# ULTRA CLEAN FUELS VIA MODIFIED UAOD PROCESS WITH ROOM TEMPERATURE IONIC LIQUID (RTIL) & SOLID CATALYST POLISHING

by

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# DEDICATION

To my parents,

Hsiu-Chen Ou and Kuang-Yu Cheng,

To my sister,

Ting-Yu Cheng

For their support, patience, and love throughout my life.

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# ABBREVIATIONS

| | |
|---|---|
| [BMIM][$OcSO_4$] | 1-Butyl-3-Methylimidazolium Octyl Sulfate |
| [BMIM][$PF_6$] | 1-Butyl-3-Methylimidazolium Hexafluorophosphate |
| [EDMIM][$EtSO_4$] | 1-Ethyl-2,3-Di-Methylimidazolium Ethyl Sulfate |
| [EMIM][$EtSO_4$] | 1-Ethyl-3-Methylimidazolium Ethyl Sulfate |
| [EMIM][$EtSO_4$] | 1-Ethyl-3-Methylimidazolium Ethyl Sulfate |
| [$TBMNH_4$][$MeSO_4$] | Tri-Butyl Methyl Ammonium Methyl Sulfate |
| [TBMP][$MeSO_4$] | Tri-Butyl Methyl Phosphonium Methyl Sulfate |
| 2ET | 2-Ethyl Thiophene |
| 2MBT | 2-Methyl Benzothiophene |
| 2MT | 2-Methyl Thiophene |
| 4,6-DMDBT | 4,6-Dimethyl Dibenzothiophene |
| $AlCl_3$-TMAC | Tri-Methylammonium Chloroaluminate |
| ASTM | American Society of Testing and Materials |
| BDS | Biodesulfurization |
| $BF_4^-$ | Tetrafluoroborate Anion |
| BT | Benzothiophene |
| BTO | Benzothiophene Sulfone |
| CARB | California Air Resource Board |
| $CH_3CN$ | Acetonitrile |
| $Cl^-$ | Chloride ion |
| $CoMO/Al_2O_3$ | Catalyst Contain Alumina |
| DBT | Dibenzothiophene |

| | |
|---|---|
| DBTO | Dibenzothiophene Sulfone |
| DMF | N,N-Dimethylformamide |
| DMSO | Dimethylsulfoxide |
| EPA | Environmental Protect Agency |
| FID | Flame Ionization Detector |
| GC | Gas Chromatograph |
| $H_2O_2$ | Hydrogen Peroxide |
| HBP | 2-Hydroxybiphenyl |
| HDS | Hydrodesulfurization |
| HF | Hydrogen Floride |
| HPLC | High Performance Liquid Chromatography |
| ILs | Ionic Liquids |
| L/L | Liquid-Liquid |
| LSD | Low Sulfur Diesel |
| MBSL | Multiple-Bubble Sono-Luminescence |
| MeCN | Acetonitrile |
| MS | Mass Spectroscopy Detector |
| NaOH | Sodium Hydroxide |
| NDXRF | Non-Dispersive X-Ray Flurescence |
| Ni/ZnO | Nickel / Zinc Oxide |
| NiS | Nickel Sulfide |
| NMO | *N*-Methylmorpholine *N*-Oxide |
| $NO_x$ | Nitric Oxides |
| NRLM | Land-Based Non-Road, Locomotive And Marine Fuels |

| | |
|---|---|
| $NTf_2$ | Bis-(trifluoromethanesulfonyl)imide |
| O/W | Oil-in-Water |
| ODS | Oxidative Desulfurization |
| OH | Hydroxyl Radical |
| OSCs | Organic Sulfur Compounds |
| PAH | Polycyclic Aromatic Hydrocarbons |
| $PF_6^-$ | Hexafluorophosphate |
| PFPD | Pulse Flame Photometric Detector |
| PM | Particulate Matter |
| PTA | Phase Transfer Agent |
| PTC | Phase Transfer Catalysis |
| QAS | Quaternary Ammonium Salts |
| RMIM | Alkyl-Imidazolium |
| RPY | Alkyl-Pyridinium |
| RTI | Research Triangle Institute |
| RTIL | Room Temperature Ionic Liquid |
| SARS | Selective Adsorption For Removing Sulfur |
| SCD | Sulfur Chemiluminescence Detector |
| SL | Sonoluminescence |
| SLFA-20 | Sulfur-in-Oil Analyzer |
| $SO_x$ | Sulfur Oxides |
| T | Thiophene |
| TAM | Tetra-Alkylammonium |
| TAP | Tetra-Alkylphosphonium |

| | |
|---|---|
| TfO | Triflate |
| Ti-B | Titanium Beta |
| TMC | Transition Metal Catalyst |
| TOAF | Tetraoctylammonium Fluoride |
| TPA | Tri-Fluoro Acetic Acid |
| TReND | Transport Reactor For Naphtha Desulfurization |
| TS-1 | Titanium Silicates |
| UAOD | Ultrasound Assisted Oxidative Desulfurization |
| ULSD | Ultra Low Sulfur Diesel |
| VOCs | Volatile Organic Compounds |
| VPT | Vapor Phase Transport |
| W/O | Water-in-Oil |

# ABSTRACT

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 fluidized bed reactor (FBR), which has been considered as one of the innovative schemes related to the desulfurization. In this respect, ionic liquid, oxidant, phase transfer catalysis, stirring, sonication, and acid catalyst have been combined in the modified UAOD process specifically. Thus, mild conditions have also provided high desulfurization efficiency.

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.

Various levels of sulfur content are contained, and can be observed in diesel fuels. Valley Oil, JP-5, and Treated Valley Oil 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.

In the pilot study, treatment tank, a pipeline system, as well as, high shear mixer has been created for the development of practical application of a batch-type continuous flow system. During these developments, appropriate time and mild conditions were given during the operations. The results show 99.9% of desulfurization efficiency can be achieve by the process. Moreover, utilization of ionic liquid and acid catalyst had been done at a less extent by the pilot study, as compared to the batch study.

