Petroleum Research

Petroleum Research 2018(June-July), Vol. 28, No. 99. 6-9

DOI: 10.22078/pr.2017.2732.2260

An Investigation of the Effect of Interfacial Tension on the Ultrasound Assisted Oxidative Desulfurization (UAOD)

Mohammad Reza Jalali and Mohammad Amin Sobati*

School of Chemical, Petroluem and Gas Engineering, Iran University of Science and Technology (IUST), Tehran, Iran

Sobati@iust.ac.ir

Received: April/06/2017 Accepted: September/19/2017

Abstract

Ultrasound assisted oxidative desulfurization (UAOD) is a new process for the sulfur removal from different middle distillate cuts. In the UAOD process, at first, the sulfur-containing compounds are oxidized using a suitable oxidation system under ultrasound irradiation. Then, the oxidized sulfur-containing compounds are separated by solvent extraction. In the present study, the effect of interfacial tension between aqueous and hydrocarbon phases on the sulfur removal of diesel fuel has been investigated for the first time. The selected oxidation system was hydrogen peroxide/ formic acid system. In this regards, three different surfactants including anionic, cationic, and nonionic surfactants have been evaluated. The results revealed that the application of sodium dodecyl sulfate (SDS) as an anionic surfactant and cetyltrimethylammonium bromide (CTAB) as a cationic surfactant leads to the sulfur removal of 82.65 and 83.10% after oxidation followed by solvent extraction respectively. The sulfur removal in the absence of surfactants was 81.61% in the same oxidation and extraction conditions. The application of span 60 as a nonionic surfactant leads to a decrease in sulfur removal to % 78.65 in the same oxidation and extraction conditions. However, the application of span 60 leads to about 3% increase in the sulfur removal in comparison with the case without surfactant after the oxidation step. Therefore, the addition of surfactants can lead to a positive effect on the oxidation step due to decreasing the interfacial tension between aqueous and hydrocarbon phases and a negative effect on the extraction step of the UAOD process.

Keywords: Interfacial Tension, Oxidative Desulfurization, Ultrasound Waves, Extraction, Diesel.

Introduction

Sulfur-containing compounds are one of the important components available in the petroleum derived fuels. In other words, sulfur is the third significant element after carbon and hydrogen which composes crude oil [1]. The presence of this element in fossil fuels leads to environmental problems. Deactivation of emission control catalysts in the internal combustion engines, SO_x emissions and also various problems in general health are cases in this point [2]. Considering these issues, nowadays, very stringent worldwide regulations on the sulfur content of transportation fuels have been legislated. Therefore, removal of sulfur-containing compounds from middle distillate fuels is necessary in order to produce clean fuels. Ultrasound Assisted Oxidative Desulfurization (UAOD) is a new technology to produce clean fuels. UAOD is a two-stage process. In the first stage (i.e., oxidation stage), the sulfur-containing compounds present in the middle distillate fuel are oxidized to their corresponding sulfoxides and sulfones. In the second stage (i.e., separation stage), the polar oxidized products are separated using different separation processes, such as solvent extraction and adsorption [3].

Ultrasound effects are attributed to the phenomenon called cavitation which is the formation, growth, and collapse of the microbubbles in the liquid medium that generates an excessive local temperature and pressure in the reaction media [4]. In general, the use of ultrasound irradiation in sonochemistry can improve chemical reactions by acceleration and initiation of alternative pathways of reactions [5]. One of the effective parameters in the cavitation phenomenon is interfacial tension which substantially affects mass transfer, heat transfer and also bubble cavitation formation. Due to the fact that the influence of interfacial tension over aqueous and hydrocarbon phases in UAOD has not been investigated yet, a study into the effect of interfacial tension was conducted here in details.

Methodology

In the present work, UAOD of gas oil with sulfur content of 1550 ppmw was investigated using a mixture of hydrogen peroxide and formic acid as the oxidant and catalyst, respectively. The reactions were done under the reaction temperature of 50°C, oxidant to sulfur molar ratio of 27.5, formic acid to sulfur molar ratio of 70, sonication time of 10 min, gas oil to surfactant mass ratio of 320 and ultrasound power per gas oil volume of 5 W/mL. Also, the oxidized gas oil was extracted using acetonitrile as solvent for 30 min according to the solvent to gas oil volume ratio of 1 in a single extraction stage at ambient temperature.

To investigate the influence of the interfacial tension on UAOD performance, an experimental test was conducted in which three surfactants of anionic, cationic and nonionic were utilized as additives. These additives which were included SDS[1] (as anionic), CTAB[2] (as cationic) and Span-60 (as nonionic) were added to the system to reduce the interfacial tension of the two phases.

Discussion and Results

The amounts of the interfacial tension between the two phases either with or without surfactant are presented in Figure 1.

