Ultrasound-Assisted Oxidative Desulfurization Process of Gas Oil

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ABSTRACT

The ultrasound-assisted oxidative desulfurization process was used for gas oil sulfur removal. The effective factors such as reaction time (5 and 10 minutes), temperature (8-65°C), type of extraction solvent and catalyst in present of ultrasonic irradiation (400 W and 24 kHz) were considered for decreasing the amount of sulfur. In this study, the highest removal was achieved during 10 minutes of process at 65°C when extraction was done by methanol. In this work, two phases was separated and ASTM 3120 method was used for analyzing oil phase.

INTRUDUCTION

Sulfur compounds are one of the major contaminants in petroleum and are significantly transferred to fuels during refining processes [1]. These compounds include sulfides, thiols, thiophenes, substituted benzothiophen and dibenzothiophenes (BTs and DBTs), benzonaphthothiophene (BNT), and etc. [2].
Sulfur compounds in petroleum fractions have poisoning effects on catalytic converters and cause the corrosion problems in combustion engines.
During diesel combustion, sulfur compounds are converted to sulfur oxides (SO_x) that are environmentally detrimental. Nowadays, many countries have limiting acts on the sulfur content of fuels and environmental regulations have been issued to control the sulfur levels in gas oil and diesel fuel. Latest environmental regulations (June 2006) need some special deep desulfurization processes to meet the ultra-low sulfur diesel (ULSD) specifications (15 ppm). Currently, ULSD production is in limited quantities, which is relying on enhanced hydro-treating technology [2,3]. The new regulations that control fuel quality have made some operational and economical challenges for petroleum refining industry. The main industrial method of eliminating aliphatic and acyclic sulfur-containing compounds from diesel oil is Hydro-desulfurization (HDS). The traditional HDS process has enough efficiency for mercaptans, thioethers, sulfides and disulfides removal but it is not satisfactory in the case of treatment of aromatic sulfur compounds such as thiophene, benzothiophene (BT) and dibenzothiophene (DBT). Moreover, refractory aromatic sulfur compounds that are a significant portion of sulfur in fuels, have low reactivity in HDS process. Additionally, this process requires special operating conditions such as high temperature (about 400 °C), high hydrogen pressure (up to 100 atm), the use of metallic catalysts (e.g. CoMo and NiMo-type), large reactors and excessive residence time, which impose higher operating costs. Another important point to make is that in the HDS process removal of sulfur compounds occurs by their conversion to H_2S, which is also undesired [1,3].
In the past decades, alternative desulfurization techniques have been studied widely such as bio-desulfurization, ionic liquid catalysis, selective adsorption, microwave catalytic desulfurization, oxidative desulfurization, as well as ultrasound-assisted oxidative desulfurization. Among these, oxidative desulfurization has been given growing interests. Oxidative desulfurization (ODS) is been considered as a promising technique for deep desulfurization because of its ability to be performed under relatively mild conditions such as low temperature, pressure and cost of operation in comparison with HDS. The oxidative desulfurization method is based on oxidation of sulfur compound resulting in formation of highly polar sulfoxide or sulfone, which could be easily removed by solvent extraction or adsorption

methods, because of their polarity. Therefore, the practicability of an ODS method depends on kinetics and selectivity of the oxidation of organic sulfur compounds (OSCs) to sulfones [1-4].

A powerful oxidant agent of sulfur compounds is hydrogen peroxide. The performance of several combinations of H_2O_2 with other substances, such as H_2O_2/Na_2CO_3, H_2O_2/heteropolyanion catalysts and phase transfer agent, H_2O_2/inorganic acids, H_2O_2/formic acid, and H_2O_2/acetic acid has been investigated. The reaction of hydrogen peroxide and a carboxylic acid produces peroxyacid. This in-situ product contributes to reaction of oxidation of sulfides to sulfoxides and sulfones. As mentioned before, these oxidized molecules have high polarity in comparison with respective sulfides and solvent extraction technique could be an easy method for selectively removing the oxidized sulfur compounds from oil phase [1]. N-methyl pyrrolidone, acetonitrile (MeCN), N,Ndimethylformamide, methanol (MeOH) and water could be used in such solvent extraction method [3].

Ultrasound-assisted oxidative desulfurization (UAOD) is a new technique to perform the oxidation reaction rapidly, economically and safely, under mild operating conditions. In this process, practically effective factors are ultrasonic frequency and power, oxidants, catalysts, phase-transfer agent and extractant, which affect reaction kinetics, product quality and recovery [2].

The oxidation of sulfur compounds, which could occur at the interfacial area or in the bulk of the solvent phase, requires well-dispersed solvent and fuel phases. Ultrasound improves the liquid–liquid interfacial area by emulsification, which is important for viscous films that are containing gas-filled bubbles and cavitation bubbles .Phase transfer agents (PTA) are surface-active species mitigating surface tension and allowing easy formation of micro-bubbles under ultrasound. UAOD process selectively oxidizes sulfur of thiophenes in diesel to respective sulfur oxides or sulfones [2,4].

