

# Sulfur Removal of Crude Oil by Ultrasound-Assisted Oxidative Method

Hossein Hosseini and Abdolghader Hamidi

**Abstract**— Because of high percentage of sulfur in crude oil, sulfur gases are produced and polluted the environment and ultimately can also cause problems during processing. Therefore, in this study a method for the removal of sulfur from sour crude oil using ultrasound-assisted oxidative process has been proposed. This method is actually a combination of oxidative and applying ultrasonic waves to achieve very low sulfur content of crude oil.

**Keywords**—Sulfur removal, Crude Oil, Ultrasound-assisted oxidative.

## I. INTRODUCTION

**C**RUDE oil is the world's largest and most extensive source of energy that is consumed as vehicle fuels such as gasoline, jet fuel, diesel and so on. As we know crude oil is a sulfur-containing organic and inorganic compound [1]-[2]. The amount of sulfur is one of the most important factors of crude oil's price. There are a variety of sulfur compounds in crude oil that can be divided into four general categories as follows:

Mercaptanes, sulfides, disulfides and thiophenes.

Figure 1 shows chemical structure of some of the organic sulfur compounds.

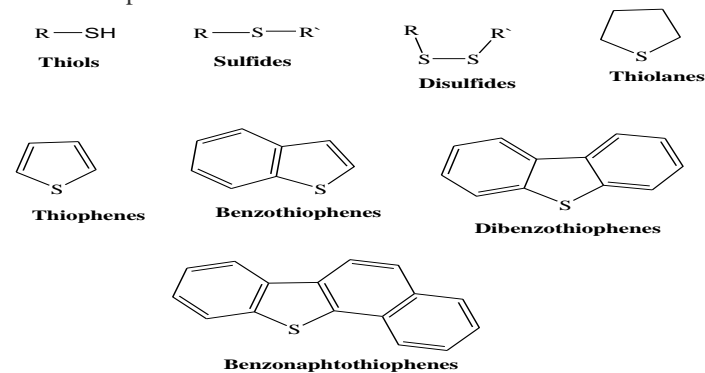


Fig.1. Chemical structure of some of the organic sulfur compounds

Sulfur compounds in the refining process are undesirable because it can lead to deactivation of the catalyst and also causes environmental pollution. Presence of sulfur in heavy petroleum fractions leads to emission of SO<sub>x</sub> which endanger public health. Today, due to stringent environmental regulations there is a strong incentive to reduce sulfur in fuels.

In order to control air pollution because of heavy petroleum fractions combustion, most of the countries released a new regulation requiring the use of low-sulfur petroleum fractions.

H.Hosseini is with Department of Chemical Engineering, Abadan Branch, Islamic Azad University, Abadan, Iran (phone: +986314460117; e-mail: h.hosseini@iaubadan.ac.ir).

A.Hamidi is with Omidieh Branch, Islamic Azad University, Omidieh, Iran.

It means that the sulfur content of petroleum fractions used in vehicles be limited to 15 ppm.

Hydrodesulfurization process has been a part of refineries for years, but new rules impose a better technology in this field. During the past years, alternative technologies have been studied by many researchers [3]-[4]-[5], among which ultrasound-assisted oxidative desulfurization has found a wide attention. Ultrasound-assisted oxidative desulfurization method for sulfur omission has main benefit compared to other common methods like HDS. Oxidative desulfurization technology as a promising method for deep removal of sulfur under mild conditions has been discussed. This method in comparison to HDS requires much less pressure, temperature and operating costs. This method is based on the oxidation of sulfur compounds and finally the formation of sulfoxides or sulfones. These materials are highly polar and therefore more easily by extraction with solvent or adsorption can remove them from the oil.

In the present work, the ultrasound-assisted oxidative desulfurization of crude oil was studied. And also, the factors that affect on this process such as frequency, power, catalyst, temperature and time are investigated.

## II. EXPERIMENTAL

### A) Material and Instruments

Crude oil, acetic acid, hydrogen peroxide and formic acid were provided from Abadan Refinery Company. An ultrasound apparatus manufactured by Sonics and Materials Inc. with power of 400w and frequency of 24 kHz has been used. The sulfur compounds in the feed were analyzed by sulfur analyzer manufactured by Horiba Company in Abadan Refinery. Properties of used crude oil are shown in Table 1.

TABLE 1  
PROPERTIES OF SOUR CRUDE OIL

SG	0.88
Water	% 0.1
API	28
Salt	18 gr/cm <sup>3</sup>
Vapor pressure	6.4 psi
Sulfur content	5.2 wt%

### B) Procedure

In this procedure 15 ml acetic acid and 10 ml of hydrogen peroxide and 25 ml of oil was used. Ultrasonic waves during different time intervals from 1 to 50 min were applied to the reaction mixture. And then the efficiency of the reaction and

the parameters of ultrasonic irradiation time, range of ultrasonic irradiation, and the role of each of the reagents in the reaction (acetic acid and hydrogen peroxide) were studied. And the best efficiency (optimum conditions) was selected for the process.

