

嘉南藥理科技大學專題研究計畫成果報告

石化產業有害廢氣排放逸散之特徵研究

(整合型計畫第二年)

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子計畫(2/3)－柴油以超音波輔助氧化脫硫以達二氧化硫減量之研究

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柴油以超音波輔助氧化脫硫以達二氧化硫減量之研究

中文摘要

二氧化硫來自於石化工業的製程及燃油燃燒之廢氣，是酸雨主要來源。若以避免產生污染源的角度思考，燃料油經過脫硫技術處理，可有效改善二氧化硫的生成。加氫脫硫法是目前工業界廣泛使用的脫硫方法，然其操作控制具有高危險性及高成本等限制因素。因此，如何以更有效率、更安全及符合經濟效益的脫硫方式，解決加氫脫硫所產生之問題，一直是學者研究之重點。

本研究以氧化脫硫方式，輔以超音波之協助去除柴油中的有機硫；該技術結合超音波學、介面活性催化作用及過度性金屬催化氧化反應等三項技術，在常溫常壓下及10分鐘的反應時間內，以雙氧水(H_2O_2)為氧化劑，將Bnzothiophenes和Dibenzothiophenes等有機硫化合物氧化成其氧硫化合物(Sulfone)；並配合極性溶液之液體/液體萃取法(Liquid/Liquid Extraction)將Sulfone自柴油中去除，以達產生低硫份柴油之目的。

反應物及產物之定性及定量主要將以Sulfur-in-Oil Analyzer、氣相層析儀配合脈衝式火燄光度檢測器及離子阱質譜儀等為之。實驗中將探討超音波之輔助效應、介面活性化學、過度金屬催化作用及整體氧化脫硫之反應機制，並建立適當之氧化脫硫操作條件，以提高有機硫之氧化效率。

關鍵詞: 超音波、氧化脫硫、活性介面劑、過度金屬催化劑、二氧化硫

Ultrasound Assisted Oxidative Desulfurization (UAOD) Process for Diesel to Eliminate the Formation of SO₂

Abstract

Sulfur dioxide, emitted from the petroleum refining industrials and combustion engines, is mainly the source of acid rain. Eliminating the contamination source is a way to be deeply considered. The desulfurization of fossil fuel oil was successfully decreased the formation of sulfur dioxide during the combustion process. Recently, hydrodesulfurization was widely used among all the refining industrials. However, conventional hydrodesulfurization has its limitations, such as new catalysts, higher hydrogen pressure, higher temperature, and high capital cost etc. How to develop a new technology which can safely, effectively and economically remove the sulfur form fossil fuel oil is a rising research topic among the world.

This research is mainly focused on Ultrasound Assisted Oxidative Desulfurization (UAOD) process which is designed to combine three complementary techniques, including ultrasonication, phase transfer catalysis, and transition metal catalyzed oxidation. This process can oxidize both the families of benzothiophene and dibenzothiophene to their corresponding sulfone by operating with hydrogen peroxide as oxidant in 10 minutes reaction time under ambient temperature and pressure conditions, and combine with liquid/liquid extraction to easily take off sulfone, thus fulfill the requirements of ultra-low sulfur diesel.

The qualitative and quantitative analysis of reactants and products will be examined by Sulfur-in-Oil Analyzer, GC-PFPD, and GC/MS. The effects of operating parameters, including sonication phenomenon, phase transfer catalysis, transition metal catalysis, and the conceptual model of UAOD process will be evaluated. The optimization of operating conditions will be examined to enhance the efficiency of oxidation process.

Keywords: RF plasma; Sulfur Dioxide; Catalyst; Decomposition; Conversion

Introduction

Diesel fuels are complex mixtures of alkanes, cycloalkanes and aromatic hydrocarbons with carbon numbers in the range of C₉-C₂₈ and with a boiling-range of 150-390 °C. Their relative distribution depends on the feedstock, refining process and blending schemes based on commercial demand. Due to the higher boiling range, the sulfur compounds in diesel are mostly alkylbenzothiophenes (BTs) and alkyldibenzothiophenes (DBTs). Recent studies on HDS indicated that organic sulfur compounds (OSCs) remaining in diesel fuel at sulfur level lower than 0.1 wt % are alkyl-DBT with alkyl substitutions at 4- and/or 6- position. Those compounds are lower in HDS reactivity and are classified as the most refractory compounds in Conventional HDS.

Sulfur compounds are known to be slightly more polar than hydrocarbon. However, oxidized sulfur compounds such as sulfones or sulfoxides are substantially more polar than sulfides. More importantly, the oxidation of sulfides to sulfoxides or sulfones is usually much easier and faster than the oxidation of most hydrocarbons (Bortolini, et al. 1985; Campestrini, et al. 1988; Ballistreri, et al. 1992). Therefore, ultrasound-assisted oxidative desulfurization (UAOD) process operating at ambient temperature and atmospheric pressure permits the selective removal of sulfur compounds from hydrocarbons by a combination process of selective oxidation and solvent extraction or solid adsorption (Mai, 2003). For convenience, solvent extraction was used as the separation method in this study.

Before fully investigating the desulfurization process, this study first examined whether this process can damage other fuel components. This was essential since many processes end up destroying hydrocarbons, which ultimately affects the performance and energy content of the fuel. Therefore, a study of the selectivity of this oxidative process is very significant, since the UAOD process cannot remove any other hydrocarbons in the diesel fuels.

In this chapter, an ultrasound-assisted oxidative desulfurization (UAOD) process operating at low temperature and atmospheric pressure for given time was executed. The effect of this process on commercial diesels, which include marine logistic fuels (F76, MGO and JP5) and transportation fuel (76 diesel), were evaluated. The selectivity of the oxidation of organic sulfur compounds to sulfones was characterized by GC-PFPD and GC/MS analysis.

Materials

Three marine logistic fuels with sulfur content of 4,222 ppm (F76), 1,710 (MGO) and 113.7 ppm (JP5), respectively, were received from Long Beach. Moreover, the transportation diesel with sulfur content of 259 ppm was purchased from a 76-gas station, Los Angeles. Those diesel fuels were used as the feedstock in this study. Phosphotungstic acid (TMC) and tetraoctylammonium fluoride (PTA) were obtained from Aldrich

Chemical. Acetonitrile, the polar solvent for extraction, and hydrogen peroxide (30 vol % solution) were obtained from VWR Inc.

Experiment Methods

The oxidation procedure of commercial diesel is described as follows. An appropriate volume of the diesel oil containing tetraoctylammonium fluoride (0.1 g) and an equal volume of hydrogen peroxide (30 vol. % solution) containing phosphotungstic acid (0.2 g) were added to the glass reactor. The mixture was irradiated by 20 kHz ultrasound for 10 min with temperature at 70 ± 2 . After cooling and separation of oil/water, the oxidized diesel was extracted with acetonitrile four times. Acetonitrile was chosen because it has a relatively low boiling point at 355 K and can be easily separated by distillation from the sulfones with boiling point ranging from 550 K to 950 K. Each time the solvent-to-oil (S/O) ratio was kept at 1:1 by weight (i.e., 5 g diesel per 5 g acetonitrile) and the mixture was shaken vigorously for 1.5 min at room temperature before the oil and solvent layers were separated.