FBR has been used to pass the oxidized organic compounds that have came 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 dissertation that sulfur removal from the diesel fuels can be done effectively by the employment of modified UAOD process and FBR. In addition, new environmental standards can be met easily by the production of ULSD fuel by the utilization of appropriate design, as well as, chemicals during the process.

# CHAPTER 1

# INTRODUCTION

## 1.1 General Overview

Diesel fuel and gasoline are the two main transportation fuels used today. They are derived from a common source, crude oil. Share similarities in physical properties and chemical composition. The environmental consequences of sulfur and nitrogen containing compounds in gasoline initiated the ground breaking environmental regulations collectively known as the various "clean air acts" of the late 20th century. The focus today is to achieve similar goals for diesel fuels. This introduction will describe the physical and chemical composition of diesel fuels, emphasizing proposed environmental regulations regarding the sulfur containing constituents and the current technologies employed to meet these goals.

## 1.2 Diesel Fuel

Diesel fuel is produced from petroleum. The density of diesel fuel (Simetric. Co. Uk) is between 820 to 950 grams per liter (g/l), somewhat heavier than the density of gasoline (Simetric. Co. Uk) which is between 710 to 740 grams per liter. The average empirical formula for diesel fuel lies in the range of $C_{10}H_{22}$ to $C_{15}H_{32}$. Diesel fuel is predominantly a mixture of 75% aliphatic hydrocarbon (Speight, et al. 2002) and 25% aromatic hydrocarbons (Speight, et al. 2002). Aliphatic hydrocarbons include paraffins (alkanes) and naphthalenes (cycloalkanes), and aromatic hydrocarbon includes alkyl-benzene and olefins (styrene).

Polycyclic aromatic hydrocarbons (PAH), are aromatic hydrocarbons that contain one or more “benzene” ring structures. PAH have a higher density than aliphatic hydrocarbon and produce more soot in burning. From these emissions, pollutants such as sulfur dioxide will cause environmental hazards; some unregulated pollutants are mutagenic in the Ames test (Yen, et al. 1999).

Recently, a great deal of attention has been placed on diesel engines with respect to fuel availability and fuel economy. The major drawback of diesel engines, is the environmental concern of the emission of high amounts of particulate matter (PM) and nitric oxides ($NO_x$). Figure 1.1(a) shows the $NO_x$ emissions trend for diesel vehicles and Figure 1.1(b) shows the PM emission trend for diesel vehicles from the early 1970’s to the late 1990s (NAPET). Due to these environmental and health issues, increasingly restrictive legislation has applied.

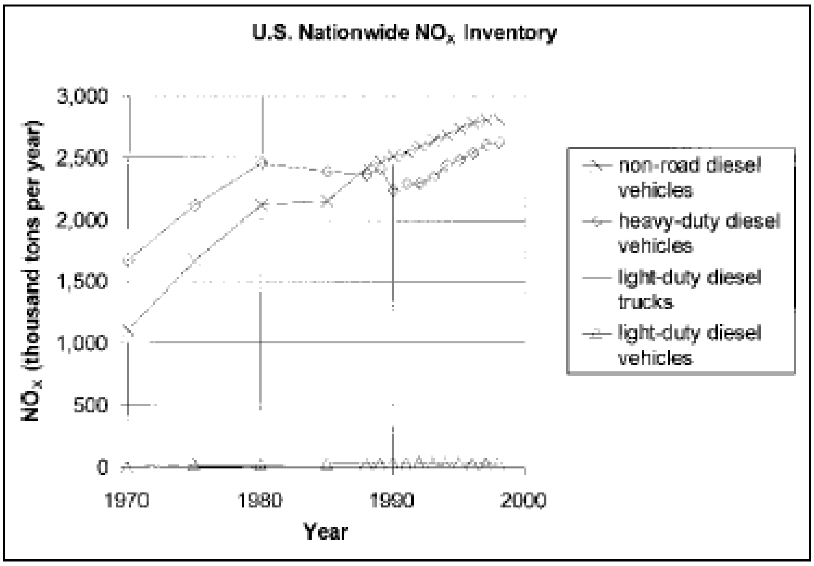


Figure 1.1 (a) Diesel NO$_x$ emissions of non-road and highway vehicles.(NAPET)

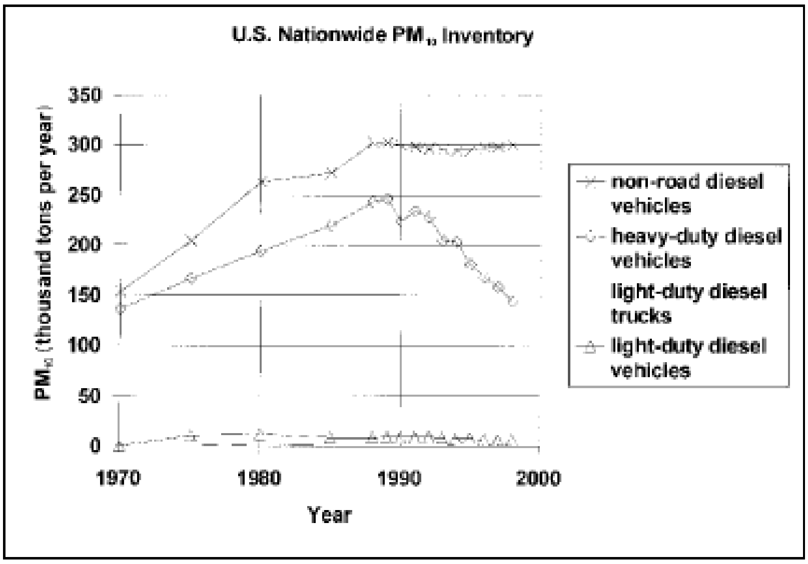


Figure 1.1(b) PM emissions of non-road and highway vehicles.(NAPET)

The presence of organic sulfur is one of major factors that correlate to the emission of particulate matter (sulphate particulate matter) and sulfur oxides (SO$_x$). Sulphate particulate matter includes PM$_{2.5}$ and PM$_{10}$ emissions that contribute health and environmental effects. Sulfur oxides can further react with water vapor in the atmosphere to form acid rain with its well known environmental consequences; building corrosion and damage to forest and crops. Within the diesel engine, sulfur damages the catalytic converter, acidifies the lubricating oil, and reduces the fuel economy.

