study of ultrasound-assisted oxidative desulfurization process applied to the utilization of pyrolysis oil from waste tires. Journal of Cleaner Production 18 (2010) 1850-1858.

أكسدة و إزالة الكبريت من النافتا الثقيلة المحسنة بواسطة الموجات فوق الصوتية

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جامعة بغداد, قسم الهندسة الكيمياوية

ألخُلاصة

تبعاً لزيادة ألطلب العالمي على أستخدام وقود أقل ظرراً بالبيئة وبأقل تكلفة ممكنة من ألجانب ألاقتصادي, فأن هذا ألعمل يركز على عملية كفوؤة وقليلة ألكلفة من أجل إزالة ألكبريت من وقود ألنفثا ألثقيلة عن طريق عملية أكسدة مركبات ألكبريت ألمعززة بالموجات فوق ألصوتية حيث أثبتت هذه ألعملية كفائتها في إزالة عميقة للمحتوى ألكبريتي.

بأستخدام نظام ألاكسدة ألمكون من بيروكسيد ألهيدروجين وحامض ألخليك كعامل مساعد من أجل أكسدة مركبات ألكبريت ألعضوية وتحويلها ألى سلفونات حيث تتم إزالة ألاخير بواسطة ألكاربون ألنشط.

ألموجات فوق ألصوتية تزيد من ألمساحة ألسطحية لتلامس نظام الاكسدة مع ألطور ألنفطي في ألنظام ثنائي ألطور وألتي تؤدي لزيادة معدل ألاكسدة لمركبات ألكبريت وبالتالي زيادة كفائة ألازالة وبدون أي تأثير على ألخواص ألكيميائية او ألفيزيائية للوقود.

في هذا ألعمل إزالة ألكبريت بواسطة ألاكسدة هي ألعملية ألرئيسية وقد أختُبرت مع عدة متغيرات والتي تؤثر في كفائة ألإزالة ومِن هذهِ ألعوامل وقت ألتفاعل (5–40 دقيقة), مقدار طاقة ألموجات فوق ألصوتية (20–60 %), كمية ألكاربون ألمنشط (0.01–0.75 غم), كمية ألعامل ألمؤكسِد هيدروجبن بيروكسيد (1–30 مل) وكمية حامض ألخليك (1–15 مل).

في ما يتعلق بتأثير ألعامل ألمؤكسد فقد لوحظ أنه بزيادة كمية ألهيدروجين بيروكسيد تؤدي لزيادة معدل إزالة ألكبريت نظراً لِزيادة مُعدل ألاكسدة لِمركبات ألكبريت ألعظوية وإن ألكمية ألمُناسِبة لِمعالجة 100 مل من ألنفثا ألثقيلة هي 10 مل من هيدروجين بيروكسيد.

في ما يتعلق بتأثير حامض ألخليك فقد لوحِظ بِأنهُ يجب أن تكون كميتهُ مُحددة وهي 7.5 مل من حامض ألخليك لكل 10 مل من ألهيدروجين بيروكسيد حيثُ أن زيادة كمية ألحامض أكثر من ألكمية ألمُحددة تؤدي لِحصول تأثير عكسي وبالتالي تُقلل مِن كفائة ألإزالة للكبريت.

ألكاربون ألمنشط كسطح ممتز وجِد أنَ ألكمية ألمُناسِبة ل100 مل مِن ألنفثا هي 0.1 غم مِن ألكاربون ألمُنشط.

زيادة وقت ألتعرُض لِلموجات فوق ألصوتية يؤدي لِزيادة مُعدل ألاِزالة وقد وجِد أنهُ أفضل فترة زمنية مناسبة هي(10 دقيقة) لِمُعالجة ألنفثا ألثقيلة.

مقدار طاقة ألموجات فوق ألصوتية مؤثر مهم في هذه ألعملية حيث وِجد أنهُ 30% من ألمقدار ألكُلي لِطاقة جهاز ألموجات فوق ألصوتية هو ألمقدار ألمناسب لِأزالة ألكبريت مِن ألنفثا ألثقيلة وفي حالة أستخدام طاقة أعلى فَإن ذلك يؤدي لحدوث تأثير عكسي يؤدي لِتقليل كَفائة إزالة ألكبريت.

على كُلِ حال فإنهٌ أمكن ألحصول على إزالة تصل إلى 89% مِن ألمحتوى ألكبريتي وذلِك عند تطبيق جميع ألمقادير ألمِثالية لِلمتغيرات. إن تفاعُل ألاكسدة ألمعززة بِالموجات فوق ألصوتية لِإزالة ألكبريت من النفثا ألثقيلة هوتفاعل من ألدرجة ألأولى.

الكلمات الدالة: إزالة ألكبريت, ألاكسدة, موجات فوق الصوتية