Application of Ultrasound Waves to Increase the Efficiency of Oxidative Desulfurization Process

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Received 2 December 2011; accepted 17 December 2011.

Abstract
One of the key factors for increasing the efficiency of reactions in which catalysts are involved is to increase the contacts and exposure of reagents to the catalysts. Using ultrasonic waves to destabilize the boundary layer between solid catalysts and reagents and mixing the homogeneous catalysts and reagent can increase the rate of reaction. Based on this fact, many industrial processes including desulfurization are enhanced by sonication. In this study a sono desulfurization unit with the capacity of 5 bbl per day, in which oxidative desulfurization is the main mechanism, is designed and tested. Also, the influence of different parameters on the efficiency of the reactions is investigated.

Key words: Ultrasonic waves; Desulfurization; Catalyst; Oxidant

INTRODUCTION
In the past three decades, world population growth has resulted in a dramatic increase of fossil fuels consumption. This high need for oil derivatives such as gasoline and diesel oil have led to an environmentally critical situation because of the contaminating effects of fossil fuels. So, designing processes related to fuel have become important in terms of expenses and environmental concerns. One of the key processes in oil industries is the desulfurization process. This process is important because sulfur components produce SO$_x$ during combustion reactions and when they go into the atmosphere they cause acid rain and many corrosive effects on the environment and industries.

Many processes have been developed in order to separate sulfur components from fuel oils such as: HDS (Hydrodesulphurization)\cite{1}, ODS (Oxidative Desulfurization)\cite{2}, Bio desulfurization\cite{3}, Liquid-Liquid extraction\cite{4}, and adsorptive desulfurization\cite{5-7}. Among these methods, HDS is the most common method for desulfurization of oil fractions. However, Hydrodesulphurization (HDS) usually operates at high temperature (320–380°C) and high pressure (3–7 MPa) over sulfided CoMo or NiMo catalysts\cite{8, 9}. As it was mentioned, this process needs a huge high pressure-high temperature reactor and, as it works under high pressure of Hydrogen, it is a risky process due to potential leakage and explosion.

The major sulfur compounds existing in current liquid hydrocarbon fuels after undergoing the HDS process are Thiophenic compounds and their alkyl-substituted derivatives such as benzothiophene (BT), 2-methylbenzothiophene (2-MBT), 5-methylbenzothiophene (5-MBT) and dibenzothiophene (DBT), that still remains in the fuel depends on the type of fuel and Thiophenes that the fuel contains\cite{10}.

Recently, the ODS method has flourished and it is considered as a promising method for deep desulfurization technology because it can be carried out under mild conditions, such as relatively low temperature, pressure and cost of operation in compared with HDS\cite{11, 12}.

Many oxidative desulfurization (ODS) methods, which convert the thiophenic compounds in the fuels to the sulfoxides and/or sulfones, and then, remove them by abstraction, distillation or adsorption, have been explored.
During all these investigations, Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) was the most common oxidizing agent\textsuperscript{[13]}. Typically, hydrogen peroxide is used in the presence of a catalyst such as acetic acid\textsuperscript{[14-16]}, formic acid\textsuperscript{[17-19]}, phosphotungstic acid\textsuperscript{[20]}, and solid catalysts\textsuperscript{[21-24]}.

The efficiency of total desulfurization by an ODS process is lower than an HDS process because an ODS method removes mostly thiophenic compounds. To overcome this weakness, the application of ultrasonic wave technology for optimizing the governing reactions in ODS process has been proposed by different researchers\textsuperscript{[25-29]}.

In this study all the efforts were based on designing a process to industrialize UAOD (ultrasonic assisted oxidative desulfurization). To this aim, a bench scale ultrasonic reactor with volume of 1.5 liter, which could give 5 barrels per day of desulfurized diesel, was used. The details of experimental setups are discussed in the experimental section.

1. EXPERIMENTAL SECTION

1.1 Experimental Set-Up

As it was mentioned previously, ultrasonic wave can increase the rate of a reaction of catalytic reactions. To investigate the effects of sonication on the oxidative desulfurization process, a specially designed ultrasonic reactor was assembled and consisted of five main parts:

1) Grade 316 stainless steel reactor with sight glass: The net volume of the reactor after connecting all parts is 1500 cc.