In order to study the effect of oxidation on the efficiency of liquid/liquid (L/L) extraction, original diesel samples were also extracted by acetonitrile using the same procedure as described above. Original diesel, oxidized diesel, extracted diesel, and oil extracts from each extraction step were collected and prepared for GC/PFPD and GC/MS analysis.

The selective ion monitoring (SIM) technique in GC/MS analysis was employed to trace the change of organic sulfur compounds (OSCs) and hydrocarbons in diesels throughout the UAOD process. Four types of compounds including *n*-paraffins, *n*-alkyl cyclohexanes, *n*-alkyl benzenes and alkyl-naphthalenes were selected to present both saturated and aromatic hydrocarbons. The changes of these compounds in UAOD process were monitored at molecular level by using SIM technique in Varian, Saturn GC/MS workstation.

Results and Discussion

Characterization of Diesel Fuels

Diesel fuels consist mainly of saturated paraffins and naphthens, and aromatic hydrocarbons. Their relative distribution depends on the feedstocks, refining process and blending schemes based on market demand. Basically, there are two types of sulfur compounds with different aromatic skeletons in diesel fuels. Figure 1 shows the composition and distribution of organic sulfur compounds (OSCs) in GC-PFPD chromatograms. The first type is the retention time before 20 minutes, which is alkyl-benzothiophenes (BTs) with alkyl carbon from 0 to 5. The second type is the retention time after 20 minutes, which is alkyl- dibenzothiophenes (DBTs) with alkyl carbon varying from 0 to 6.

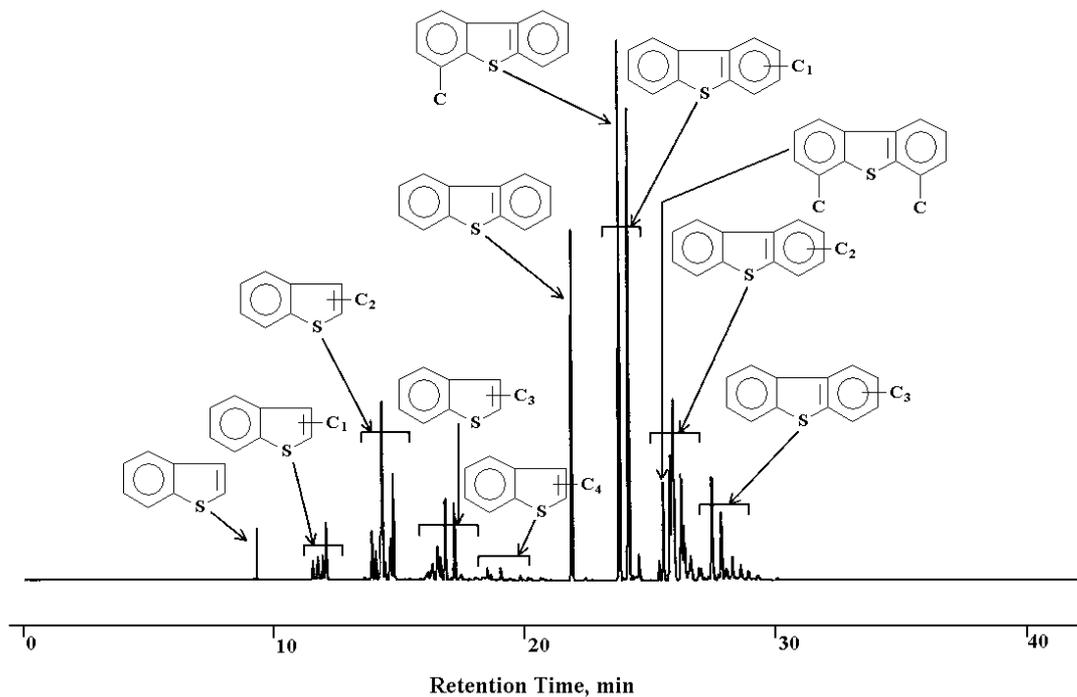


Figure 1 Composition and distribution of organic sulfur compounds in diesel fuels

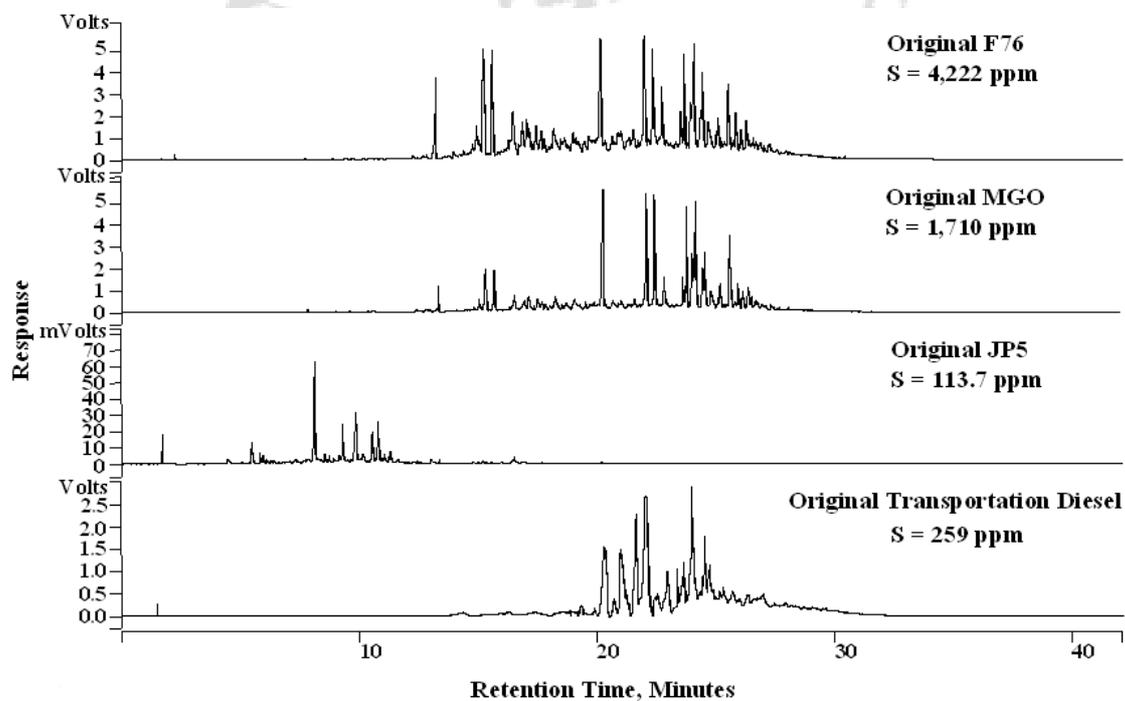


Figure 2 Composition and distribution of organic sulfur compounds in F76, MGO, JP5 and transportation diesel

Primary fuel support for sea-based aircraft shall be high flash point kerosene-based fuel, designated JP5. Conventional powered ships shall use a distillate-type fuel, such as F76 for propulsion. Military Sealift ships may use commercial marine fuels for propulsion, such as MGO. Moreover, most of the commercial trucks need the transportation diesel as their fuel supply. In order to differentiate basic compositions of different diesels, the GC-PFPD graph of F76, MGO, JP5 and transportation diesel are showed as Figure 2. It is estimated that F76 has 45% BTs and 55% DBTs of total sulfur content, while MGO has 30% BTs and 70% DBTs of total sulfur content. However, unlike F76 and MGO, BT and methyl-BTs are the most abundant species in JP5, while the DBT and methyl-DBTs are the most abundant species in transportation diesel. Neither sulfides nor alkylthiophene were found in the original diesel sample.

