Ultra Clean Fuels via Modified Ultrasound Assisted Oxidative Desulfurization process

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Introduction

Limitation of 15 ppm has been considered for the content of sulfur in the diesel fuel due to the sulfur regulation by the EPA. However, ultra low sulfur diesel (ULSD) fuel has not been produced sufficiently by the current desulfurization technology.

In this study, a new desulfurization technology has been development, this include modified ultrasound assisted oxidative desulfurization (UAOD) process and fixed bed reactor (FBR), which has been considered as one of the innovative schemes related to the desulfurization. A block diagram of the modified UAOD process is shown in Figure 1.

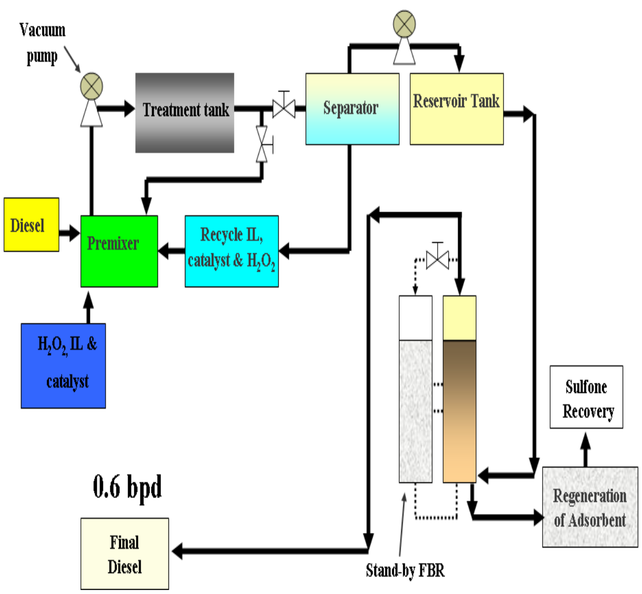

Figure 1 A Block diagram of continuous modified UAOD process.

Experimental Procedures:

Model Sulfur Compound and Diesel Fuel

Sulfur model compound was dissolved into toluene to make a stock solution with given sulfur content approximately 500 ppm. The oxidation and extraction procedure of sulfur model compounds is described as follows. An equal weight ratio of 5 gram of hydrogen peroxide (H_2O_2), 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] and model sulfur compound were prepared. H_2O_2 and 3 gram acid catalyst were add into the beaker, the mixture was stirred at room temperature for 5 minute, leading to solution A. Solution B was prepared with sulfur model compound stock solution that mix with 0.3g of TOAF (tetra-octyl ammonium floride). Solution B was added to solution A. Finally, [BMIM][PF_6] ionic liquid was slowly added into the mixture. The mixture has three phases. The mixture was first heated to 50^{o}C water bath and than irradiated by probe type ultrasound reactor for 10 minutes. During the sonication, the mixture was emulsified and all the mixture becomes one phase. After the sonication, the mixture was stirred under 50^{o}C water bath for certain time, than the phase was separated by centrifuge and the top organic phase was used for quantitative and qualitative analysis. The bottom phase of ionic liquid was extract with polar solvent for further analysis.

The experimental procedure has been repeat with different variable, this include: mixing method, catalyst selection, ionic liquid type and oxidant concentration. An efficient protocol condition of modified UAOD process has been development for both model compound and real diesel study.

Fixed bed reactor

Two glass vessels were purchased from Chem-Glass, with 55 mm in diameter and 150 mm in length. The glass vessels were used to pack the alumina. To avoid the loss of alumina or leak out, glass fiber wool was placed at the bottom of the vessels. The on the top of glass wool, at mean time, fresh alumina was added; toluene was added to keep the alumina free from air bubbles. Once both glass vessels were filled with alumina, they were connected and sealed with a clamp.

Results and Discussion:

During the study, proper oxidant, catalyst, as well as, ionic liquid was utilized during the demonstration under the modified UAOD process, specifically for model sulfur compounds. It has been observed that duration of three hours has been enough for desulfurize 99.9% of various type of model sulfur compound. Figure 2 shows the results of desulfurization of various model sulfur compounds under protocol condition.

