

Novel Methods for Desulfurization of Fuel Oils

H. Hosseini

Abstract—Because of the requirement for low sulfur content of fuel oils, it is necessary to develop alternative methods for desulfurization of heavy fuel oil. Due to the disadvantages of HDS technologies such as costs, safety and green environment, new methods have been developed. Among these methods is ultrasound-assisted oxidative desulfurization. Using ultrasound-assisted oxidative desulfurization, compounds such as benzothiophene and dibenzothiophene can be oxidized. As an alternative method is sulfur elimination of heavy fuel oil by using of activated carbon in a packed column in batch condition. The removal of sulfur compounds in this case to reach about 99%. The most important property of activated carbon is ability of it for adsorption, which is due to high surface area and pore volume of it.

Keywords—Desulfurization, Fuel oil, Activated carbon, Ultrasound-assisted oxidative desulfurization.

I. INTRODUCTION

PRESENCE of sulfur in heavy fuel oils leads to emission of SO_x which endanger public health. In order to control air pollution because of heavy fuel oils combustion, most of the countries released a new regulation requiring the use of low-sulfur fuel oils. It means that the sulfur content of fuel oils 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 [1-7], among which ultrasound-assisted oxidative desulfurization has found wide attention.

In the present work, the ultrasound-assisted oxidative desulfurization of Naphtha and Pentane was studied in the Hydrogen peroxide / Acetic acid system. And also, as a alternative technology desulfurization in the activated carbon and molecular sieve packed beds have been studied and the results is compared to ultrasound-assisted oxidative desulfurization.

II. EXPERIMENTAL

A. Material and Instruments

Naphtha, pentane, acetic acid, hydrogen peroxide, activated carbon in powder and granulated form, molecular sieve, dimethyldisulfide and silica gel were provided from Abadan and Tabriz Petrochemical Companies.

Seven fuel oils with different sulfur contents at 530 ppm, 22 ppm, 17 ppm, 5.8 ppm, 3.5 ppm, 5 ppm and 6.30 ppm have been used for experiments.

An ultrasound apparatus manufactured by Sonics and Materials, Inc. has been used. The sulfur compounds in the feed were analyzed by gas chromatography in Tabriz

Petrochemical Company. And also, It is used a pilot plant (length: 1m, width: 10cm) for batch desulfurization of naphtha and pentane.

III. PROCEDURE, RESULTS AND DISCUSSION

At the first, 100 cc of naphtha with measured sulfur as 22 ppm was placed in ultrasound bath for 10 minutes to which 1cc acetic acid and 1 cc hydrogen peroxide was added. Purity of hydrogen peroxide was read to be 30%. Results from sulphur measurement indicated deletion efficiency to be 60% in 10 minutes which means remained sulfur to be 8.8 ppm.

Tests indicate the best results from desulfurization 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/cm² or 5-100 W/cm² 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). Desulfurization rate in low power rates (0.1-0.4 W/cm²) in Naphtha-Hydrogen Peroxide-Acetic acid system decreases with power rate. However if the ultrasonic power is higher than 200 W, we witness desulfurization rate with ultrasonic power increase which is resulted from cavitation. As well ultrasonic power is related to the solution volume. Regular ultrasonic range is 50-200 W while the solution volume ranging from 50 to 60 cc gives the best possible desulfurization. Post ultrasound solution is consisted form aqueous and organic phases. Organic phase includes sulfones obtained from oxidation reactions. We obtained sulfones using liquid-liquid extraction with the aid of dimethyl formamide polar solution. Oxidized naphtha was extracted two times with dimethyl formamide. In the second recovery naphtha was increased for about 10%. Desulfurization efficiency increased with increased solution to naphtha rate and number of extractions.

Practical problem in this method is that in oxidizing desulfurization process with the aid of ultrasound, about 80% of naphthalene alkyls may be lost in liquid-liquid extraction and operational problems appears with increased system dimension in industrial application. For this reason and to lower naphthalene alkyls lose it would be better to use solid absorption system such as alumina or zeolite for solution extraction, instead of dimethyl formamide [2].