The UAOD on F76 Marine Logistical Diesel

The total sulfur content of the F76 marine diesel is 4,222 ppm. Comparison of GC-PFPD chromatograms of original F76, oxidized F76 and desulfurized F76 in UAOD process is shown in Figure 3. Two main groups of sulfur compounds, BTs and DBTs, were oxidized to form benzothiophene sulfones (BTOs) and dibenzothiophene sulfones (DBTOs), respectively. After being extracted by acetonitrile, the sulfones in oxidized diesel partitioned into solvents and produced a diesel with total sulfur content of 211.4 ppm. The overall sulfur removal of UAOD on F76 is close to 95 %.

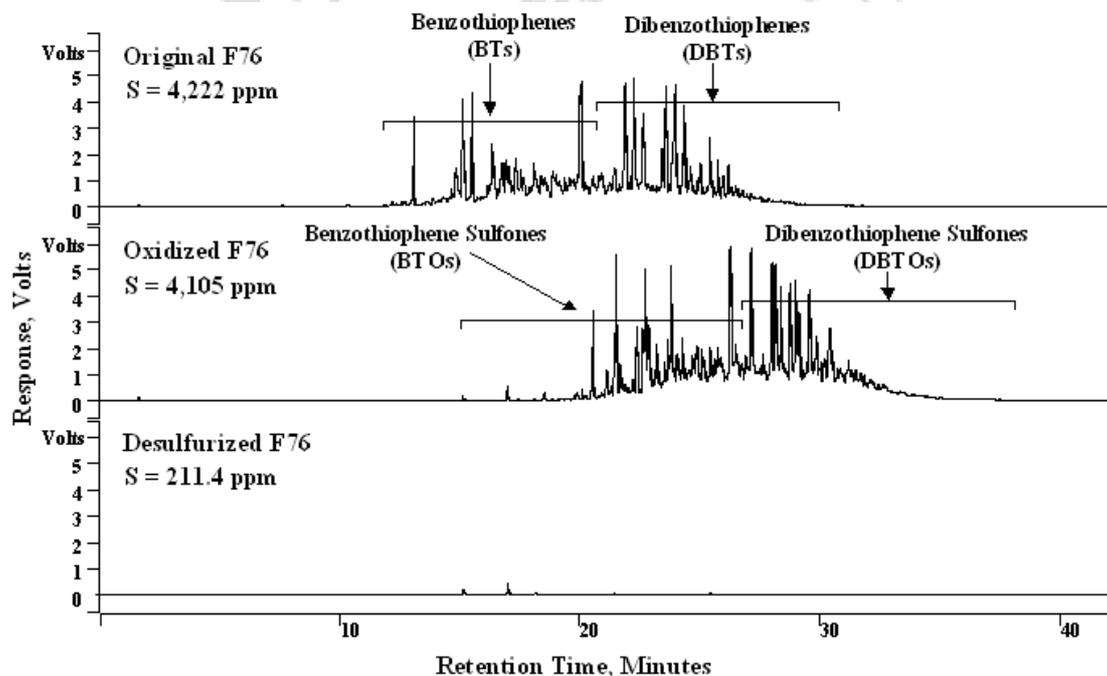


Figure 3 GC-PFPD chromatograms of F76 marine diesel in UAOD process

Organic Sulfur Compounds (OSCs) have different reactivity in oxidation and the extractability of their oxidized products also varies in solvent extraction. Figure 4 shows

that there are few unreacted BTs (with retention time before 20 mins) remaining in the desulfurized F76. The peaks with retention time after 20 mins are characterized as unreacted DBTs and unextracted BTOs and DBTOs. Based on the retention time, those four major compounds are categorized as compounds in the groups of C₃-BTs, C₄-BTs, C₅-BTs and C₃-DBTs. It is believed that further identification and quantification of individual OSC would be useful to process the kinetics study of individual OSCs in diesel fuels under UAOD conditions.

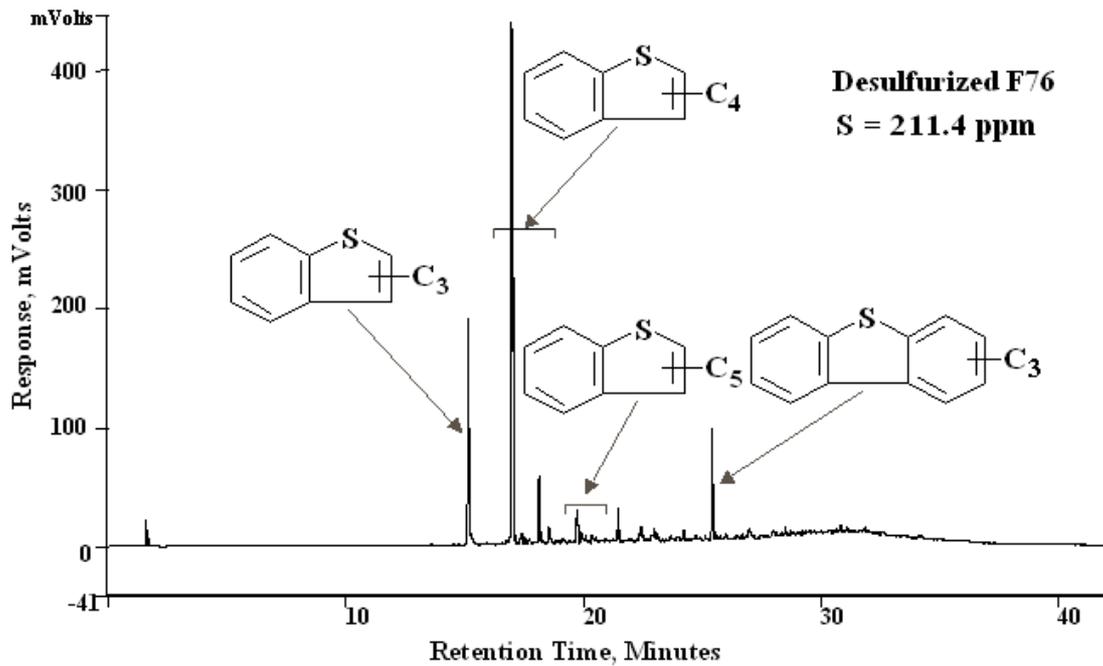


Figure 4 Organic sulfur compounds remain in the desulfurized F76 after UAOD process

The UAOD on MGO Marine Logistical Diesel

The total sulfur content of the MGO marine diesel is 1,710 ppm. Figure 5 shows the distribution of OSCs in the original MGO. It is seen that the major types of OSCs are still BTs and DBTs, and the concentrations of BTs are lower than that of DBTs. Unlike F76, DBT and methyl-DBT are the most abundant species in MGO. It is estimated that MGO has 30 % BTs and 70 % DBTs of total sulfur content. Again, neither sulfides nor alkythiophene were found in the original F76.