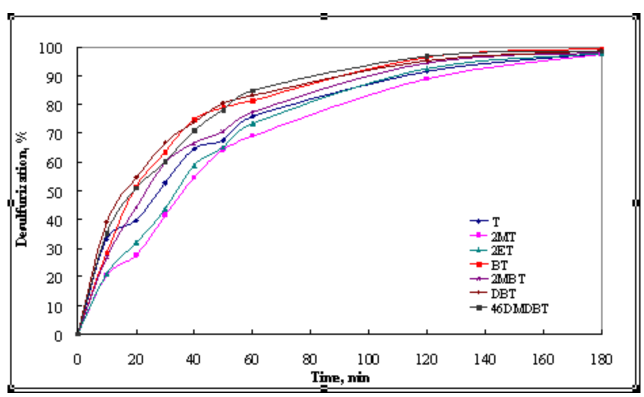

Figure 2: Desulfurization efficiency on various model sulfur compounds.

From previous work[1, 2] have already demonstrated the high desulfurization efficiency (98%) of benzothiophene and dibenzothiophene and their families by UAOD process. However, the current UAOD process, cannot achieve ultralow sulfur diesel. There are still refractory organic compounds such as C_3-BT, C_4-BT, C_5-BT and C_3-DBT that are difficult to oxidized, unless by using double or triple amounts of oxidants, catalyst and extended sonication time. Figure 3 shows the refractory organic sulfur compounds that have been left under current UAOD process that has been used since 2003 with MGO diesel sample.

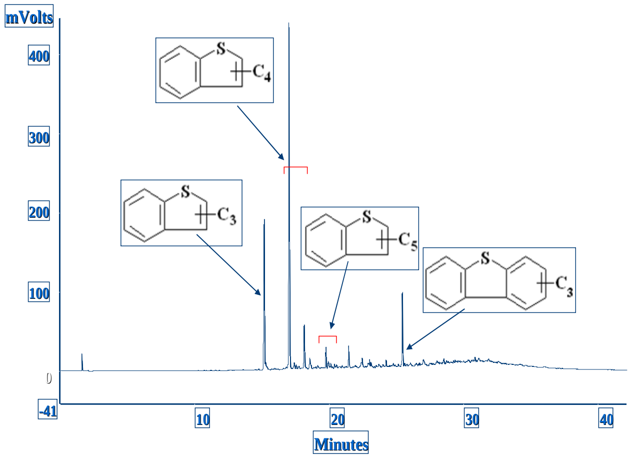

Figure 3 OSCs remaining after current UAOD process (Wan, et al. 2003)[2]

The modified UAOD process is capable of oxidizing various sulfur level diesel, this include: Valley Oil, JP-5 and F-76 are some of the levels. In this regard, 99.9% removal efficiency in the sulfur reduction can be demonstrated by the solvent extraction, as well as, solid adsorption, which has been followed by the modified UAOD process. Moreover, recycling can be done to the ionic liquid and acid catalyst, which is usually contained in the spent aqueous phase. Interestingly, high efficiency, as well as, high selectivity can be exhibited by the same. Figure 4 shows the chromatogram of different stages with original, oxidation, solvent extraction on the OSCs distribution that was found in the F-76. It has been an observation that equivalent and parallel BTOs, as well as, DBTOs were formed after the oxidation of both elements in the F-76. Subsequently, removal of formed sulfones in the F-76 was done by the solvent extraction of Acetonitrile. In the result, production of desulfurized F-76 takes place, and 0 ppm is found to be the total sulfur content of the outcome. The overall sulfur removal by modified UAOD process on F-76 is 100%.

Fixed bed reactor (FBR) has been used to pass the oxidized organic compounds that have come out from the batch-type continuous flow system. Moreover, acidic alumina can adsorb almost 99.9% of oxidized sulfur, as indicated by the results. Additionally, recycling has also not affect the adsorption capacity of adsorbent. It has been shown by the results of this study that sulfur removal from the diesel fuels can be done effectively by the employment of modified UAOD process and FBR. It has been noted that setup, compact, convenience, and installing of the continuous desulfurization units are very easy to be done, which has been considered as one of the significant and imperative discoveries of present technology.

