DESULFURIZATION OF FUEL OILS USING AN ADVANCED OXIDATION METHOD

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Introduction

The sulfur content reduction in fuel oils is traditionally carried out by hydrodesulfurization (HDS), where the C-S bond is broken by hydrogenolysis to produce H_2S and sulfur-free hydrocarbons[1]. However, side reactions occur during the process, such as, hydrogenation and cracking; therefore, high concentration of H_2 and drastic experimental conditions (over 350ºC and 100 bar) are needed in order to eliminate considerable amounts of sulfur.

An interesting alternative for sulfur elimination is the oxidative desulfurization using Fenton-like catalysts and hydrogen peroxide[2-6]. In this case, hydrogen peroxide reacts with the catalyst to generate hydroxyl radicals (·OH), a very strong oxidant agent that reacts with the sulfur compounds to yield sulfoxides and/or sulfones. These compounds are more polar than the no oxidized species, so they can be extracted with a polar organic solvent, like acetonitrile and alcohol, or by passing through an ionic column. This process is achieved at mild reaction conditions (less than 100ºC and atmospheric pressure), but it proceeds very slow.

On the other hand, it has been also found that hydroxyl radical can be produced by ultrasound through cavitations in liquid solutions. It is believed that ultrasonic waves generate and collapse microbubbles very fast, and temperatures around 5000ºC and pressures over 300 bar are reached in the liquid-gas interphase[7-13]. These drastic conditions are able to break molecules to generate free radicals in the following way:

$$H_2O \longrightarrow H\cdot + OH\cdot$$

$$H_2O_2 \longrightarrow 2OH\cdot$$

$$RR' \longrightarrow R\cdot + R'\cdot$$

So, hydroxyl radicals are generated, and the oxidative desulfurization process can be carried out. Additionally, dyhydrogenation and recombination reactions can occur through the free radical mechanism[10-13].

In the present work, the oxidative desulfurization of fuel oils assisted by ultrasound was analyzed. It was studied the effect of hydrogen peroxide concentration, the fuel oil to aqueous solution volumetric ratio, and type of catalyst. The Fenton-like catalysts studied were ferric chloride and cupper sulfate.

Experimental

Fuel Oil Samples. Heavy fuel oil was got from Altamira Refinery (Tamaulipas, Mexico) and used as received. Diesel was purchased in a gas station and used as received.

Reactants. Deionized water was obtained *in situ* by passing distilled water through an ionic bed column. Acetonitrile (HPLC grade), hydrogen peroxide solution (30 wt%), ferric chloride (reactant grade) and copper sulfate (reactant grade) were purchased from J. T. Baker and used as received.

The experiments were made in a Cole Palmer apparatus, model 8890R-MTH, at constant frequency of 47 kHz and using a mechanical stirrer with a variable speed rate.

The experimental procedure consisted on preparing an aqueous solution with or without H_2O_2 and catalyst. This solution was added to the fuel oil and mixed using the mechanical stirrer. Then, the reactive mixture was put in the ultrasonic bath, and the ultrasonic energy was applied during the desired time. After the reaction period, it was allowed the separation between the aqueous phase and the organic phase. Next, the organic phase was washed with acetonitrile and mechanical agitation to extract the oxidized sulfur compounds. Finally, the fuel oil was separated from the acetonitrile solution and its sulfur content was determined.

The sulfur content in fuel oil was determined according to the ASTM-D129 Method.

Results and Discussion

The initial sulfur content in the heavy fuel oil and diesel was 3.85 and 0.04475 wt%, respectively. To determine if the acetonitrile could extract sulfur compounds from the fuel oil, samples of each fuel oil were washed once with acetonitrile. For the heavy fuel oil, the sulfur reduction due to acetonitrile washing was 18.4%; on the other hand, no sulfur reduction was obtained in diesel.

The effect of reaction time was studied for both fuel oils using a 3 wt% hydrogen peroxide aqueous solution without catalyst, and a fuel oil to aqueous solution volumetric ratio of 2. The experimental results are shown in **Figure 1**. The reduction of sulfur was greater in diesel than in heavy fuel oil. This can be explained by the complexity of the sulfur compounds in the heavy fuel oil compared to those in diesel. In the case of heavy fuel oil, the sulfur compounds are more hindered, so the oxidation by the hydroxyl radical is more difficult. On the other hand, it was found that the amount of sulfur eliminated from the heavy fuel oils decreased as the reaction increased from 7.5 to 20 min. This could be due to secondary reactions during the ultrasound treatment. In addition to the oxidation reaction, the ultrasound promotes dehydrogenation, cracking and recombination of heavy molecules, so the large hydrocarbon chains can react to make less available the sulfur compounds, and more difficult to extract during washing with acetonitrile. Also, an increase in the viscosity of the heavy fuel oil was observed after 20 min of ultrasonic treatment, which confirm that some changes in the physicochemical properties have occurred. Therefore, even in the case the sulfur compounds had been oxidized, their extraction with acetonitrile would be more difficult due to mass transfer problems. For diesel no appreciable effect was observed as the reaction time increased, and the small decrease was attributed to experimental error during the experimentation and sulfur content analysis.

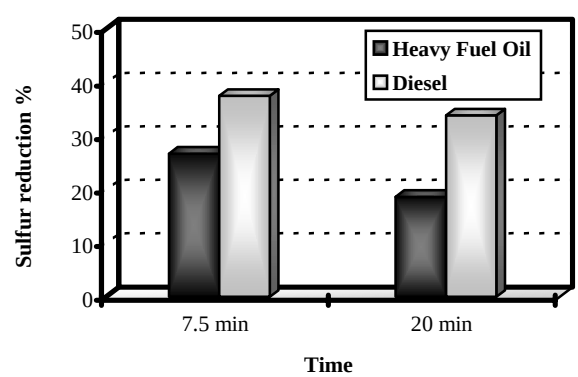

Figure 1. Effect of reaction time in the reduction of sulfur for heavy fuel oil and diesel.

