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 that 7.5 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]. Sulphur 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].
Oxidation desulphurization considered an efficient process to remove Sulphur compounds that can't be removed by the HDS process such as benzo thiophenes 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       | H₂O₂    | Hopkin and Williams, England |
| Acetic acid       | Increase oxidation| 60               | 99       | C₄H₆O₄  | Riedel-De Haen, Germany |
| 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).

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](image)

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.

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.

\[ \text{H}_2\text{O}_2 + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} \]  

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.

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.
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 desulphurization efficiency, 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.

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

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الخلاصة

تبعاً لزيادة أطمب العالمي على استخدام وقود أقل ظرراً بالبيئة وبأقل تكلفة ممكنة من أجل الجانب الاقتصادي، فإن هذا العمل يركز على عملية كفوؤة وقليلة تكلفة من أجل إزالة الكبريت من وقود ألبنتا أنقليلا عن طريق عملية أكسدة مركبات الكبريت المعززة بالموجات فوق الصوتية حيث أثبتت هذه العملية كفاءتها في إزالة عميقة للمحتوى الكبريت.

باستخدام نظام أكسدة ألمكون من بيروكسيد الهيدروجين وحامض الخليك كعامل مساعد من أجل أكسدة مركبات الكبريت العضوية وتحويلها إلى حلول حاوية يتم إزالة الألخائر بواسطة ألكاربون النشط.

الموجات فوق الصوتية تزيد من المساحة السطحية لتلامس نظام الأكسدة مع أطور النفطي في أنظمة أثنائي أسعار التبادل وتؤدي لزيادة معدل الأكسدة وبالتالي زيادة كفاءة إزالة وتقليل أي تأثير على الخواص الكيميائية أو الفيزيائية للمواد.

في هذا العمل إزالة الكبريت بواسطة الأكسدة هي العملية الرئيسية وقد أختبرت مع عدة متغيرات والتي تؤثر في كفاءة إزالة و من هذه العوامل وقت التفاعل (5-40 دقيقة)، مقدار طاقة الموجات فوق الصوتية (20-60 %)، كمية ألكاربون المنخفض (0.10-0.75 غم)، كمية ألكاربون المؤكسد بيروكسيد (1-30 مل) وكمية حامض الخليك (1-15 مل).

في ما يتعلق بتأثير ألكاربون المؤكسد فقد لوحظ أن زيادة كمية الهيدروجين بيروكسيد تؤدي لزيادة معدل إزالة الكبريت نظراً لزيادة معدل الأكسدة لمركبات الكبريت العضوية وان الكمية المناسبة لمعالجة 100 مل من ألبنتا النقلية هي 10 مل من هيدروجين بيروكسيد.

في ما يتعلق بتأثير حامض الخليك فقد لوحظ بأن تكون كمية محددة وهي 7.5 مل من حامض الخليك لكل 10 مل من الهيدروجين بيروكسيد حيث أن زيادة كمية الحامض أكثر من الكميات المحددة تؤدي لحصول تأثير عكسياً وبالتالي تقليل من كفاءة إزالة الكبريت.

كل الكاربون المنخفض كسطح ممتز وجد أن الكميات المناسبة ل100 مل من ألبنتا هي 0.1 غم من ألكاربون المنخفض.
زيادة وقت التعرض للموجات فوق الصوتية يؤدي لزيادة معدل الإزالة وقد وجد أنه أفضل فترة زمنية مناسبة هي (10 دقيقة) لمعالجة النفثة الثقيلة.

مقدار طاقة الموجات فوق الصوتية مؤثر مهم في هذه العملية حيث وجد أنه 30% من المقدار الكلي لطاقة جهاز الموجات فوق الصوتية هو المقدار المناسب لإزالة الكبريت من النفثة الثقيلة وفي حالة استخدام طاقة أعلى فإن ذلك يؤدي لحدوث تأثير عكسي يؤدي لتقليل كفاءة إزالة الكبريت.

على كل حال فإنه من الممكن الحصول على إزالة تصل إلى 89% من الكبريت وذلك عند تطبيق جميع المقدار المناسبة بالموجات فوق الصوتية لإزالة الكبريت من النفثة الثقيلة.

إن تفاعل الأكسدة المتعززة بالموجات فوق الصوتية لإزالة الكبريت هو تفاعل من الدرجة الأولى.

الكلمات الدالة: إزالة الكبريت, أكسدة, موجات فوق الصوتية