After adding passing F-76 Naval diesel through the fluidized bed, effluent samples were collected, the sample concentration was measured by SLFA-20 sulfur analyzer. Figure 5 shows the breakthrough curve of acidic alumina for F-76 diesel fuel.

The results of the desulfurization of diesels fuels by modified UAOD process are summarized in Table 1.

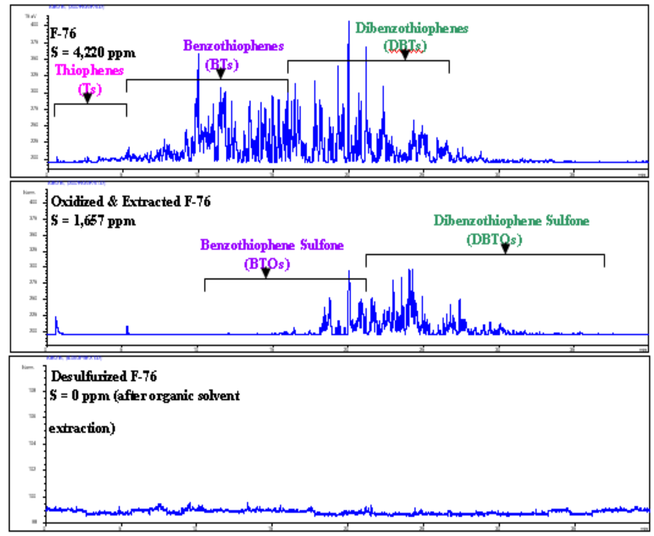

Figure 4 GC-SCD chromatograms of F-76 under modification UAOD process

Table 1 Desulfurization efficiency of Modified UAOD process on diesel fuels

Diesel Fuels	Sulfur Content (ppm)			Sulfur Removal (%)
	Original	After Oxidation	After Extraction	
JP-5	740	120	<1	99.9
Treated Valley Oil	560	84	<1	99.9
F-76	4,220	1,657	<1	99.9
Valley Oil	8,110	2,400 (1st) / 1,372 (2nd)	6	99.9

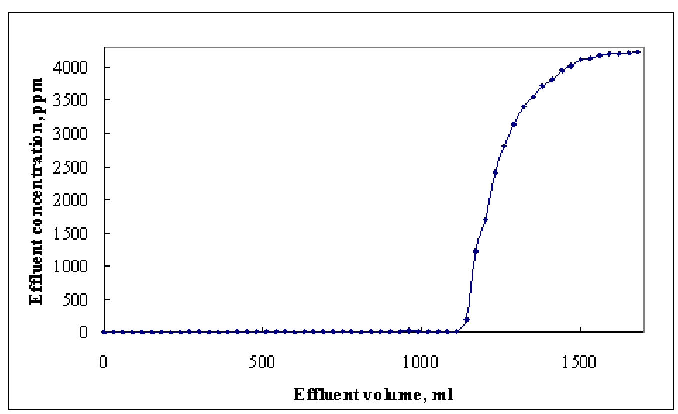

Figure 5 Breakthrough curve of acidic alumina for F-76

As shown in the breakthrough curve, it is to be noted that 1 gram of alumina can adsorb 11.82 mg of organic sulfur compound. The adsorption ability, as such is very close to the previous results by Etemadi, et al. 2007[3]. According to his thesis and published literature on MGO diesel, his adsorption ability is 12.59 mg sulfur per gram of alumina. And to make it known, this shows the results obtained by the present researcher in this study (11.34 mg sulfur / g alumina). This can be used for pilot study design consideration. The major advantage of using fixed bed reactor is: (1) the adsorb reaction time is less than the packed column procedure (usually the packed column procedure takes around 6 to 8 hours to adsorb). On the contrary, fluidized bed takes less time, for F-76 diesel: It takes only 3 hours. Another chief advantage is (2) it can treat large volumes of diesel in liter volumes, which is in contrast to the volume on packed column that takes small volumes for procedures.

References:

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