1. Sodium Dodecyl Sulfate
2. CetylTrimethylAmmonium Bromide

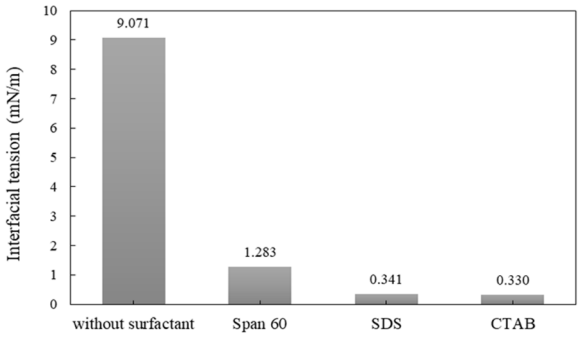

Figure 1: The interfacial tension of aqueous-hydrocarbon phases with and without surfactant.

Depending upon this figure, surfactant greatly reduces the interfacial tension between the aqueous and hydrocarbon phases.

"Figure 2" shows the effects of the presence of surfactant on the performance of the UAOD process. According to the Figure 2, one could perceive that using either anionic or cationic surfactants in the UAOD process leads the sulfur removal of the gas oil to slightly enhance.

This comes from the fact that the cavitation bubbles are formed much easier by reducing the amount of the interfacial tension. Therefore, as the interfacial tension reduces, the cavitation threshold decreases, and then cavitation is done at lower acoustic pressure [6].

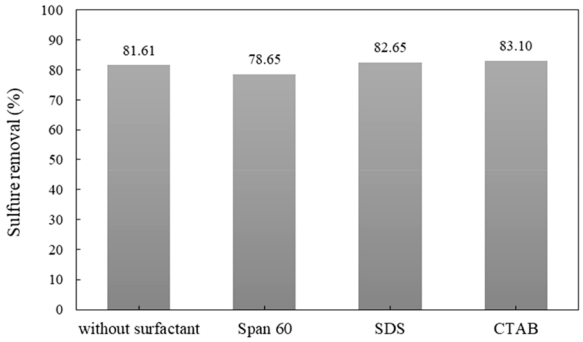

Figure 2: The performance of the UAOD process in the presence and absence of surfactant.

This results in the improvement of the desulfurization efficiency. The reduction of the sulfur removal performance when using Span 60 relates to its molecular structure. Unlike the two previous additives (SDS and CTAB), Span 60 almost diffuses to the hydrocarbon phase and interrupts the extraction operation.

Conclusions

Herein, the effect of three different surfactants on the performance of ultrasound assisted oxidative desulfurization process was studied. The main achievements obtained in this work are summarized as follows:

1- An increase in the desulfurization was observed in case of using the anionic and cationic surfactants.

2- Although enhancing the performance of the oxidation step in UAOD process, the nonionic surfactant could not increase the desulfurization efficiency because of its interruption in the extraction step.

3- The remained surfactants in the hydrocarbon phase makes the phase separation difficult after extraction step. Therefore, a centrifugal equipment is needed to separate the treated gas oil and the extracted solvent phases.

Generally speaking, while making a good impact on the oxidation step, surfactants affect the extraction step performances negatively in the UAOD process.

References

[1]. Soleimani M., Bassi A. and Margaritis A., *"Biodesulfurization of refractory organic sulfur compounds in fossil fuels,"* Biotechnology advances, Vol. 25, pp. 570-596, 2007.

[2]. Fan Q., Zhao D. and Dai Y., *"The Research of ultra-deep desulfurization in diesel via ultrasonic irradiation under the catalytic system of* H_2O_2-CH_3COOH-$FeSO_4$*,"* Petroleum Science and Technology, Vol. 27, pp. 302-314, 2009.

[3]. Jalali M. R. and Sobati M. A., *"Intensification of oxidative desulfurization of gas oil by ultrasound irradiation: Optimization using Box–Behnken design (BBD),"* Applied Thermal Engineering, Vol. 111, pp. 1158-1170, 2017.

[4]. Rahimi M., Shahhosseini S. and Movahedirad S., *"Continuous-flow ultrasound assisted oxidative desulfurization (UAOD) process: An efficient diesel treatment by injection of the aqueous phase,"* Ultrasonics Sonochemistry, Vol. 39, pp. 611-622, 2017.

[5]. Dai Y., Qi Y., Zhao D. and Zhang H., *"An oxidative desulfurization method using ultrasound/ Fenton´s reagent for obtaining low and/or ultra-low sulfur diesel fuel,"* Fuel processing Technology, Vol. 89, pp. 927-932, 2008.

[6]. Kuijpers M. W. A., Van Eck D., Kemmere M. F. and Keurentjes J. T. F., *"Cavitation-induced reactions in high-pressure carbon dioxide,"* Science, Vol. 298, pp. 1969-1971, 2002.