Besides elemental sulfur, thiols, sulfides and thiophenes (Speight, et al. 2000), can be classified as organic sulfur compounds (OSCs). There are three major types of OSCs: thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT). Table 1.1 shows the chemical structure of major types of sulfur compound in diesel. DBT have higher molecular weight due to the two “benzene” ring structure.

Figure 1.2 shows the chromatogram of a simple diesel fuel to illustrate the distribution of the OSCs. It can be seen that diesel fuels contain mainly alky-BTs and alkyl-DBTs and partially alkyl-Ts.

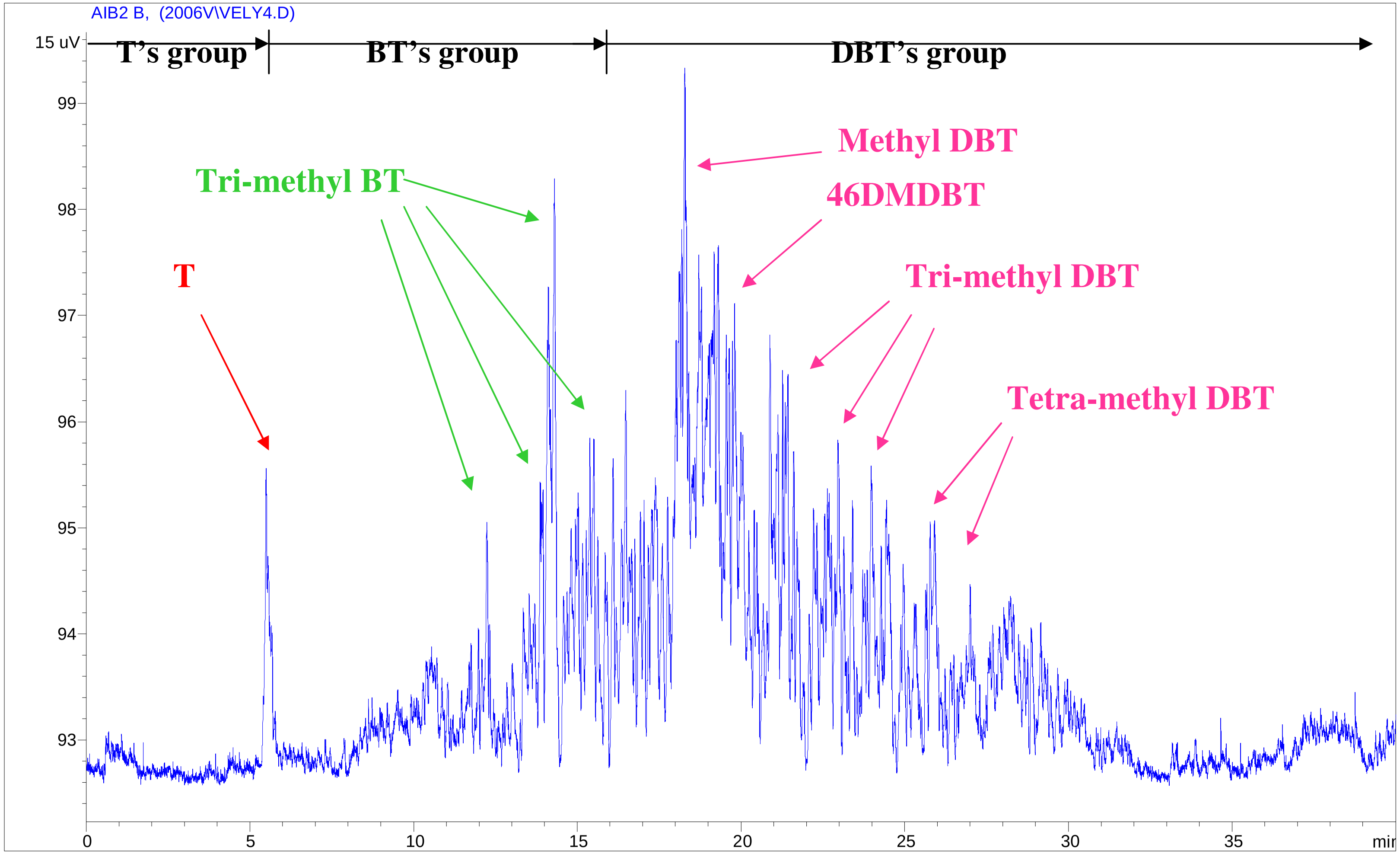
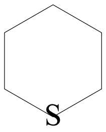
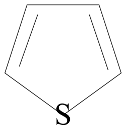
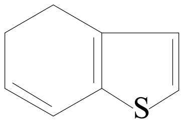
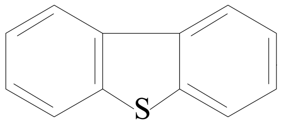


Figure 1.2 GC-SCD chromatogram of organic sulfur compounds distribution in diesel fuel

Table 1.1 Major types of OSCs in diesel fuel

| | |
|---|---|
| Thiols | RSH |
| Sulfides | RSR |
| Cyclic Sulfide |  |
| Thiophene |  |
| Benzothiophene |  |
| Dibenzothiophene |  |

## 1.3 Diesel Fuel: Sulfur Regulations

In 2006, The Environmental Protection Agency (EPA) and the California Air Resource Board (CARB) approved the new standards requiring the petroleum industry to produce Ultra Low Sulfur Diesel (ULSD) fuel containing only 15 ppm sulfur. The new regulations were designed to not only improve air quality and public health, but also vehicle performance. ULSD fuels will enhance the efficiency and durability of engines, and allow the use of more advanced emission control devices, thus assuring dramatic reductions in PM and $NO_x$ emissions. Table 1.2 summarizes the new sulfur standard for both highway diesel fuels and non-road diesel fuels (U.S EPA. 2000).