Figure 5 also shows the changes of organic sulfur compounds in MGO after oxidation and solvent extraction. It is demonstrated that both BTs and DBTs oxidized to form corresponding BTOs and DBTOs, respectively. After solvent extraction by acetonitrile, the sulfones in the oxidized MGO were essentially removed. As a result, the total sulfur content of desulfurized MGO was 20.9 ppm. The overall sulfur removal of UAOD on MGO was 98.8 %.

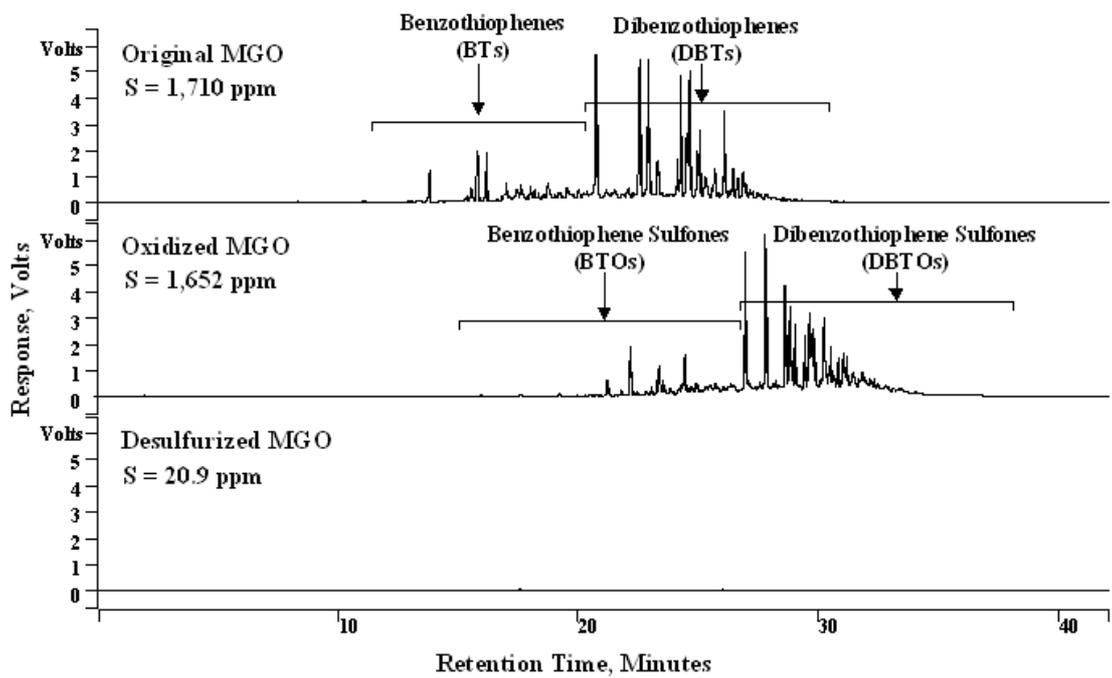


Figure 5 GC-PFPD chromatograms of MGO Marine diesel in UAOD process

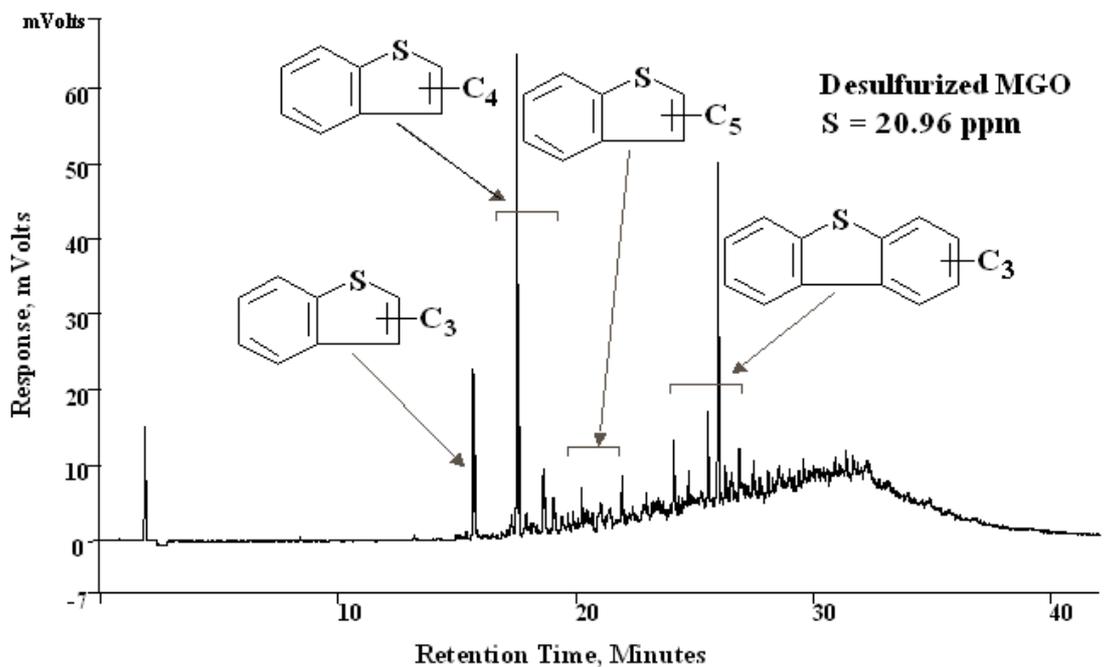


Figure 6 Organic sulfur compounds remain in the desulfurized MGO after UAOD process

Figure 6 indicates that there are four major sulfur compounds left in the desulfurized MGO. Based on the retention time, these four sulfur compounds are categorized into groups of C₃-BTs, C₄-BTs, C₅-BTs and C₃-DBTs. It is believed that further structural characterization of these four Sulfur compounds is essential to process design and optimization.

The UAOD on JP5 Marine Logistical Diesel

The total sulfur content of the JP5 Marine diesel is 113.7 ppm. Figure 7 shows the distribution of organic sulfur compounds in the original JP5. Clearly, unlike F76 and MGO, BT and methyl-BTs are the most abundant species in JP5. Again, neither sulfides nor alkylthiophene were found in the original F76. Moreover, as shown in Figure 7, most BTs in the JP5 were oxidized into corresponding sulfones within 10 min and subsequently removed by solvent extraction. The total sulfur content in the desulfurized JP5 was 27.7 ppm. The overall sulfur removal of UAOD on JP5 was close to 87.5 %.