2) Peristaltic pumps: For pumping the oxidants with variable flow rates.

3) Ultrasonic generation system composed of a MPI Ultrasonic wave generator with variable powers ranging up to 3000 watts: A 20 kHz MPI Ultrasonic wave transducer, which converts electrical waves to mechanical wave and an amplification and horn system, designed by ultrasonic Research Group to transfer the wave to the fluids contained in the reactor,

4) Digital thermometers: To measure and record the temperature at every 5 minutes.

5) Cooling and recirculation system: It condenses the evolved gases and injects the condensed liquid into the reactor.

Figure 1: Schematic of Ultrasonic Assisted Oxidative Desulfurization Reactor

The ultrasonic horn that is used has a unique hammer structure which provides us with cylindrical propagation of ultrasonic waves. It is made of grade 1060 aluminum which is ionized in order to reduce the corrosion of the horn. A schematic of the experimental set-up is illustrated in Figure 1.

1.2 Reaction Materials

The feedstock used in the sono-reactor was 7240 ppm diesel fuel. The water injected into the system for making an emulsion was deionized distilled water. As oxidant agent, thirty percent Hydrogen peroxide was added to the sono-reactor with peristaltic pump with a 10 cc/min flow rate. The catalyst used in this set of experiments was phosphoric acid with 99% purity and Fe\textsubscript{2}SO\textsubscript{4} was used as the phase transfer agent. In the experiments where Phase Transfer Agent (PTA) was used, the catalyst and phase transfer agents were mixed together and injected into the sono-reactor through one of the peristaltic pumps.

1.3 Experiments Design and Procedure

The knowledge of the contribution of individual factors is a key to deciding the nature of the control to be established on a production process. In this study, six main factors seem to have a high significance in the success of the operation of the UAODS process. These factors are type and amount of oxidant, wave intensity and radiation time, water cut and catalyst to diesel volume ratio\textsuperscript{[2, 5, 8]}. All the experiments were performed in atmospheric pressure and the wave was radiated continuously. The experiments were done based on the following procedure:

1) Diesel and water were mixed and dispersed together by ultrasonic radiation for 1 minute.

2) PTA and catalyst were injected into the vessel and fluid was heated to reach thirty degrees centigrade temperature. Then, the ultrasonic generator started radiation and the test was initiated.

3) In order to control the reaction, oxidant was injected into a sonoreactor at a constant rate of 10 cc per
minute.

4) At 5 minute intervals, 100 ml were taken.

5) The samples were quickly cooled to ambient temperature, in order to avoid expulsion of light components in gaseous form.

6) Then, the sulfur contents of the sample were removed in an LL extraction process twice. Methanol was used as the extractor in a ratio of 1:1 with the sample. Then the oil layers (upper layer) were collected for further analysis and the solvent in the lower layers was recycled.

1.4 Analysis

The total sulfur content of the treated diesels was analyzed by RX-360SH of Tanak. RX-360SH determines the total sulfur amount in petroleum products, such as gas oil, fuel oil, crude oil and naphtha, using an energy dispersive X-ray fluorescence (EDXRF) method, which is an accurate, non-destructive, economical and yet quick method prescribed in ISO 8754 and ASTM D4294-03.

Based on the primary experimental studies, some parameters can have significant roles on the rate of reactions in the UAODS process. These parameters are: 1) Catalyst, 2) Phase transfer agent, and 3) Oxidant. Types and fractional volumes of these parameters can change the reaction rate and ensure that the reaction proceeds with the highest efficiency towards the desired output products, producing the highest yield of product while requiring the least amount of an ultrasonic wave’s energy to operate. In addition to these parameters, there are two other parameters which seem to have marked importance. These are the amount of water that was added to diesel fuel to make an emulsion of the two liquids and the wave intensity.

To investigate the role of each of these parameters, with the aim of obtaining the optimum conditions for the UAODS process, sets of experiments were designed and performed.