The present paper shows that using solid absorbents has no negative effect on the main fuel hydrocarbons and the unit scale is made more practical as the result of very low solid volume used compared with the liquid solution.

Another reason for using such solid absorbent, like Alumina, is their capability in easy reduction with calcinations operation. Meantime sulfones are destructed thermally in this temperature. Using Hydrogen Peroxide-Activated Carbon-Acetic Acid system, percentage of the remaining sulfur would

be much lower after desulphurization compared with the usage of Hydrogen Peroxide-Acetic Acid system.

In another test 100 cc naphtha with measured sulfur as 22 ppm was placed in ultrasound bath for 10 minutes to which 1 cc hydrogen peroxide was added. Purity of hydrogen peroxide as read to be 30%. Results from sulfur measurement indicated the omission efficiency to be 20% in 10 minutes.

In the third test 2 cc hydrogen peroxide and 2 cc acetic acid was added to 100 cc of naphtha with measured sulfur as 17 ppm. Hydrogen peroxide purity was 30%. Remainder sulfur was 7 ppm so omission efficiency was 58% in this test.

In the fourth test 5 cc acetic acid was added to 100 cc naphtha with measured sulfur of 28 ppm. Sulfur measurement indicated the omission efficiency to be 7%. Results indicate hydrogen peroxide to have significant role in omission of sulfur.

In the next test 100 cc of pentane with measured sulfur of 3.5 ppm was added to the bed consisted from 10 gr active carbon. Therefore omission efficiency is amounted to 57%.

In the sixth test 100 cc of pentane with measured sulphur as per 3.5 ppm was added to the bed consisted from 20 gr active carbon. Sulfur measurement results after one hour indicated omission efficiency to be about 100% so that the remainder sulfur was ppb. It shows that absorbent rate has significant role in sulfur omission efficiency.

In the seventh test 240 cc pentane with measured sulfur of 5.8 ppm was quickly passed through 50 gr of activated carbon. Results from measuring sulfur indicated the remainder sulphur to be 3.9 ppm with omission efficiency of 32.76%.

In the eighth test 750 gr of granular activated carbon was weighted and added to decanter. 500 cc pentane was passed through activated carbon bed. 300 cc pentane was used for saturation of activated carbon. Pentane sample contained 6.5 ppm of sulfur which was reduced to 1.5 ppm after omission. Therefore omission efficiency was 77%. Benzene was measured by GC to be ppb while no benzene related peak was appeared after omission. Therefore, results indicated that activated carbon is able to omit pentane sulphur intermittently.

Two absorbent beds were selected in the ninth test. One contained 570 gr of activated carbon and the other had 554 gr of molecular sieve. At first 400 cc pentane passed through the molecular sieve bed. 250 cc of pentane obtained from the first bed (containing molecular sieve) passed through the second bed containing activated carbon, resulted in delivery of 150 cc of pentane. Analysis results indicate that pentane water level was 20 ppm in the zero time (before omission). It was 10 ppm leaving the first bed and reached 5 ppm passing through the second bed. Sulfur rate was 5 ppm in the feed and was finally less than 1 ppm in the second column output (activated carbon bed). In the tenth test 25 gr of activated granular carbon and 25 gr of powder activated carbon were weighted. Then 100 cc pentane was placed near powder activated and granular activated carbon separately for one hour. The sulfur rate was 5 ppm in the feeding. Sulfur rate in the pentane sample adjacent to the powder activated carbon was 1.34 while the rate was reported to be 2.4 ppm in the pentane sample adjacent to granular activated carbon. In the eleventh test 25 gr of granular activated carbon and 25 gr of powder activated carbon were weighted. Then 100 cc pentane was placed near powder activated and granular activated carbon separately for