### 1.3.1 Highway Diesel Fuels

Since October 1993, sulfur content regulation for highway diesel fuels was 500 parts per million (ppm) also known as Low Sulfur Diesel (LSD). LSD is regulated by the EPA. In January 2001, the EPA established new regulations for highway diesel fuel with maximum sulfur content of 15 ppm (ULSD). By June 2006, all the highway diesel fuel produced from refineries must meet standards (U.S EPA. 2000). In 2007, all the light and heavy duty diesel engines will only use ULSD fuels instead of LSD fuel.

### 1.3.2 Non-road Diesel Fuels

Non-road diesel fuels include land-based non-road, locomotive and marine fuels (NRLM). Since 1993 to 2000, the legislation of sulfur content for non-road diesel fuels is 5000 ppm. With new EPA regulation, two steps are involved to achieve 15 ppm sulfur standard. In June 2007, the sulfur content for non-road diesel fuels was limited to 500 ppm. In June 2010, land-based non-road diesel fuels must meet 15 ppm ULSD fuels standard. By June 2012, locomotive and marine diesel fuels must meet 15 ppm ULSD fuels standard (U.S EPA. 2000).

Table 1.2 U.S. EPA Diesel Fuel Sulfur Standards (U.S. EPA. 2000)

| Diesel Type | Implementation Date | Maximum Sulfur Level (PPM) |
|---|---|---|
| Highway | 1993 | 500 |
| Highway | 2006 (June) | 15 |
| Land-base non-road | 1993 | 5,000 |
| Land-base non-road | 2007 (January) | 500 |
| Land-base non-road | 2010 (June) | 15 |
| Non-road (locomotive & marine) | 2012 (June) | 15 |

## 1.4 Desulfurization Technologies

To meet the technological and environmental concerns, various processes have been employed.

### 1.4.1 Hydrodesulfurization (HDS)

Hydrodesulfurization (HDS) also know as a hydrotreating process, is one of the most common desulfurization methods that have been used in refinery processes since the 1950s. HDS takes place in a fixed bed reactor. The mixture of sulfur bearing hydrocarbon feed and hydrogen gas enters the reactor: the sulfur bearing hydrocarbon feed will pump up to pressure ranging from 13 to 130 atmospheres. The higher pressure feed will join with hydrogen gas and then pass through a heat exchanger to heat up the liquid-gas mixture with temperatures ranging from 300 to 400°C. In the reactor, catalyst contains alumina ($CoMO/Al_2O_3$) base with cobalt and molybdenum was used to speed the reaction which results OSCs to hydrogen sulfide. Figure 1.3 shows the reaction pathway for various OSCs under catalytic reaction.

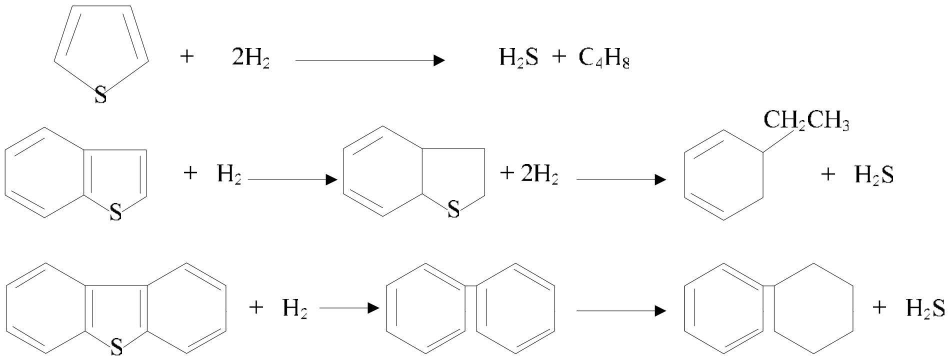


Figure 1.3 OSCs under $CoMO/Al_2O_3$ catalytic reaction

The resulting gas/liquid mixture of hydrogen sulfide, hydrogen gas and liquid fuel were separated by a gas separator vessel, the reaming hydrogen gas was recycled and passed through amine tower for purification to give sulfur free hydrogen gas. The hydrogen sulfide is oxidized to sulfur dioxide by air and sulfur is formed. This process is called the Claus process. The overall reaction is show below.

$$2H_2S + SO_2 \rightarrow 3S(s) + 2H_2O$$

The fuel separate from gas separator vessel were passed though stripper distillation tower. This is the final stage for HDS. Inside the distillation tower, sour gas (hydrogen sulfide, methane, ethane and some volatile organic gas) is removed from liquid fuel. Some of the sour gas can be reused for further purpose like refinery fuel gas. Figure 1.4 gives a process flow of typical HDS unit in a refinery.