2. RESULTS

2.1 Water to Fuel Ratio Role

Based on knowledge and primary experiments, the presence of water in emulsion form in diesel fuel makes a convenient condition for the reaction. This is due to the ultrasonic wave effects that make a stable emulsion of two immiscible liquids. The emulsion of two liquids might advent if the polarity of two liquids is close to each other. The ratio of water to fuel is one of the key parameters in ultrasonic assisted oxidative desulfurization.

To prove this claim, a set of experiments was designed. In these experiments, 500 mL of H₂O₂ as oxidant, 750 mL of diesel as fuel, and 60 mL of phosphoric acid as catalyst were used. Waves were radiated with the resonant frequency of the fluid system, which was measured to be 22.5 kHz. The ultrasonic wave generator was set to work with 50% of its maximum nominal power. The value of output power was calculated to be 650 watts based on calorimetry experiments at 50% level. For more information about the calorimetry method used, researchers can refer to Kikuchi and Uchida (2011)\[30\].

Figure 2
Role of Volume of Water Emulsified in 750 ml of Diesel on Desulfurization Process

Figure 2 shows the result of water to fuel ratio experiments. As shown, the presence of 50ml of water in diesel in emulsion form reduces the sulfur content of fuel by an average of 4.5% more at each time of radiation, in comparison to the case in which there is no emulsified water. Increasing the water to fuel ratio to 2/15 leads to an increase in efficiency of the UAODS method. But it seems that there is no marked difference between the results of a 2/5 water to fuel ratio with that of 4/15. Besides, an increase in water to fuel ratio would lead to complexities in separating water from fuel in the extraction part of this experiment. From an industrial point of view, this means an increased capital investment for a water-fuel extraction unit.

2.2 Catalysts Role

In reactions that occur in fuel processing, the use of a catalyst to accelerate the reaction and helping selectivity is ordinary. In UAODS, two immiscible liquid phases exist and the reaction takes place on the interface of these two liquid phases. The role of a catalyst in UAODS helps the oxidant components to decompose faster so more free radicals could exist on the interface.

Figure 3
Possible Reaction Pathways for the Sulfur Compounds Oxidation Reaction in Ultrasound (Fe²⁺) System\[1\]
To investigate the role of catalyst amount on the process of ultrasonic assisted oxidative desulfurization, three experiments were performed in which 20, 60 and 100 mL of phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) were used as the catalysts. Other parameters were kept constant in the experiments. In all three experiments 500 mL of hydrogen peroxide as oxidant, 100 mL of water and 750 mL of diesel are used. The resonant wave frequency was 22.5 kHz. The power was set at 50% of the maximum nominal power. The samples were taken at 5, 10, 15, 20 and 25 minute intervals at the beginning of the experiments.

As shown in Figure 4, there is an optimum value for the volume of catalyst used. In fact, if the amount of catalyst is too high, adverse reactions will occur in the aqueous phase due to the reaction between the catalyst and the oxidant and, in this condition, the reaction is distorted from its main path. On the other hand, if the amount of catalyst becomes lower than that specified amount, there will be a deficiency in radical exchange terminals to exchange the radicals between two surfaces.

In other experiments, 250 mL of hydrogen peroxide oxidant and 100 mL of water were used in order to remove the sulfur content of 750 mL of diesel fuel. The wave properties were the same as previous experiments: Wave frequency = 22.5 kHz and power = 50% of the maximum nominal power. This experiment was done by using different volumes of catalysts. The results are shown in Figure 5.

In the second experiment, the behavior of the catalyst is the same as the first experiment. It is obvious that the extent of catalyst does not mean more conversion in these types of reactions and these reactions need an optimum amount to show the best yield. In Figure 6, the conversion is different from Figure 5 and this is because of the fuel to oxidant ratio. As it is shown, if the amount of oxidant to fuel increases the conversion will increase. This behavior of system will be described extensively in the “oxidant agent role” section. By considering the rate of decrease of the sulfur content after 10 minutes and by a comparison with Figure 4, the deficiency of the oxidant for the reaction is deduced.