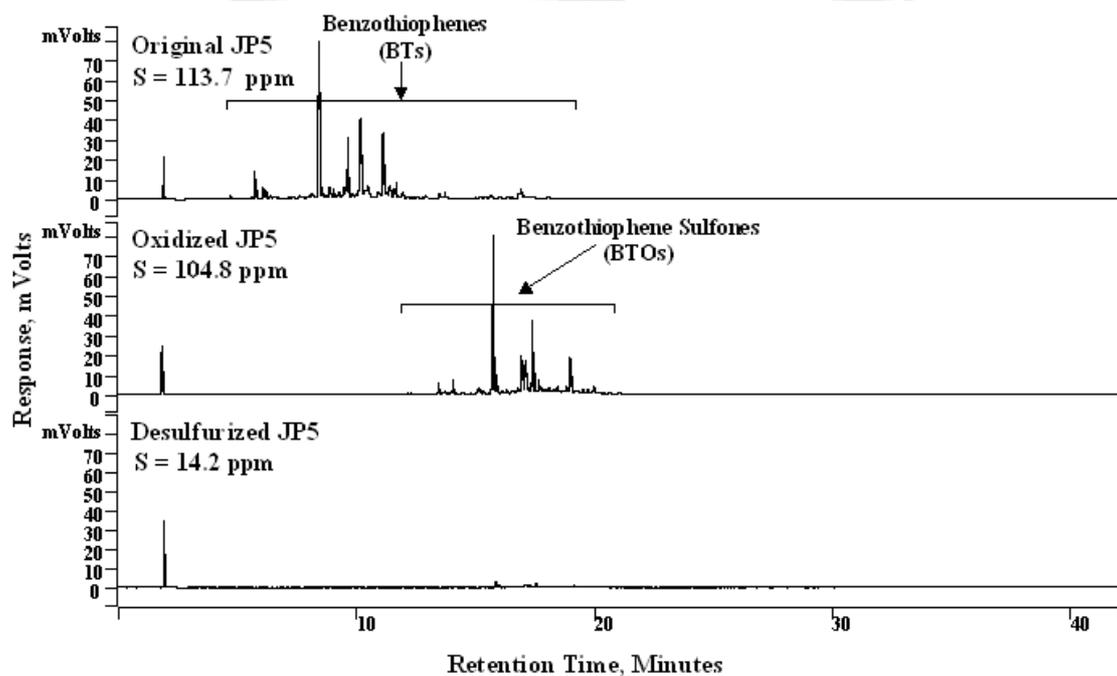


Figure 7 GC-PFPD chromatograms of JP5 Marine diesel in UAOD process

Figure 8 indicates that there are two major BTs left in the desulfurized JP5, including C₃-BTs and C₄-BTs groups. Interestingly, these two BT compounds in the desulfurized JP5 were identified as the same sulfur species in the desulfurized F76 and desulfurized MGO. Therefore, It indicates that marine diesel fuels, with different composition, distribution of OSCs and total sulfur content, may lead to very similar low sulfur diesels (LSD) with respect to the remaining sulfur species after UAOD process.

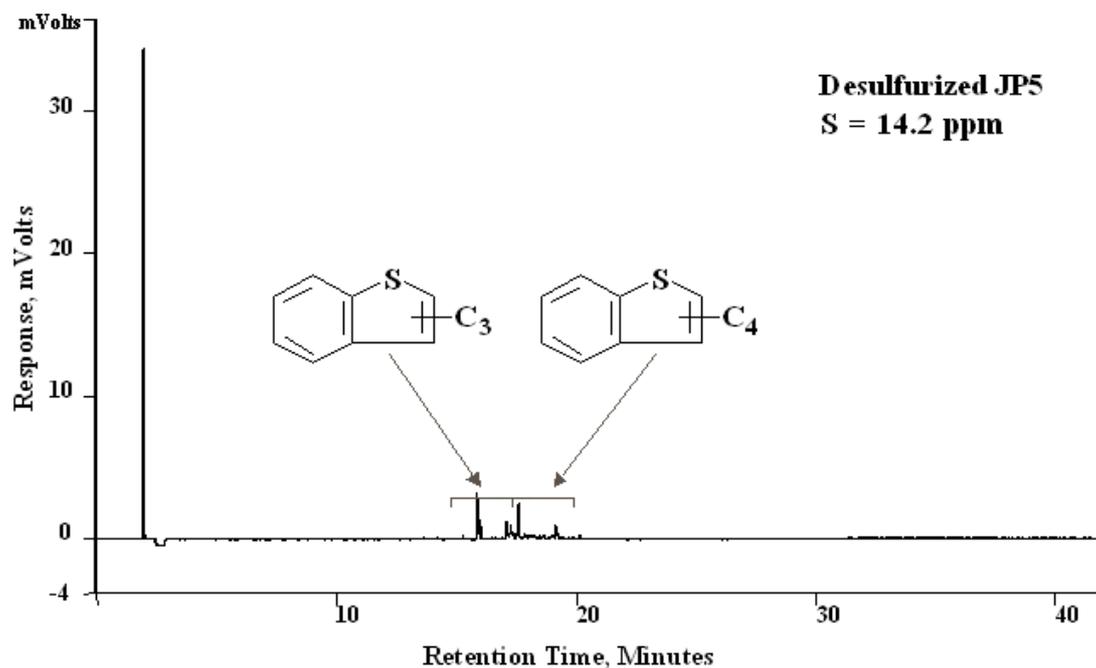


Figure 8 Organic sulfur compounds remain in the desulfurized JP5 after UAOD process

The UAOD on Transportation Diesel

The total sulfur content of transportation diesel is 259 ppm. Comparison of GC-PPFD chromatograms of original diesel, oxidized diesel and desulfurized diesel in UAOD process is shown as Figure 5.9. Two main groups of sulfur compounds, BTs and DBTs, were oxidized to form benzothiophene sulfones (BTOs) and dibenzothiophene sulfones (DBTOs), respectively. After being extracted by acetonitrile, the sulfones in oxidized diesel partitioned into solvents and produced a diesel with total sulfur content of 10 ppm. The overall sulfur removal of UAOD on transportation diesel is close to 96.1 %.

Organic Sulfur Compounds (OSCs) have different reactivity in oxidation and the extractability of their oxidized products also varies in solvent extraction. Figure 10 shows that there are some small amounts of unreacted BTs and DBT that remained in the desulfurized diesel, including the groups of C₄-BTs and C₃-DBTs. It also indicates that transportation diesel with different composition, distribution of OSCs and total sulfur content than marine diesel fuels, may lead to very similar low sulfur diesels (LSD) with respect to the remaining sulfur species after UAOD process. Therefore, for diesel fuels containing various levels of sulfur content and different composition and distribution of organic sulfur compounds, through the use of catalytic oxidation and sonication, sulfur removal efficiency can reach or exceed 95 % in a short contact time at ambient temperature and pressure. This process can be a simple approach for future application to obtain the ultra-low sulfur diesel.