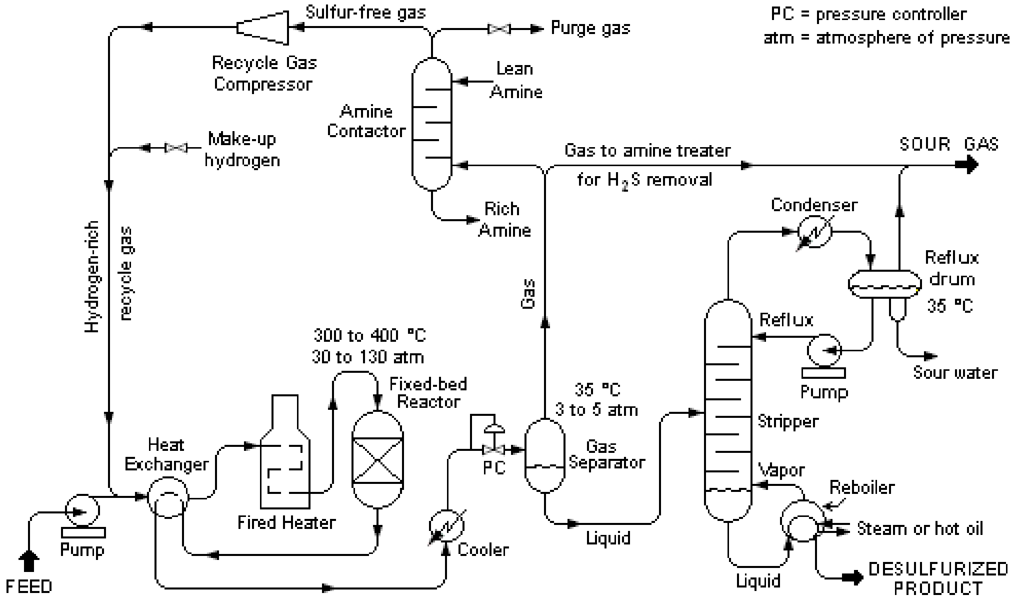


Fig 1.4 HDS unit

The disadvantages of HDS process are described as follow: (1) HDS requires operating at high temperature and pressure, which results in high cost and an explosive environmental process. (2) Some of the gas and heat of the waste gas stream cannot be reused, resulting in poor energy efficiency and creating new environmental concern. (3) The capital costs are high to build reactor, pipe and land usage.

To produce ULSD fuel from HDS is not easy, from the early research, the reactivities of OSCs decrease in order of one to three rings: Thiophenes >

benzothiophenes > dibenzothiophenes. According to recent studies, hydrotreating diesel fuel with 500 ppm sulfur content, alkyl-DBTs compounds were the refractory compounds that have great difficulty to desulfurize by HDS (Ma, et al. 1994 & Speight, et al. 2000); especially alkyl group at 4 and/or 6- position have low reactivity due to steric hindrance, electronic density, bond order and stacking degree of catalyst (Dagge, et al. 1994), Figure 1.5 is the schematic drawing of 4,6-dimethyl dibenzothiophene (4,6-DMDBT). (2) For new EPA sulfur regulations, the traditional HDS refinery can only produce LSD fuel. To meet the new regulations, it needs deeper HDS by increasing catalyst to fuel ratio, modification of catalysts, increasing hydrogen usage, and new reactor configuration is necessary. Studies shows doubling the amount of catalyst usage will only reduce sulfur content by 100 ppm with LSD fuel by current HDS unit, in other words, adding six or seven times of catalyst for HDS will meet the new sulfur standard (Whitehurst, et al. 1998). This will increment the cost of catalyst which is not economical. Hydrogen consumption is the main operating cost for HDS, to produce ULSD (15 ppm) fuel instead of LSD (500 ppm) fuel, it require addition 25 to 45 percent more hydrogen consumption (Charles River Associates, Inc). The new design of fixed bed reactor that can operate at pressures between 1,100 and 1,200 psig would be required. The reactor requires a thick wall to handle high pressure conditions, so it takes time and cost to manufacture (National Petroleum Council). Therefore, desulfurization the remaining sulfur of the distillate streams will be a challenge for refining industry.

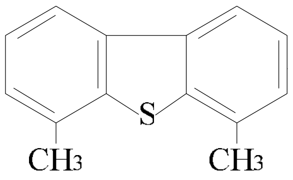


Figure 1.5 4,6-DMDBT

### 1.4.2 Biodesulfurization (BDS)

Biodesulfurization uses naturally occurring bacteria to act as biocatalysts to remove OSCs within diesel fuel. During the process, oil feed stock is mixed with a water phase that contains biocatalysts. The oil/water mixture was operated inside bioreactor under ambient temperature and pressure, during the desulfurization, air or oxygen is pumped into reactor to consumption of sulfur. OSCs such as DBT or alkyl-DBTs are oxidized through multi stage enzymatic reaction, Figure 1.6 shown the multi-enzyme pathway of the reaction using DBT as the model sulfur compound and *Rhodococcus* sp. strain IGTS8 as the biocatalyst. DBT is oxidizing into following order: sulfoxide, sulfone, sulfinic acid, 2-hydroxybiphenyl (HBP) and sulfate salt. The biocatalyst speed up the conversion of DBT to HBP by a multi-enzyme pathway, this involving two mono-oxygenases and a desulfinase, the final reaction catalyzed by the desulfinase is the rate limiting step. At end, inorganic sulfate salt can be easy removed because it is a water-soluble product (Gray, et al. 1996).

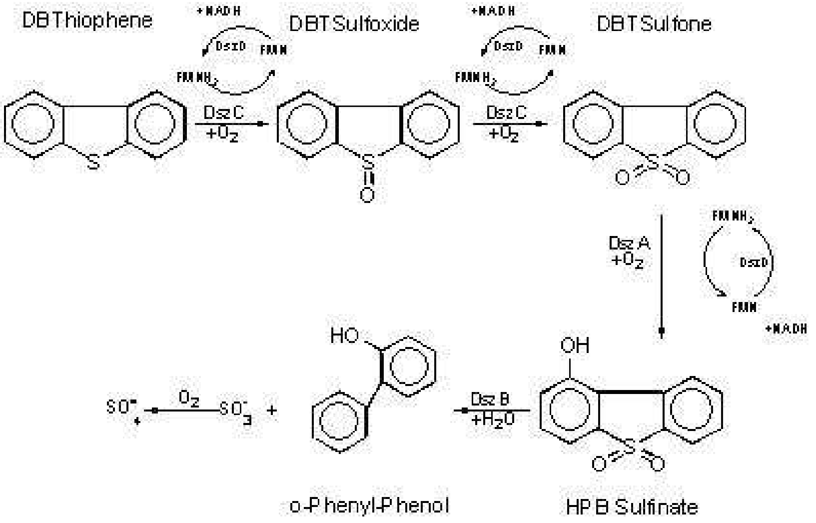


Figure 1.6 BDS of DBT by multi-enzyme pathway (Gray, et al. 1996)

Biocatalysts have high enzymatic activity and selectivity to oxidize OSCs without degrading the fuel value of the hydrocarbon matrix, therefore, BDS can be another alternative desulfurization technology. However, biocatalyst life is sensitive to environmental conditions such as reaction temperature, sterilization and solvent tolerance. Also, BDS have only tested in bench study, pilot or scale up application are still in developmental phase.