The effect of hydrogen peroxide concentration was studied in both fuel oils. The volumetric fuel oil to aqueous solution was 2 in all experiments, and the reaction time was 7.5 min. The experimental results are shown in **Figure 2**. In absence of H_2O_2 in the reaction mixture, the sulfur was not eliminated from diesel, and the reduction of sulfur from heavy fuel oil was minimal, and even less than when it was just washed with acetonitrile. Again, this could be explained by secondary reactions that impedes the elimination of sulfur polar compounds during the washing stage. As the amount of H_2O_2 increases from 0 to 6 wt%, the reduction of sulfur content increased for the heavy fuel oil. This can be attributed to the generation of more hydroxyl radicals from the H_2O_2, which oxidize more sulfur compounds. Further increase to 10 wt% (not shown in Figure 2) did not enhance the sulfur reduction. On the other hand, the sulfur reduction on diesel enhanced when the H_2O_2 concentration increase to 3 wt%, but further increase in the H_2O_2 concentration to 6 wt% did not improve the sulfur reduction, and even it decreased a little, which was attributed to the experimental error that occurred in both experiments during the reaction and analytical stages.

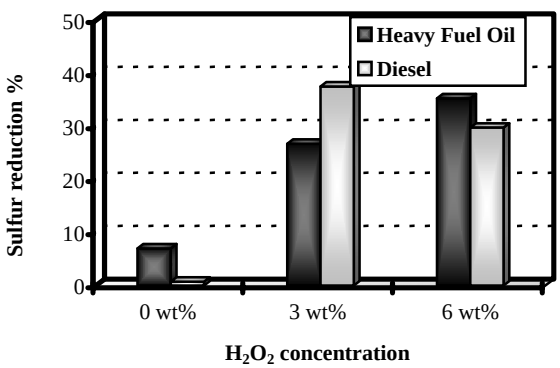

Figure 2. Effect of H_2O_2 concentration in the reduction of sulfur for heavy fuel oil and diesel.

The use of Fenton-like catalysts was studied for the sulfur reduction in heavy fuel oil and diesel at different conditions. The studied catalysts were $FeCl_3$ and $CuSO_4$. In the case of heavy fuel oil, when H_2O_2 was added to the reaction mixture, its concentration in the aqueous phase was 6 wt%. Conversely, for experiments with diesel the concentration of H_2O_2 was 3 wt% when it was included in the reaction mixture. In both cases the reaction time was 7.5 min. The experimental results are shown in **Figure 3**. In the case of heavy fuel oil, it was observed that the absence of H_2O_2 slightly improved the sulfur reduction, and almost the same catalytic activity was observed for both catalysts, around 34%. On the other hand, for diesel no sulfur reduction was observed in the absence of H_2O_2; also, the only active catalyst was $FeCl_3$ getting around 70% of sulfur reduction, and only around 5% of sulfur reduction was obtained when $CuSO_4$ was used.

Finally, the effect of the oil:aqueous solution volumetric molar ratio was studied for heavy fuel oil and diesel at different conditions. In the case of heavy fuel oil, experiments were carried out without catalysts and with a H_2O_2 concentration of 6 wt%; for diesel, the experiments were achieved using $FeCl_3$ and a H_2O_2 concentration of 3 wt%. In both cases, the reaction time was 7.5 min. The experimental results are presented in **Figure 4**. In the case of heavy fuel oil, when the amount aqueous solution increased up to a volumetric molar ratio of 1:1, the sulfur reduction slightly improved from 35 to 39%; however, further addition of aqueous solution decrease the sulfur reduction to 19% when the volumetric molar ratio of oil/aqueous solution was 0.5. On the other hand, for diesel the sulfur reduction always decreased as the amount of aqueous solution augmented in the reaction mixture.

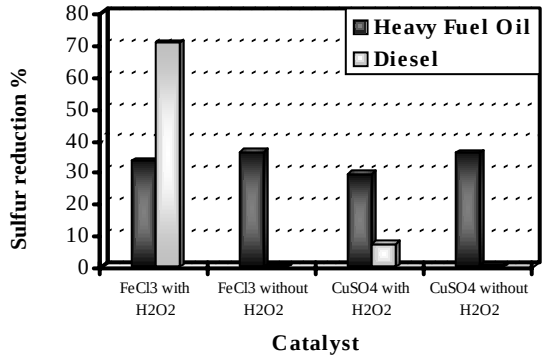

Figure 3. Effect of addition of catalyst in the reduction of sulfur for heavy fuel oil and diesel.

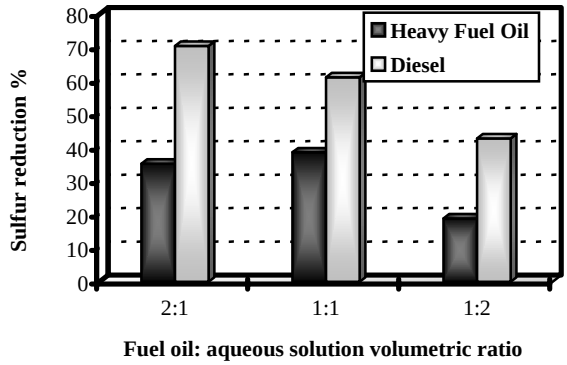

Figure 4. Effect of fuel oil to aqueous solution volumetric ratio in the reduction of sulfur for heavy fuel oil and diesel.

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