Decreasing the Sulfur Content of Crude Oil by Ultra-Sound and Activated Carbon Assisted Oxidative Method

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Abstract. There is a large amount of sulfur compound in crude oil, sulfur gases such as H2S for example are emitted and can affect the environment and finally can cause problems during the processing operation of crude oil. Therefore, in this study, a method for the removal of sulfur from crude oil using an ultrasound device has been proposed. This method is a combination of oxidative method and applying ultrasonic waves to achieve the allowable sulfur content in crude oil. Samples of crude oil have been taken that we got from an Al-Najaf refinery to study the effect of three parameters (activated carbon weight, hydrogen peroxide volume, and acetic acid volume) at 50°C on the desulfurization process. The optimum result of desulfurization has been found to be (81.325%) at activated carbon amount of (9gm) with (H2O2/acetic acid)(40/30)ml.

I. Introduction

The development of technology and the growing desire to crude oil derivatives have led to the increasing amount of sulfur content in the crude oil resulting in poor oil quality [1]. Poor oil quality is because of the presence of some dissolved sulfide, for instance hydrogen sulfide, sulfoether, mercaptan, disulfide, and thiophene [2]. Sulfur components that exist in crude oil are unfavorable in refining process because they lead to first suppression of some of the catalysts used in crude oil processing and second cause erosion problems in pipeline, pumping, and refining equipment [3]. By nature, sulfur compounds that are maintained in fuels cause to release acid gases like sulfur oxides. water Reacting with these gases to form acid rain which harms the buildings and glaze finishes as well [4]. The percent of sulfur content in crude oil is varying between 0.04% w/w for crude oil with low density to about 5% w/w for crude oil with high density [5].

The sulfur compound that exist in crude oil is produced by the process of putrefaction of organic substance, sulfur compound can be segregated from the oil in a shape of hydrogen sulfide which emerges in the correlating gas, an amount of it remains in the liquid [6].Sulfur compounds in crude oil are found in many types such as: Free sulfur is scarcely present in crude oil [7].The appearance of unleashed sulfur is linked to the denudation process of extra complicated sulfur compound [8]. H2S is a harmful, colorless, blazing gas which smells as rotten eggs [9]. Thiols are organosulfur compounds which consist of a sulfhydryl group [10]. The sulfides with linear structure are considered a compounds of organosulfur. Thus, to minimize the effect of the sulfur...
compounds that exist in crude oil and petroleum fractions, several desulfurization methods have been used around the world in the last and current century. such as:

1. Hydrodesulfurization (HDS) method which needs rigorous conditions of operation [14].

2. Adsorptive desulfurization the effectiveness of this method depends on the quality of the sorbent material [14].

3. Oxidative desulfurization is considered to be an auspicious one for its profound desulfurization technology so it can be accomplished under moderate situations [14]:

Otsuki et al. (2000) has used a blend of H2O2 and HCOOH to oxidize a model of diesel (dibenzothiophene derivatives, benzothiophene derivatives, and thiophene derivatives), gas oil (S: 2.17 wt %) come from vacuum process and light gas oil come from atmospheric process (S: 1.35 wt %), he also has tested the relationship between the electron density of the sulfur atoms and the reactivity of the different sulfur-containing compounds and thiophene are usually oxidized with hardness because of lower electron densities while BT as well as other sulfur compounds that have higher electron densities are oxidized to erect their conformable sulfones [12]. Flores et. (2004). Have studied oxidative desulfurization to heavy fuel oil and diesel using Fenton-like catalysts and hydrogen peroxide followed by extraction with acetonitrile [13]. Oxidative desulfurization of a commercial diesel fuel has been studied by Yu et al. (2005). (The content of sulfur, 800 wt. ppm) using hydrogen peroxide, activated carbon, and formic acid system [14]. Oxidative desulfurization has been used by Reda (2006) and that 35 kHz ultrasonic irradiation supports this process to lower the sulfur proportion of the crude oil of Baghdad. The empirical results show the highest rate of the elimination efficiency is was about 76% at 60 oC, 80W/cm2 sonication energy density that is applied for 12 minutes [15].