### 1.4.3 Adsorption Desulfurization

#### 1.4.3.1 S Zorb Sulfur Removal Technology

S Zorb sulfur removal technology is developed by ConocoPhillips to produce low sulfur gasoline (Gislason, et al. 2002). In 2001, ConocoPhillips start to operate and commercialize S Zorb unit in Borger refinery in Texas, USA, the production rate is about 6,000 barrels of gasoline per day (Gispason, et al. 2002). Figure 1.7 shows S Zorb process flow diagram.

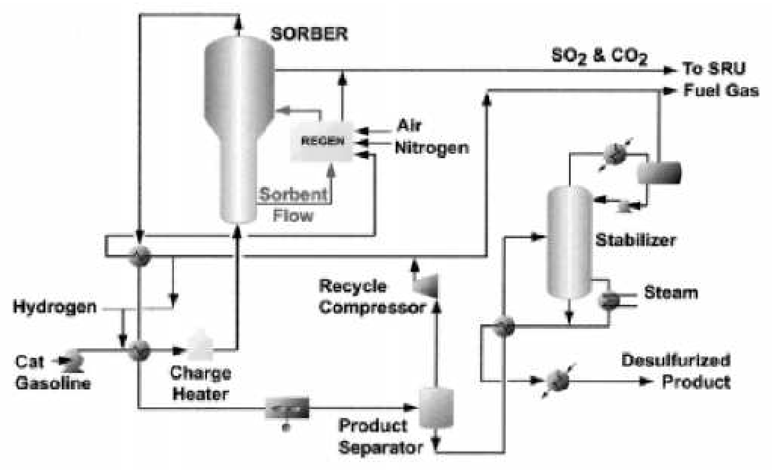


Figure 1.7 S Zorb sulfur removal technology flow diagram (Gispason, et al. 2002)

The adsorption process uses a proprietary sorbent to adsorb sulfur atom from OSCs, the adsorption reaction takes place in fluidized bed with presence of hydrogen, hydrogen attacks the sulfur compounds that results in weakening the sulfur atom's atomic bond that allows the reaction with the sorbent. A catalytic reaction occurs between the raw gasoline feed and hydrogen from the bottom of the fluidized bed reaction column and the sorbent is add at the top, the sulfur atom is remaining on the sorbent and hydrocarbon matrix is released back into the process stream. During the process, the sorbent that has adsorbed sulfur compounds is continuously conveyed to the regeneration unit where the sulfur is removed as sulfur dioxide under air oxidation, the sulfur dioxide gas is sent to the sulfur plant. The cleansed sorbent is reconditioned by purging with nitrogen and hydrogen to ensure that is returned to its original state and transferred back to the reactor for more desulfurization. In other words, adsorption reaction and regeneration of spend sorbent occur simultaneously. The rate of sorbent regeneration and adsorption process are carefully controlled to ensure the desired sulfur concentration in the product (ConocoPhillips). Figure 1.8 is an example of the sulfur removal by S Zorb.

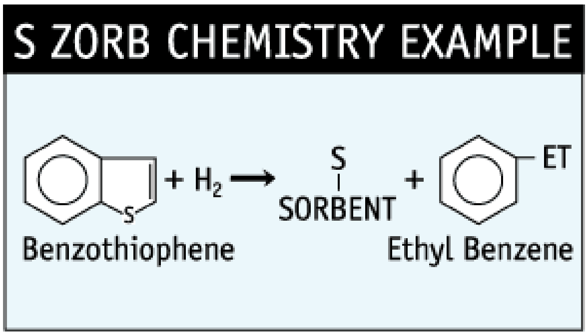


Figure 1.8 S Zorb Reaction Formula (ConocoPhillips)

S Zorb Sulfur Removal Technology did not produce hydrogen sulfide compare to HDS, therefore, product stream avoid recombination reactions of hydrogen sulfide and olefins to make mercaptans: which would increase the effluent sulfur concentration (ConocoPhillips).

#### 1.4.3.2 Transport Reactor for Naphtha Desulfurization (TReND)

TReND was developed by Research Triangle Institute (RTI), metal oxide-based sorbent is used to adsorb sulfur in a high throughput transport reactor, Figure 1.9 shows the schematic drawing of TReND process (Turk, et al. 2001). The liquid naphtha feed mix with hot hydrogen stream and vaporize within mixing zone: depending on the OSCs composition, if liquid naphtha contains mercaptan type sulfur and no aromatic sulfur, the TreND process do not require hydrogen gas. A pre-heater brings the naphtha feed to the absorber with operating temperature 600$^{o}$F to 1,000$^{o}$F: the absorber act as transport reactor that naphtha feed contact with adsorbent. In absorber, the adsorption reaction time is short and enables sufficient removal OSCs from the naphtha feed. A cyclone unit is equipped with transport reactor that allows separates the sorbent for regeneration, finally, cleansed sorbent are conveyed back to the standpipes. The desulfurization naphtha is then condensed by cooling tower, separate excess hydrogen gas and light ends, the light ends and hydrogen gas are recycled back to the incoming feed (Turk, et al. 2003).