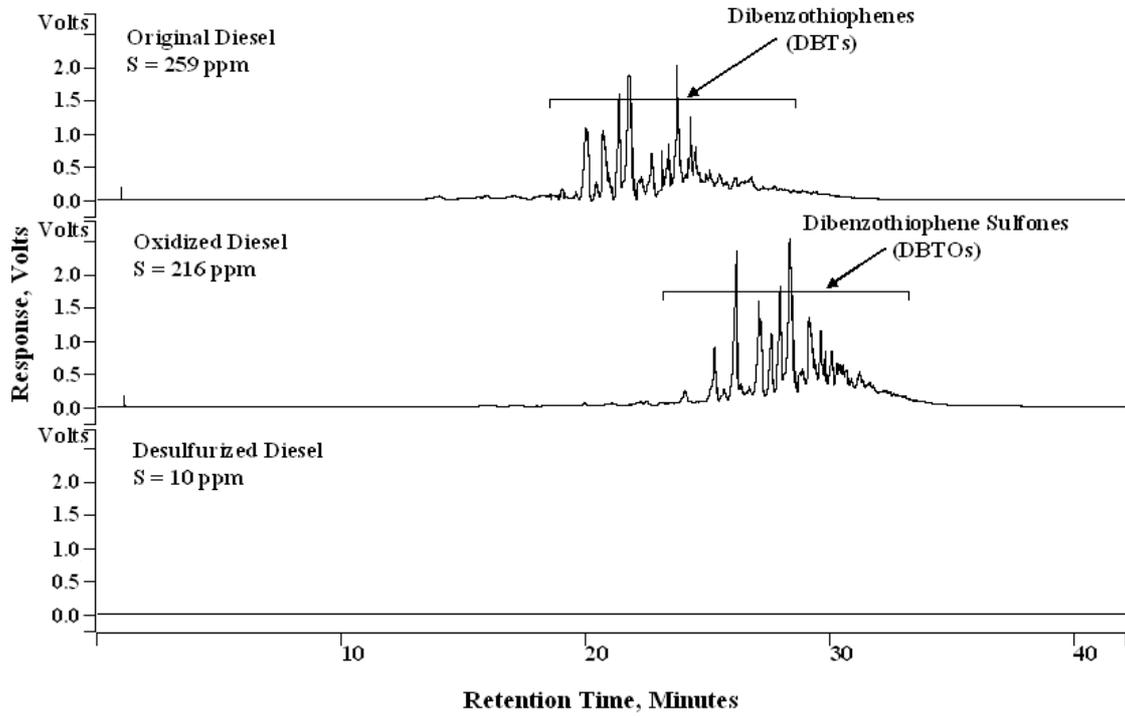


Figure 9 GC-PFPD chromatograms of transportation diesel in UAOD process

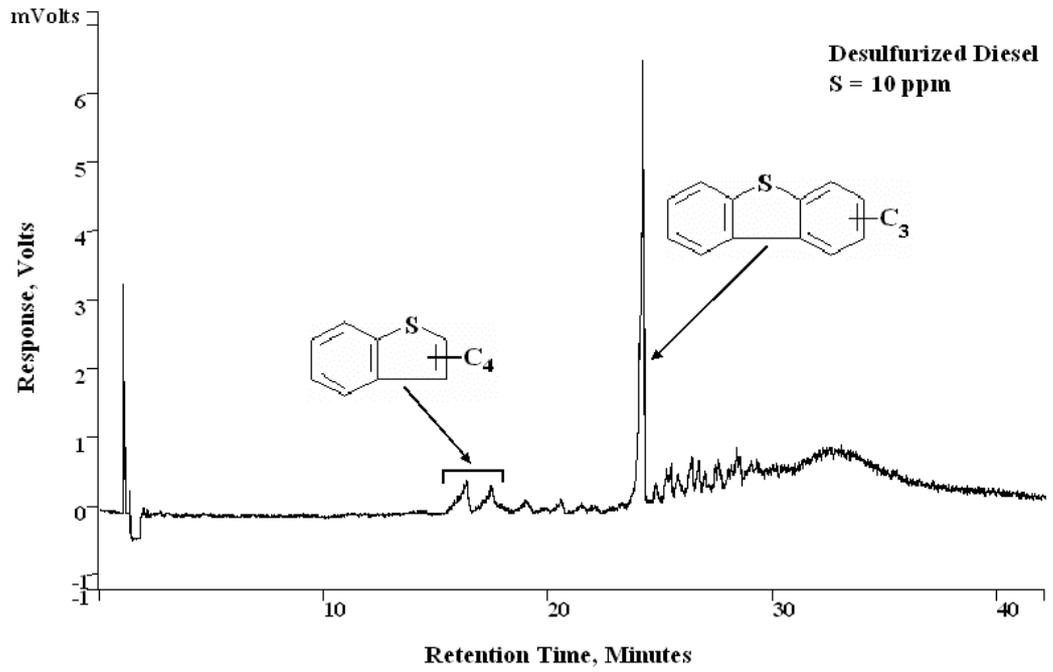


Figure 10 Organic sulfur compounds remain in the desulfurized transportation diesel after UAOD process

Effects of UAOD on Main Hydrocarbons in Diesel Fuels

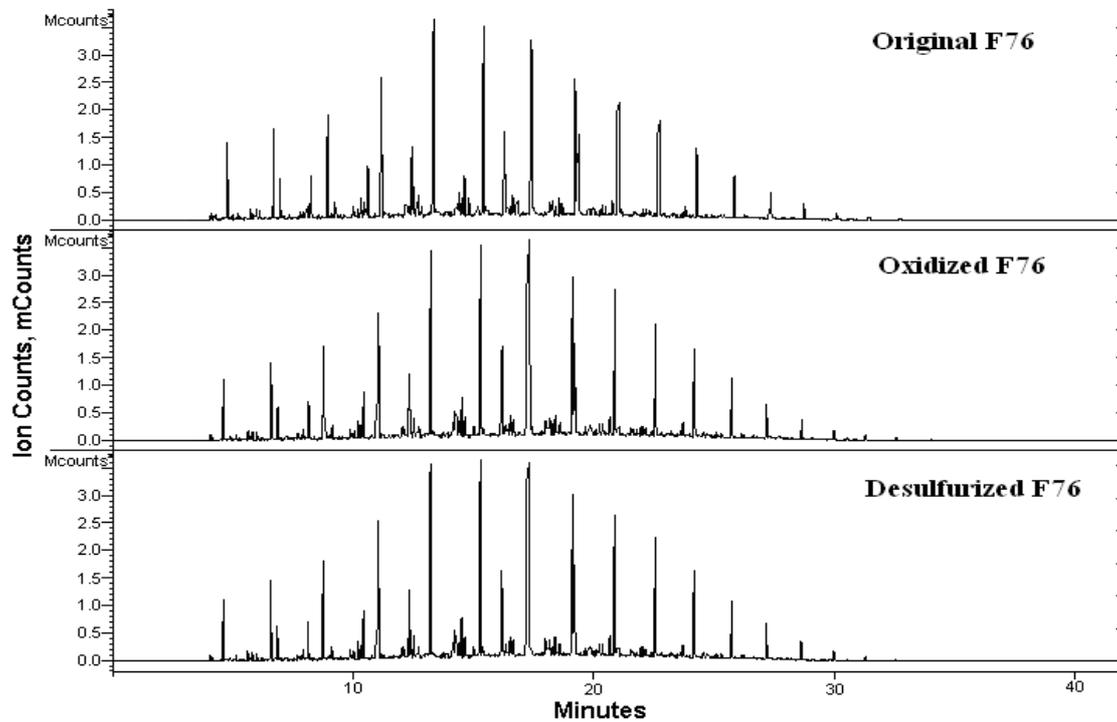
The main components of diesel fuels are saturated and aromatic hydrocarbons. Saturated hydrocarbons are dominant diesel components that include normal paraffins (*n*-paraffins), isoparaffins and cycloparaffins (naphthenes). Aromatic compounds in diesel fuels are mainly alkylbenzenes, florenes, phenanthrens, anthracenes and naphthenophenanthrens. Diaromatic hydrocarbons with naphthalene-type structure are the more abundant aromatic components in diesel fuels. Traces of polycyclic aromatic hydrocarbons (PAH) such as chrysens, pyrenes, benzanthracenes, and perylenes may also be present (Song, 2000).