It is scientifically clear that ultrasonic irradiation can effectively improve the reaction yield in chemical synthesis. This is mainly due to cavitation when mechanical vibrations are generated into the liquid as ultrasonic waves. When liquids are subjected to high intensity ultrasonic waves, acoustic cavitation is made. This phenomenon is the formation and succeeding violent collapsing of cavitation bubbles, creating shock waves, preparing a great set of conditions for chemical reactions and increasing the chemical reactivity in the system. During this process, short-term localized hot spots could be produced. The violent collapse of each bubble causes locally high temperature (up to 5000 K), high pressure (up to 1000 atm) and drastic liquid jets. This microenvironment, with extreme local conditions, is suitable for creation of active intermediates permitting the reaction to progress rapidly [3].

Ultrasound-assisted oxidative desulfurization (UAOD) has been presented using hydrogen peroxide, phosphotungstic acid/acetic acid and a PTA (e.g. tetraoctylammonium bromide and/or fluoride or acetonitrile), a biphasic diesel–acetonitrile system with hydrogen peroxide, sodium carbonate and Fenton's reagent. Ultrasound effect is applied to increase reaction rate due to the formation of radicals, cleavage of bonds and enhancement of mass transfer, providing unique chemical effects. Despite the great advantages provided by the use of ultrasound, in the last years, few studies related to its direct application in petroleum industry have been published [1].

In this work, the ultrasonic power was used for the oxidation of sulfur components in gas oil. The effect of parameters such as reaction time, temperature and type of extraction solvent were investigated in ultrasound-assisted oxidative desulfurization (UAOD) process, which was carried out in present of hydrogen peroxide as oxidant and acetic acid as pH controller.

EXPERIMENTAL METHOD

Instrument

In this work, an ultrasound apparatus (UP400S) manufactured by Hielscher, was used. An ultrasonic probe with a 0.5 in. threaded end titanium tip was 'dipped' into 30 ml of reaction mixture, where it was able to produce ultra-fine emulsion by introducing high intensity ultrasound irradiation to the system. The wave frequency and the wave generator were 24 kHz and 100% of the nominal power of 400 W, respectively.

Analysis

After performing UAOD process, two phases (i.e. aqueous and oil) were separated. Eventually, the oil phase was analyzed using ASTM 3120 method.

Reagent and material

The feedstock treated in this study was gas oil containing 9500 ppm of sulfur. The properties of the gas oil are shown in Table 1. Hydrogen peroxide (30 % w/w) was used to the sono-reactor as the oxidant agent and $FeSO_4$ was applied as the catalyst. In addition, acetonitrile was added as the phase transfer agents.
Ferrous ion (from $FeSO_4$) was added into the reactor in the form of aqueous solution. In this set of experiments, the pH value of the aqueous phase was adjusted because the activity of catalyst was depended on acidity of the solution and its value should be kept less than 3 [5]. The experiments were performed according to the following procedure:

1) PTA and acetic acid were added into the reactor,
2) Catalyst was injected and then the H_2O_2 was added,
3) After ultrasonic process, the sulfur contents of the sample were extracted in a Liquid-Liquid extraction process three times.

In the last step, methanol and water were used as the extractor. The oil layer (the upper one) was separated for analysis.

Table 1
Properties of the gas oil

Parameter	Unit	Specification
Density @ 15°C	g/cm^3	0.82-0.86
Total Sulfur	mg/lit	9500
FBP	°C	385
Flash Point	°C	54-62
Pour Point	°C	(-4)-(-2)

RESULTS AND DISCUSSION

Effect of aqueous pH on catalytic activities of metal ions

When the reaction is catalyzed by metal ions, hydrogen peroxide decomposition rate to hydroxyl radicals depends on the aqueous phase pH value. To study the effect of this phenomenon on UAOD, the oxidation reactions of diesel fuel in presence of hydrogen peroxide were performed under various aqueous phase pH values. The pH values were set with acetic acid. It is obvious in figure 1 that the rate of ODS of diesel fuel at pH value of 2.1 is higher than smaller values.