two hours. The sulfur rate was 6.3 ppm in the feeding. Sulfur rate in the pentane sample adjacent to the powder activated carbon was 1.6 while the rate was reported to be 1.8 ppm in the pentane sample adjacent to granular activated carbon. In the twelfth test, pentane omission pilot was made (in length of 1 meter and 10 cm width). Two columns were selected. 1 kg of silica gel of 5x type from Olefin unit and 0.5 kg of Norit granular activated carbon was added to the first and second columns respectively. 5 liters of pentane containing 5 ppm sulfur was passed through the two said beds. Discharge rate was set at 30 ml/min. After omission of the sulfur it reached the ppb. In the thirteenth test 1 kg of silica gel of 5x type from olefin unit was added to the 1st column and 0.5 kg of Norit granule activated carbon was added to the second column. 5 Lit of pentane containing 50 ppm sulphur passed through the said two beds. Discharge rate was set at 100 ml/min. After omission of sulfur it reached 17 ppm.

In the fourteenth test 1 kg of silica gel of olefin 5x type was added to the 1st column and 0.5 kg of powder activated carbon from recovery unit was added to the second column. 5 Lit of pentane containing 5 ppm sulfur passed through the said two beds. Discharge rate was set at 100 ml/min. After omission of sulfur it reached ppb.

In the last test 3 droplets of dimethyldisulfamide was added to 50 cc of pentane. Measured sulfur was reported to be 530 ppm. 50 cc of the sample was added to Jurget balloon 500 and reached to 500 cc. Then the sulfur was measured and reported to be 50 ppm which means the omission to be about 90%.

As indicated in fig.1 increased molar rate of hydrogen peroxide to sulfur up to 0.02, discharged sulfur from naphtha would increased too while with higher rate sulfur discharge would be decreased.

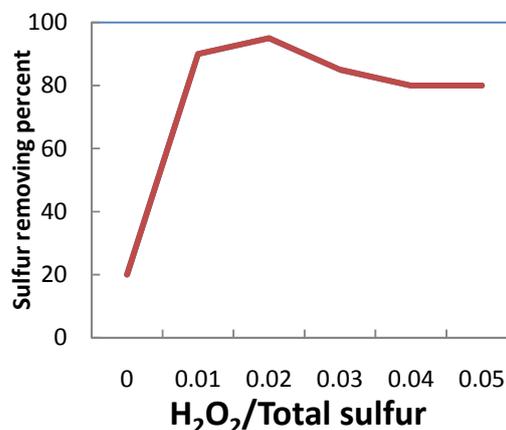


Fig. 1 Sulfur removing percent versus mole fraction changing

IV. CONCLUSION

In this research project the ultrasound-assisted oxidative desulfurization was compared to activated carbon packed bed system for removal of sulfur from naphtha and pentane. Primary tests indicate that when using hydrogen peroxide without acetic acid, removed sulfur would be very low (about 20%), but the rate would significantly increase (60%) under similar conditions when using acetic acid. As well further tests indicated that when using activated carbon the highest rate of

sulfur omission can be seen (100%) under batch state while when using the system continuously sulfur omission rate would decrease. Ultrasound-assisted oxidative desulfurization method for sulfur omission has main benefit compared to other common methods like HDS. In this method tests can be made in atmospheric pressure and relatively low temperatures. As well no metallic catalyst is necessary in this method for sulfur removal. The present research work indicates that ultrasound method and activated carbon packed bed are suitable alternatives for removal of sulfur from different oil compounds.

REFERENCES

- [1] Song, C. et al., Ultra deep desulfurization by selective adsorption, *Catalysis Today*, 111, 74-83, 2006.
- [2] Wu, Z. et al., *Ultrasonics Sonochemistry*, 17, 1027-1032, 2012.
- [3] Yu, G. X. et al., *Energy Fuels*, 19, 447-452, 2005.
- [4] Brink, P. J. , Catalyst for the Selective Oxidation of Sulphur Compounds to Elemental Sulphur, Process for Preparing Such a Catalyst and Method for the Selective Oxidation of Sulphur Compounds to Elemental Sulphur, US Patent. No 5,286,697, Feb 1994.
- [5] Mei, H. et al., *Fuel*, 82, 405-414, 2003.
- [6] Aida, T., *Europa Patent* 565324, 1993.
- [7] Tu, S.P. et al., *Journal of Environmental Engineering Science*, 1, 237-246, 2002.