Before fully investigating the desulfurization process, a study of the selectivity of this oxidative process is very significant. It is known that a single mass chromatogram of a common characteristic fragment can present the distribution of a whole class of diesel components. For example, all of the *n*-paraffins yield m/z 57 fragment ions, *n*-alkyl cyclohexanes yield m/z 83 fragment ions and *n*-alkyl benzenes yield m/z 92 fragment ions. Therefore, m/z 57, 83, and 92 mass chromatograms can exhibit the whole class of *n*-paraffins, *n*-alkyl cyclohexanes, *n*-alkyl benzenes, respectively. For alkylnaphthalenes, the combination mass chromatogram of molecular ions, m/z 128, 142, 156, 170, and 184 presents the distribution of alkylnaphthalenes with alkyl carbon atom from 0 to 4.

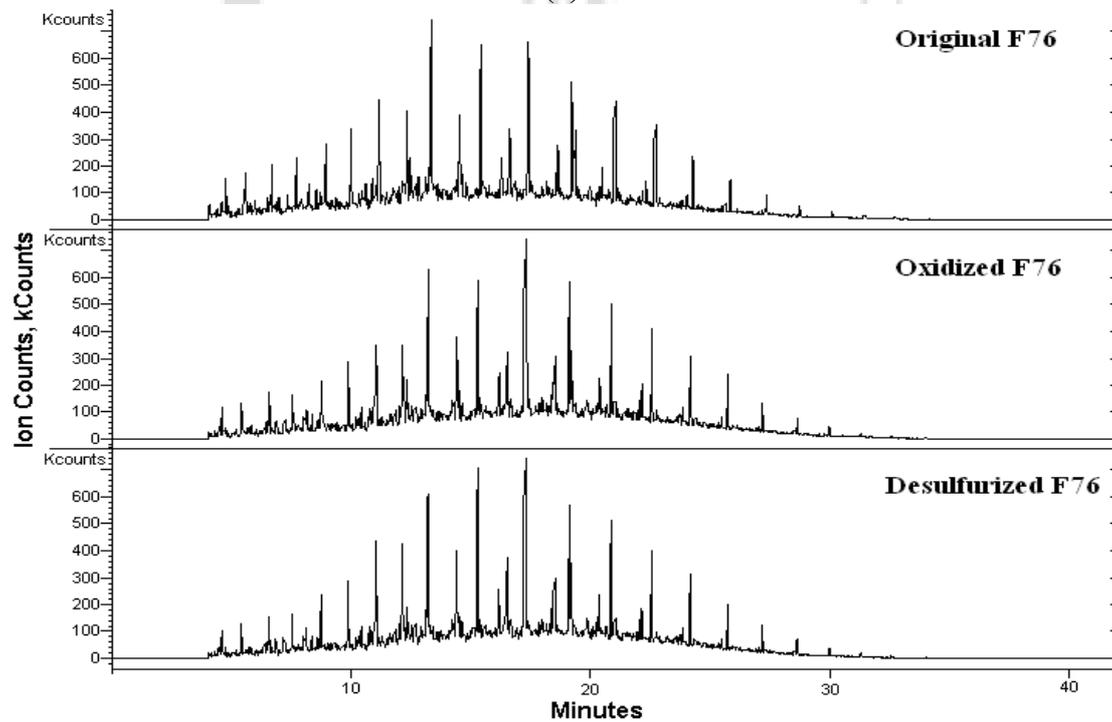
Figure 11 shows that there are no significant changes in both distribution and intensity of *n*-paraffins peaks (Figure 11a) in the original F76, oxidized F76 and desulfurized F76. The selected ion chromatograms (SICs) of 83 Da ion (Figure 11b) and 92 Da ion (Figure 12a), extracted from GC-MS analysis of F76 at different stages of UAOD, also follow the same pattern. This indicates that *n*-paraffins, *n*-alkyl cyclohexanes, and *n*-alkyl benzenes were not subject to any negative effects in both oxidation and solvent extraction steps in UAOD process.

However, Figure 12b indicates that even though alkylnaphthalenes did not undertake significant changes in the oxidation steps, the intensity of alkylnaphthalenes peaks in the desulfurized F76 decreased obviously due to solvent extraction. This shows that alkylnaphthalenes have relatively higher polarity than saturated hydrocarbons and benzenes, and intend to partition into polar solvents. However, this portion of aromatics can easily be recovered by distillation of solvent extract.

For MGO JP5 and transportation diesel, the SIM analysis indicated similar distribution and intensity to F76 for four selective compounds. The pattern of *n*-paraffins, *n*-alkyl cyclohexanes, and *n*-alkyl benzenes in both oxidation and solvent extraction steps in UAOD process were not subject to any negative effects. The intensity of alkylnaphthalenes peaks in the desulfurized diesels decreased due to solvent extraction. An alternative way is to change the solubility parameter of acetonitrile by blending with another solvent. These experimental findings should be optimized against the solubility of alkyl aromatics.