Chan et. (2008). expound potassium superoxide as a substitutional oxidizing agent for the desulfurization process. Sulfur removal has reached the high is percent that is about 99% For epimine compounds of benzothiophene, dibenzothiophene, as well as a number of selected diesel oil patterns [16]. A study about the process of Sulfur removal of Azeri crude oil has accomplished by Lin et al (2010) using electrical field. This process is achieved in the electrician desalination unit. The results revealed that density and viscosity of crude oil are to be decreased with the extraction of sulfur content whereas some other basic qualities of crude oil tend to be less affected by the process of desulfurization [17]. Hammad et al. (2012) deals with the feed stream of high sulfur content in crude oil by combining solvent plucking out, in addition to hydrotreating and presented a processed crude oil product that is substantially reduced from sulfur content and without any considerable volume waste [18]. Wang et al. (2013) inspected the process of synchronous elimination of sulfur and demetallization of crude oil by electrician desalination based on the corrosion of alkyl thiophene and nickel compounds with the component of Chitosan Schiff under the status of microwave irradiation. By the use of suitable conditions of the microwave irradiation, reaching up to 56 % of sulfur and 82 % of nickel, the removal proportions are accomplished for ideal compounds in crude oil patterns [19].

In the recent study, the main target of the research is to consider the desulfurization process of crude oil by the ultrasound and AC assisted oxidative desulfurization of crude oil.

2. Experimental Part:

2.1. Material and Instruments

Ten specimens of crude oil (100 ml of each sample) have been provided from al-Najaf refinery and have been mixed with activated carbon, hydrogen peroxide (H2O2) and acetic acid to shape ten mixtures as listed in Table (1)
Table 1. The used samples in this project

| Sample | H₂O₂ content (50%) | Acetic acid (ml) | AC (g) | Crude oil (ml) |
|--------|--------------------|-----------------|--------|---------------|
| 1      | 40                 | 30              | 3      | 100           |
| 2      | 40                 | 30              | 7      | 100           |
| 3      | 40                 | 30              | 9      | 100           |
| 4      | 40                 | 30              | 5      | 100           |
| 5      | 40                 | 50              | 5      | 100           |
| 6      | 40                 | 40              | 5      | 100           |
| 7      | 40                 | 20              | 5      | 100           |
| 8      | 30                 | 20              | 5      | 100           |
| 9      | 50                 | 20              | 5      | 100           |
| 10     | 60                 | 20              | 5      | 100           |

Ultrasound Device from Hans-Ulrich Petermann GmbH & Co. KG, German with a power of 400w and frequency of 24 kHz has been used. The used crude oil forms originally comprised of about 1.95 wt. % sulfur content as shown in Table (2).

Table 2. Crude oil sample properties.

| Item        | Measurement | Measurement unit | Test Result |
|-------------|-------------|------------------|-------------|
| 1           | Water Cut  | %                | Trace       |
| 2           | Salt        | PPM              | 13.27       |
| 3           | Sulfur      | %                | 1.95        |
| 4           | API@60F     | --               | 27.61       |
| 5           | Density@15C | Gm/cm³           | 0.8941      |

2.2 Procedure

All the samples (10 once) are entered into an ultrasound device (2 hrs for each sample) and then to be exposed to ultrasound waves to detach the sulfur from the crude oil. After the ultrasound, the shaker device is to be used to mix the components (2 hrs for each sample at a temperature of 50 C) to get excellent mixing state. By using Separation pipe, the crude oil is separated from the hydro solution, add (200 ml) of filtered water(for each sample) to the secession funnel and shake the funnel. Then we separate the aquatic solution again (washing process), by adding (100 ml) of Methanol (for each sample) to the funnel and shake it, after that, the second separation process stats (second washing process). Finally, a filtration paper is used the residual sample has lixiviate after them separation process (for each sample), the specimen has been entered to a sulfur analyzer device and the left sulfur content is measured after the removal process.
3. Results and Discussion

3.1. Effect of activated carbon changing

Through the present study four samples have been used of crude oil which contain steady amount of \( \text{H}_2\text{O}_2 \) and acetic acid contents with a change in activated carbon content. Thus, the results according to this study reveal that the sulfur content in crude oil samples will be decrease if the activated carbon content has increase. This is because of the growing surface area, therefore offering more dynamic spots for the bound of sulfur types. Furthermore, activated carbon stimulates the putrefaction of \( \text{H}_2\text{O}_2 \) so that hydroxyl radicals can be produced which work as strong oxidants like per hydroxyl ions (OH-2) which in turn will oxidize the uncompromising sulfur compounds with much ease into sulfones [20]. The outcomes of this study are shown in Table (2) and figure (1).