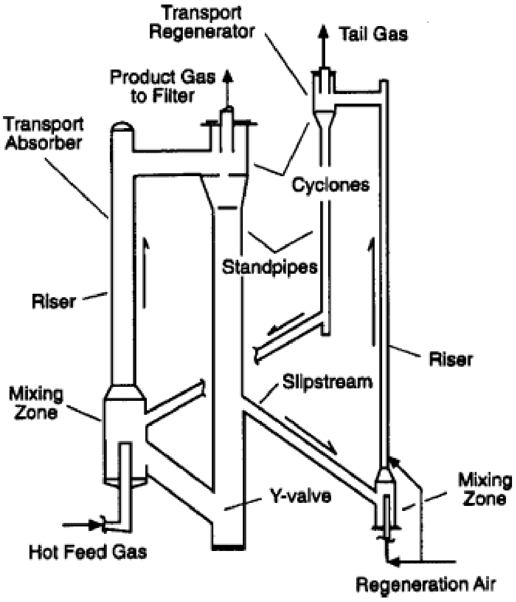


Figure 1.9 TReND process (Turk, et al. 2003)

TReND use smaller reactor size compared to the ConocoPhillips's S Zorb fluidized bed reactor with more efficient heat and mass transfer. However, the sorbent posses extremely high attrition resistance with high temperature, therefore, scale up for commercial use is still under development and not yet publicly unveiled.

Figure 1.10 shows the mechanism of adsorption desulfurization done by Tawara et al. (Tawara, et al. 2001). Based on Ni/ZnO as the sorbent to adsorptive kerosene that has previously treated by HDS, Ni reacts with sulfur to form NiS with presence of hydrogen gas, NiS then sulfur the surface of ZnO and results ZnS, finally regenerate Ni.

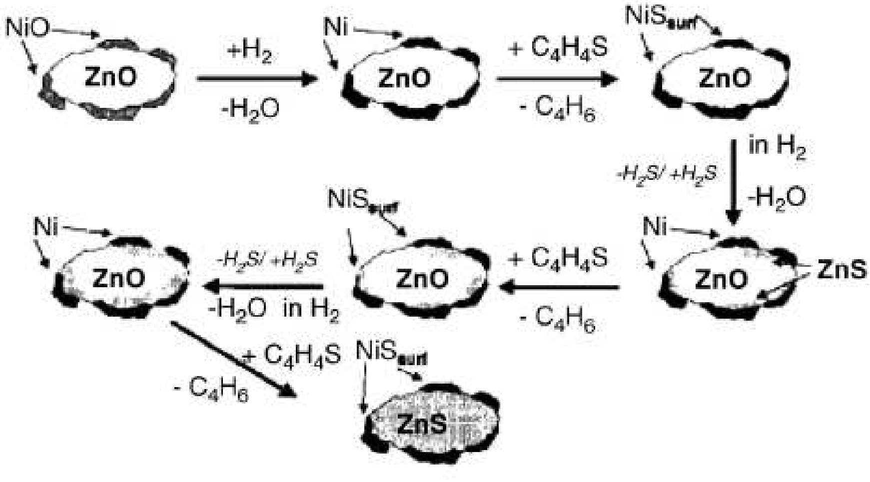


Figure 1.10. Adsorption desulfurization mechanism (Babich, et al. 2003).

### 1.4.3.3 Selective Adsorption for Removing Sulfur (SARS)

A new selective adsorption process for removing sulfur (SARS) has been developed recently by Song and Ma at Pennsylvania State University. The main objective of SARS process is to selectively adsorb OSCs from fuels, and non-sulfur-containing hydrocarbon such as aromatic, olefinic hydrocarbons and cyclic paraffinic hydrocarbons remain unchanged. A new adsorbent containing transition metal compound supported on silica gel has been used for SARS process. The adsorption experiments were accomplished under ambient temperature from room temperature to 250$^{o}$C and atmospheric pressure in a glass adsorption column. Another unique characteristic for SARS is that OSCs can be adsorb without using hydrogen gas (Song, et al. 2003). With published results (Song, et al. 2003. Ma, et al. 2002), new adsorbent is effective for remove OSCs and even the refractory sulfur compounds in fuels. Figure 1.11 shows the chromatogram of the OSCs distribution before and after SARS process.

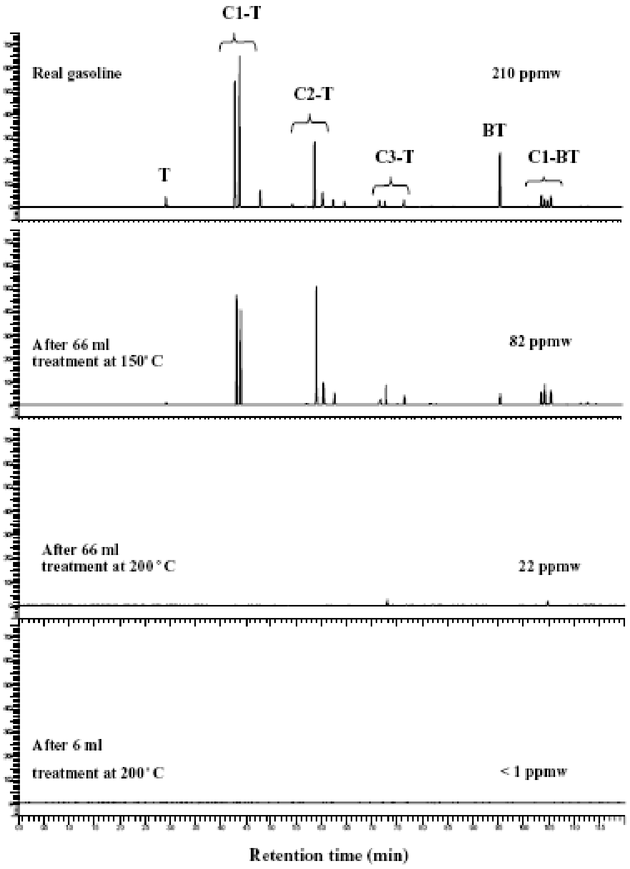


Figure 1.11 Sulfur chromatogram of gasoline before and after SARS process (Velu, et al. 2003)

### 1.4.4 Oxidative Desulfurization (ODS)

OSCs compounds are oxidized to sulfone by using a selective oxidant such as hydrogen peroxide. Figure 1.12 shows a block diagram of ODS.