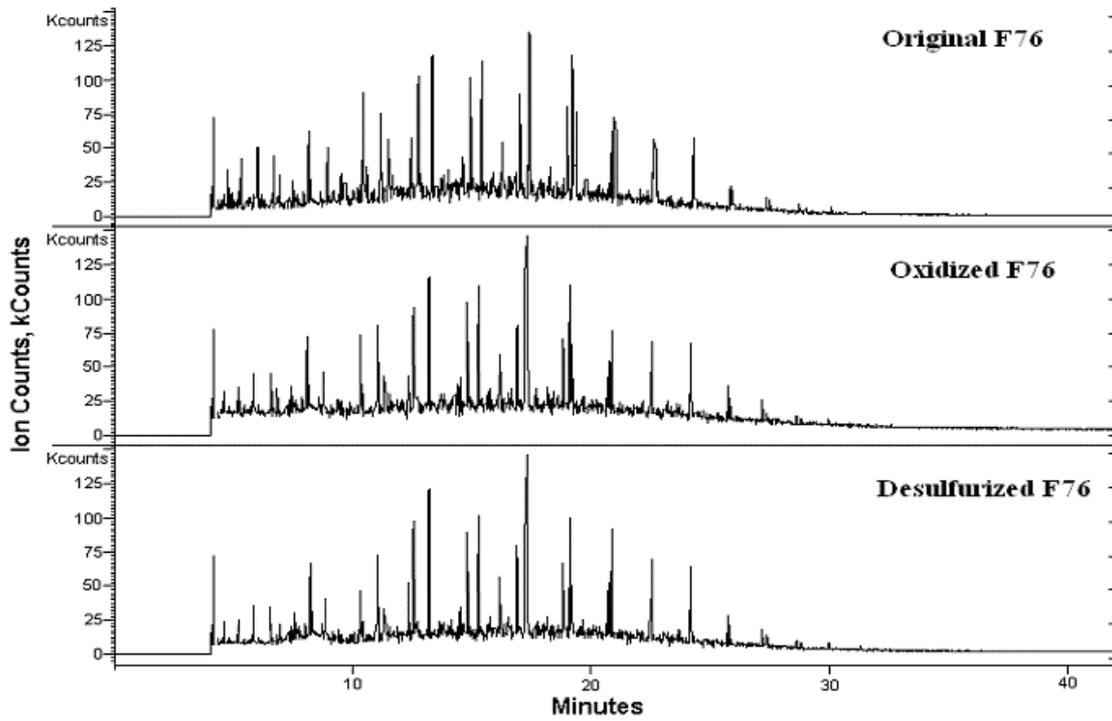


(a)

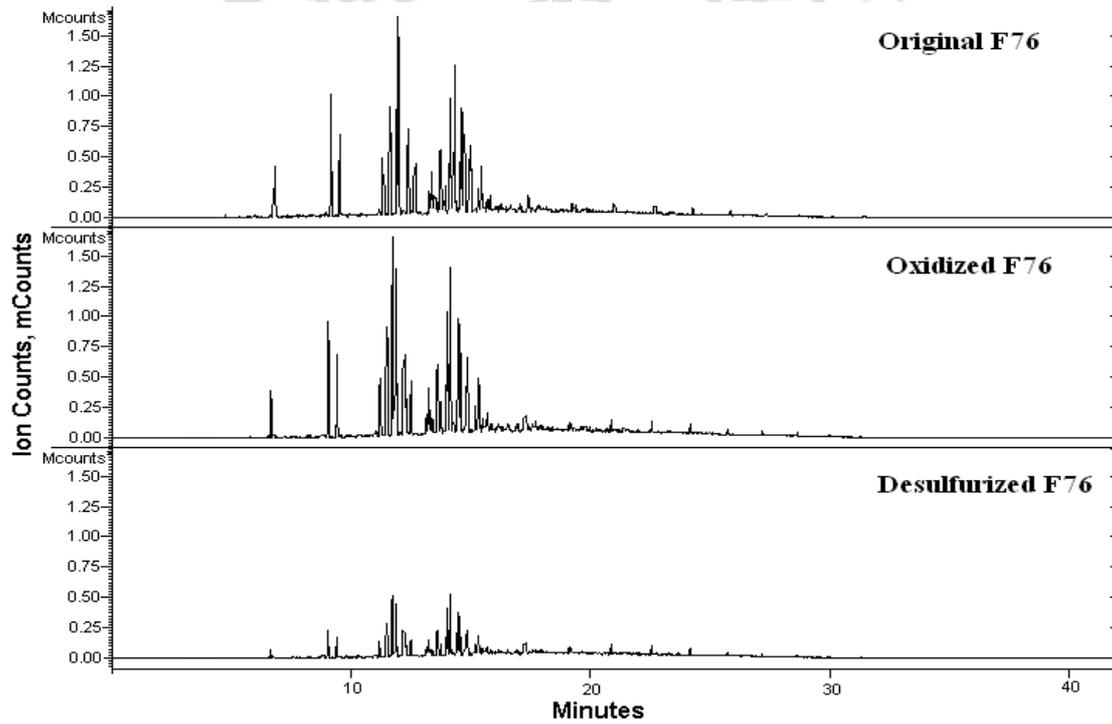


(b)

Figure 11 Effects of UAOD on saturated hydrocarbons in marine logistic fuel.
 (a) *n*-paraffins, (b) *n*-alkyl cyclohexanes



(a)



(b)

Figure 12 Effects of UAOD on saturated hydrocarbons in marine logistic fuel.
 (a) *n*-alkyl benzenes, (b) alkylnaphthalenes

Selective ion monitoring (SIM) technique in GC/MS analysis provides a unique illustration of UAOD process on diesels at a molecular level. It was employed in this study to trace the changes of OSCs as well as major hydrocarbons in diesels throughout UAOD process. It firmly demonstrated that UAOD process has high efficiency and high selectivity on oxidizing the OSCs to sulfones.

Conclusion

In this study, for marine diesel fuels and transportation diesel fuels containing various levels of sulfur content, through the use of catalytic oxidation and sonication followed by solvent extraction, removal of sulfur-bearing compounds can reach high sulfur removal in a short contact time at low temperature and atmospheric pressure. The results of the oxidative desulfurization of diesels fuels by UAOD process are summarized in Table 13.

Table13 Desulfurization efficiency of UAOD process on diesel fuels

Diesel Fuels	Sonication time (min)	Sulfur Content (ppm)			Sulfur Removal (%)
		Original	After Oxidation	After Extraction	
F76	10	4,222	4,105	211.4	95.0
MGO	10	1,710	1,652	20.9	98.8
JP5	10	113.7	104.8	14.2	87.5
Transportation	10	259	216	10.0	96.1

It is seen that there are four major sulfur organic compounds left either in desulfurized F76, MGO and JP5 or desulfurized transportation diesel. Those four sulfur compounds, which are categorized as the group of C₃-BTs, C₄-BTs, C₅-BTs and C₃-DBTs, will be among the most refractory compounds in marine logistic diesels under UAOD conditions. This information is essential to understand the reactivity of various organic sulfur compounds under oxidative conditions and to carry out the model sulfur compound study. It also provides a direction for the design and optimization of the desulfurization process.

Selective ion monitoring (SIM) technique in GC/MS analysis provides a unique illustration of the UAOD process on diesels at a molecular level. It was employed in this study to trace the changes of OSCs as well as major hydrocarbons in diesels throughout the UAOD process. It firmly demonstrated that the UAOD process has high efficiency and high selectivity on oxidizing the OSCs to sulfones.

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