Table 3. The result of changing A.C content in samples

| Original sulfur content (Weight) | H2O2 (ml) | Acetic acid (ml) | AC (g) | Remaining sulfur content | Desulfurization % |
|----------------------------------|-----------|------------------|-------|------------------------|------------------|
| 1.95                             | 40        | 30               | 9     | 0.3642                 | 81.325           |
|                                  | 40        | 30               | 7     | 0.3974                 | 79.622           |
|                                  | 40        | 30               | 5     | 0.4387                 | 77.5             |
|                                  | 40        | 30               | 3     | 0.79279                | 59.344           |

Figure 1. The relation between the percent of desulfurization and AC content in the used samples.

3.2. The effect of hydrogen peroxide

Here three samples of crude oil are used which contain a constant amount of Acetic acid and AC besides changing the amount of \( \text{H}_2\text{O}_2 \). As a result, this study shows the same behavior of AC that the sulfur content is reduced by increasing the used volume of \( \text{H}_2\text{O}_2 \). This is because of the reaction between hydrogen peroxide and hydrogen sulfide as well as Mercaptan and Diallyl Sulfides in addition
to another sulfur compounds that exist in crude oil under acid, neutral conditions to form sulfones or sulfoxides [9].

\[ H_2S + H_2O_2 \rightarrow S + 2H_2O \]

From the above reaction, it will be absorbed by AC that presents in the mixture. The results of this study are shown in Table 4 and figure 2.

Table 4. The result of changing hydrogen peroxide in the used sample

| Original sulfur content (Weight) | H\textsubscript{2}O\textsubscript{2} (ml) | Acetic acid (ml) | AC (g) | Remaining sulfur content | Desulfurization % |
|---------------------------------|-----------------|-----------------|--------|-------------------------|-------------------|
| 1.95                            | 30              | 20              | 5      | 0.6978                  | 64.215            |
|                                 | 40              | 20              | 5      | 0.630                   | 67.684            |
|                                 | 50              | 20              | 5      | 0.5854                  | 69.978            |
|                                 | 60              | 20              | 5      | 0.5692                  | 70.806            |

**Figure 2.** The relation between the percent of desulfurization and H\textsubscript{2}O\textsubscript{2} content in the used samples.

### 3.3. Effect of acetic acid

In the last three samples through this study there are H\textsubscript{2}O\textsubscript{2} and AC amount which is fixed whereas acetic acid volume is changed. Increasing the amount of acetic acid in the mixture leads to a rising in the percent of desulfurization because the acetic acid is found to have better oxidation-desulfurization effect than other acids. Also a large amount of acetic acid leads to increase in peracetic acid (CH\textsubscript{3}COOOH) amount that results from the reaction between acetic acid and (H\textsubscript{2}O\textsubscript{2}) [20]. The (CH\textsubscript{3}COOOH) will react with a large number of sulfides and will oxidize it into sulfones or sulfoxides. The results of this study are shown in Table 5 and figure 3.
Table 5. The result of changing acetic acid content in the used sample

| Original sulfur content (Weight) | H$_2$O$_2$ (ml) | Acetic acid (ml) | AC (g) | Remaining sulfur content | Desulfurization % |
|---------------------------------|-----------------|------------------|--------|-------------------------|------------------|
| 40                              | 40              | 20               | 5      | 0.6301                  | 67.684           |
| 40                              | 40              | 30               | 5      | 0.43875                 | 77.5             |
| 40                              | 40              | 40               | 5      | 0.40540                 | 79.21            |
| 1.95                            | 40              | 50               | 5      | 0.3871                  | 80.15            |

Figure 3. The relation between the percent of desulfurization and H$_2$O$_2$ content in the used samples.

4. Conclusions
Depending on this experiment and the results of sulfur removal of crude oil by ultra-sound assisted oxidative desulfurization method, it can be concluded that:

Ultrasonic irradiation enhanced desulfurization reaction and this leads to better desulfurization efficiency.

The highest Desulfurization efficiency obtained is about 81 % of activated carbon amount of (9 gm) with (H$_2$O$_2$/acetic acid) (40/30) ml.

The desulfurization efficiency has increased by increasing the used amount of (AC).

The desulfurization efficiency has increased with the increased amount of oxidant acids (H$_2$O$_2$ and acetic acid) which has been used in the mixture.
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