2.3 Phase Transfer Agent Role

A phase transfer agent (PTA) acts like a catalyst which makes a reactant migrate from one phase to another phase in which the reaction is done with more ease. PTA also helps oxidants to decompose faster. In this test based on previous studies, FeSO\textsubscript{4} is determined to be a good choice for phase transfer agent\textsuperscript{[31]}. The wave frequency was 22.5 kHz and the wave generator was set at 50% of the maximum nominal power. As oxidant agent, 500 mL of hydrogen peroxide and as a catalyst 100 mL of phosphoric acid was applied to the reaction cell. Before initiating the experiments 100 mL of water is added to 750 mL of diesel and mixed well with the ultrasonic waves.
From Figure 6, it can be concluded that the greater amount of PTA, the more conversion takes place. Figure 6 also indicates the slope of “10 grams of phase transfer agent” line descends toward zero after 15 minutes. It shows that by adding much more phase transfer agent, PTA catalyzed oxygen free radicals in an adverse reaction. By lowering the amount of oxygen radicals the conversion rate became lower.

2.4 Oxidant Role

The most important part of an ODS process is the usage of an oxidant. As this process is based on oxidative desulfurization, the type and amount of this oxidant is the main concern. In this investigation, \( \text{H}_2\text{O}_2 \) was chosen as the oxidant because of its high hydroxyl radical production; each mole of this liquid make 1mole of hydroxyl radical. On the other hand, this component is environmentally friendly as its only by-product is water. Exploring the effect of this oxidant shows that increasing or reducing the oxidant agent volume has obvious effects on sulfur components conversion. To investigate the role of an oxidant agent, 100ml, 250 mL and 500ml of hydrogen peroxide were added to the reaction vessel. The wave properties were the same as the previous experiments. Before experiments initiation 60 mL of phosphoric acid was supplied to the reaction system as a catalyst and 100 mL of water was mixed with 750 mL of diesel. The experiments are done in 0, 25%, 50% and 75% radiation conditions. Based on the calorimetry experiments, the amount of power of the system in 25%, 50% and 75% of radiation are approximately 400, 650 and 800 watts, respectively. The results are shown in Figure 8. As it can be seen, wave radiation can highly increase the recovery of sulfur removal. The selection of a power level for industrial applications needs more study to consider economic factors and energy consumption analysis.

Figure 7 also shows that by increasing the amount of oxidant, more conversion occur. However, it should be considered that by increasing its amount, the operational cost increased dramatically and it is recommended that the amount of oxidant be chosen by the commercial conditions of a project.

2.5 Role of Wave Power

One of the most important parameters in this study was the wave intensity. To investigate the role of this parameter, a set of experiments were performed. Before experiments initiation 60 mL of phosphoric acid was supplied to the reaction system as a catalyst and 100 mL of water was mixed with 750 mL of diesel. The experiments are done in 0, 25%, 50% and 75% radiation conditions. Based on the calorimetry experiments, the amount of power of the system in 25%, 50% and 75% of radiation are approximately 400, 650 and 800 watts, respectively. The results are shown in Figure 8. As it can be seen, wave radiation can highly increase the recovery of sulfur removal. The selection of a power level for industrial applications needs more study to consider economic factors and energy consumption analysis.
CONCLUSION

In this study an ultrasonic assisted oxidative desulfurization experimental setup was designed and different parameters influencing the efficiency of desulfurization were investigated. Based on the results obtained, the following conclusions can be drawn:

1. The presence of water in emulsion form leads to an increase in the efficiency of the process. The amount of water to diesel ratio must be set in order for no difficulties or excess investment in extraction units.

2. The amount of catalysts used in this process has an optimum amount. If more than an optimum amount is used, adverse reactions will take place and the efficiency of the desulfurization process reduces dramatically.

3. Using more phase transfer agents (PTAs) increases the efficiency of desulfurization process. But adding more phase transfer agent (PTAs) than required has the same results as that of catalysts too much usage.

4. A different relation between the amount of oxidant and the efficiency of the process is needed. In industrial applications, the usage of oxidants should be determined based on an economic analysis.

REFERENCES


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