And finally the oil and aqueous phases were separated, and then the oil phase using three polar solvent such as methanol, acetonitrile and water was extracted by a glass funnel. The residual sulfur concentration in the oil phase was characterized by a sulfur Analyzer device. After that, the process was carried out without applying ultrasonic waves.

### III. RESULTS AND DISCUSSION

In oxidation process, sulfides are oxidized to sulfones or sulfoxides by using proxy acids such as hydrogen peroxide and acid-carboxylic. A useful method for desulfurization of oil using organic acids and hydrogen peroxide according to the following reaction is suggested.

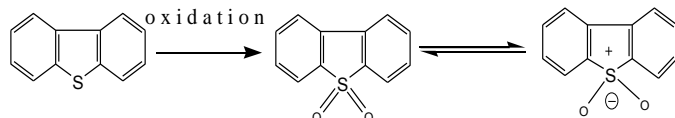


Fig. 2 Oxidation of Dibenzothiophene compounds.

Despite the good performance of this kind desulfurization (oxidation using organic acids), this method is very time consuming and it may be necessary to compensate for the use of metal catalysts. Therefore, to minimize reaction time, ultrasonic irradiation can provide the optimum conditions for chemical reactions without catalysts.

Tests indicate the best results from desulphurization to obtain in 20-200 KHz frequencies. The best conditions are preferably obtained in 20-50 KHz. The best results are obtained in power range 30-300 W/cm<sup>2</sup> or 5-100 W/cm<sup>2</sup> preferably. Generally, sonic analysis of organic contaminants in aqueous solutions in high frequencies (20-850 KHz) would result in higher efficiency than low frequencies (20-80 KHz). However if the ultrasonic power is higher than 200W, we witness desulfurization rate with ultrasonic power increase which is resulted from cavitations. In this study, ultrasonic radiation with amplitude of 70% was applied to the mixture.

Results show that in the ultrasonic irradiation time of 1 to 10 minutes early, only about 56.4% of the sulfur is removed. But after 10 minutes the slope at once to increase sulfur removal efficiency is more strongly and it took 20 minutes to reach 93.4% removal rate. However, without using of ultrasonic waves, the maximum sulfur removal is about 36%.

These results show that methanol can extract sulfur compounds, especially DBT from the organic phase to the aqueous phase.

To investigate the best acid for desulfurization process, these experiments were done by formic acid and propanoic acid too.

The results obtained in this study are shown in Table 2. Efficiency of 93% for formic acid shows the same efficiency of formic acid and acetic acid. Desulfurization efficiency by propanoic acid was less than acetic acid which is probably due to the less solubility in H<sub>2</sub>O<sub>2</sub> and reducing of sulfur contents.

TABLE II  
EFFICIENCY OF DESULFURIZATION FOR DIFFERENT  
ACIDS IN EXTRACTION PROCESS

Percent of desulfurization	Chemical structure	Acid type
93.4	CH <sub>3</sub> COOH	Acetic acid
93	HCOOH	Formic acid
66.2	H <sub>3</sub> CCH <sub>2</sub> COOH	Propanoic acid

### IV. CONCLUSION

Experiments show that ultrasonic irradiation enhanced desulfurization reaction. Moreover, the oxidation of sulfur compounds can occur at the interface or in-phase oxidants that are necessary to good dispersion. Desulfurization efficiency was about 93.2% when ultrasound was used. However, when ultrasonic irradiation wasn't used (reaction with mechanical stirring) even after 20 min, desulfurization efficiency was less than 62.5%. Based on these results, it can be suggested that oxidative desulfurization method using ultrasound is a useful method for desulfurization of crude oil.

### REFERENCES

- [1] I.V. Babich and J.A. Moulijn, "Science and technology of novel processes for deep desulfurization of oil refinery streams", *Fuel*, vol.82, pp. 607-31, 2003.  
[http://dx.doi.org/10.1016/S0016-2361\(02\)00324-1](http://dx.doi.org/10.1016/S0016-2361(02)00324-1)
- [2] F.A. Duarte, *Fuel*, vol. 90, pp.2158-2164, 2011.  
<http://dx.doi.org/10.1016/j.fuel.2011.01.030>
- [3] L. Lu et al., *Energy Fuels*, vol.21, pp. 383-384, 2007.  
<http://dx.doi.org/10.1021/ef060345o>
- [4] X.L. Ma, K. Sakanishi, T. Isoda, I. Mochida, *Energy Fuel*, vol.9 pp.33-37, 1995.  
<http://dx.doi.org/10.1021/ef00049a005>
- [5] S. Mayo, N.J. Gudde, E. Brevoord, F. Plantenga, Paper AM-02-38, National Petroleum and Refiners Association annual meeting, San Antonio, TX, pp.17-, 2002.