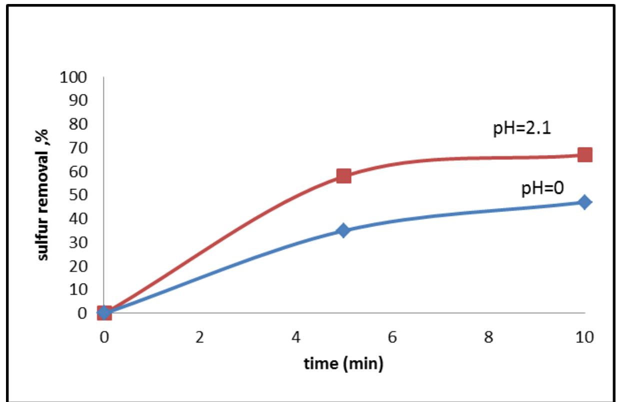

Figure 1
The effect of pH on the sulfur removal %

Effect of temperature

The temperature effect on the oxidative reaction under ultrasound has been investigated in the range of 20 to 90 °C in some literatures. The upper limit (i.e. 90 °C) is the boiling point of the most volatile component of the mixture. There are two limitations for increasing the temperature:
1) Destruction of hydrogen peroxide in high temperatures (i.e. more than 80).
2) Evaporation of light components of the gas oil.
In this study, three temperatures (i.e. 8, 47 and 65 °C) was considered and the results are shown in figure 2. It can be clearly seen that increase in temperature from 8 to 65 °C causes increase in sulfur removal from 28 to 67%.

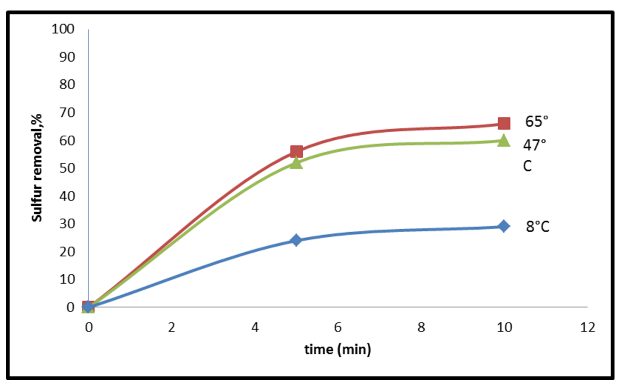

Figure 2
The effect of temperature on the sulfur removal %

Effect of reaction time

In the all of experiments, samples were taken every 5 minutes and total sulfur of them was analyzed. The experiments were carried out during 10 minutes. It is obvious from both figures 1 and 2 that the rising of time decreased the sulfur component in gas oil. Therefore, the effect of increasing time is very important on the diesel oil treating.

Actually, the increase in time was useful for this process, but to decrease the operation cost it is necessary to find the optimum time.

Role of oxidants

Hydrogen peroxide is the most common oxidant in UAOD process and it is very friendly with environment. H_2O_2 in the present of catalyst ($FeSO_4$) was decomposed to produce free hydroxyl radicals. Hydroxyl radical acts as oxidant for oxidation of sulfur components. As the amount of consuming H_2O_2 increased, the result for sulfur removal became better but according to economic consideration, it could not be used inconsiderably. In addition, it is important to minimize the use of oxidizing reagents and the consequent chemical residues [1].

Roles of extraction

After sonication process, the product mixture contains two phases, aqueous and organic. Sulfones produced by the oxidation reaction are in the organic phase. Organosulfur compounds have polar quality and a proper solvent extraction method can be used to extract sulfur compounds, mainly in oxidized form. In such a process, the solvent must have two main characteristic [1]:

1) High polarity
2) Insolubility in the oil.

Some solvents that could be utilized in liquid–liquid extraction step are methanol and water. After extraction, sulfur amount of the oil phase was determined. It was concluded that increase in solvent volume enhanced extraction efficiency.

In this work, two extractor i.e. methanol and water were used. It is clear in figure 3 that methanol was so better than water.

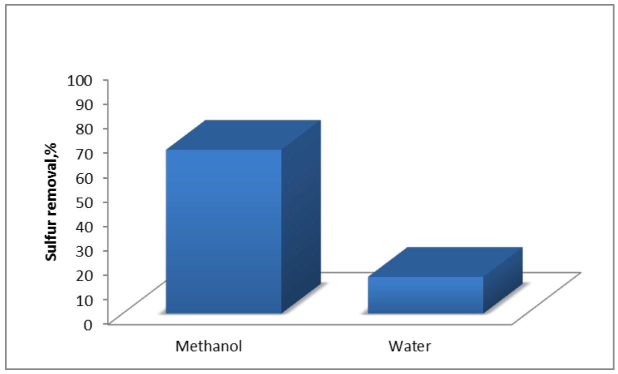

Figure3
The effect of extractor type on the sulfur removal %

CONCLUSIONS

The desulfurization was performed using UAOD process with hydrogen peroxide as oxidant, $FeSO_4$ as catalyst and methanol as an extraction solvent.

The effective factors studying in this work include time, temperature and type of extraction solvent. According to the results, increase in time and temperature caused decrease in the amount of sulfur of gas oil.

Comparison between the results that were obtained from extraction with methanol and water showed that methanol is better and has more efficiency.

UAOD process of this work has more advantages in comparison with HDS. UAOD is performed at normal pressure and relatively low temperature. In addition, the operating cost is lower and the safety is higher.

KEYWORDS

Desulfurization, ultrasonic, gas oil, oxidative.

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