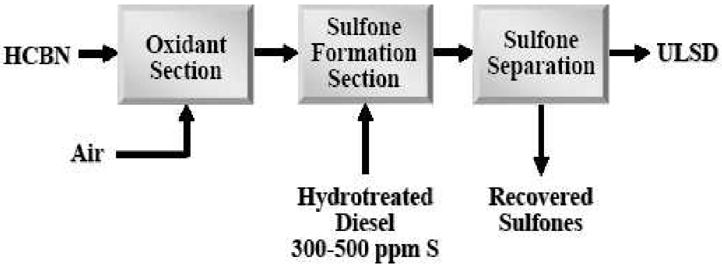


Figure 1.12 Block diagram of ODS

During ODS reaction, reaction of oxidant with OSCs occur at ambient temperature and pressure, the oxidation reaction continue until oxidized sulfur-containing compounds as knows as sulfone are confirmed, finally oxidation reaction is stopped before the oxidant attacks other, or the remaining refractory of the diesel fuel can not be oxidized under such conditions. Figure 1.13 shows the ODS reaction for BT and DBT.

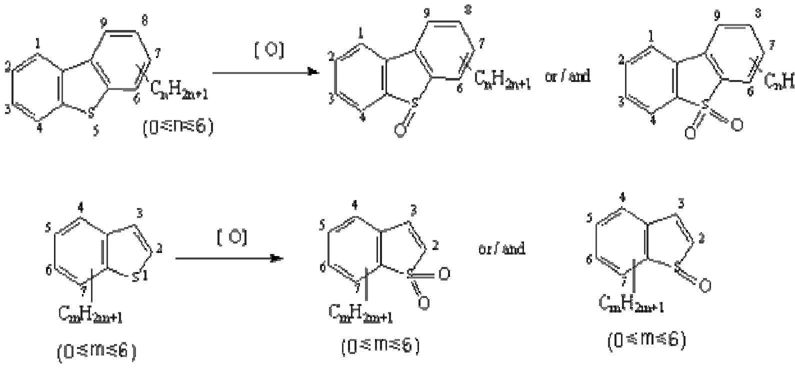


Figure 1.13 ODS reaction pathway for BT and DBT (Levy, et al. 2001)

Diesel fuel containing sulfone is separated from the depleted oxidant. The unused oxidant is then regenerated or recycles by washing, extracting and chemical post-treatment. The sulfone can be extracted from the diesel fuel by contacting with a non-miscible solvent, this is because sulfone allow extracted due to their increased relative polarity. Sulfone can be removed out from diesel fuel by liquid-liquid (L/L) extraction with solvent and settle down by centrifugation. Alternative method to removed sulfone can be achieved by absorption using silica gel and aluminum oxide. The extraction solvent is separated from the mixture of solvent and sulfone by a simple distillation and cleanse solvent can be re-used again for L/L extraction. By repeating these steps, the highest amount of undesirable compounds is extracted from the diesel fuel while doing the least amount of damage to the end product. From the literatures (Babich, et al. 2003 & Otsaki, et al. 2000), dimethylsulfoxide (DMSO), N,N-Dimethylformamide (DMF) and acetonitrile (MeCN) are used as polar solvent for L/L extraction due to high values of the Hildebrand solubility parameter higher than about 22 have been selected as be extraction solvent. Due to the close boiling point (570K) of DMSO and DMF to sulfone, they may not be reused for extraction, therefore, MeCN become the alternative extraction solvent since it has low boiling point (355K) and easy to regenerate by distillation. The only drawback for L/L extraction that some good hydrocarbon like naphthaline were also extract out by solvent that will reduce the diesel fuel quality (Mei, et al. 2003).

The advantages of ODS include: (1) Low capital cost, no need to build large hydro reactor. (2) Low operating cost because desulfurization operates at ambient temperature and pressure compare to traditional HDS. (3) No hydrogen gas required. (4) Short residence time due to highly efficiency catalyst supply. Recently, Unipure (a petroleum company) estimate capital cost at $1,000 per barrel of daily installed capacity which is half the cost of new high pressure hydrotreater (Levy, et al. 2001).

# CHAPTER 2

# THEORETICAL BACKGROUND

## 2.1 Introduction

The term Modification Desulfurization Method includes: Ultrasound, Phase Transfer Catalysis (PTC), Stir, Organic Acid Catalyst, Ionic Liquids (ILs), Oxidant, and Solid Catalyst Polish, respectively, are seven of the above mentioned techniques. Sound waves with higher frequency than the audible human frequency is being studied and applied by various experts these days. The study of these sound waves of more than 16 kHz is known as Ultrasonication. The production of emulsion, various chemical processes, drilling, clearing, and reactions rates have been increased by the above mentioned useful tool and is approved by many experts in this regard. With stir, agitating a liquid with an implement, this results in better mixing and reaction. In many areas of chemistry, Phase Transfer Catalysis is considered as a very powerful tool for the conduction of different reactions that occurs between reagents, while they are found in two or more phases. Organic acid catalyst is used for enhanced oxidation of organic sulfur compounds in to its relative sulfone. Ionic liquids are used to remove the oxidized sulfur due to it polarity, although ionic liquids can replace the organic solvent due to non volatile organic compounds (VOCs) through desulfurization and easy to handle. Various fields such as, biochemistry, analytical chemistry, catalytic and electrochemical reactions have applied it widely. The basic concepts of these techniques have been described in this chapter.

## 2.2 Ultrasound Assisted Oxidative Desulfurization (UAOD) Concept

From the previous work (Mei, et al. 2003 and Wan, et al. 2005), the combination of phase transfer agent (PTA), transition metal catalyst (TMC), and ultrasonic waves have resulted in the enhanced reaction of oxidation in organic sulfur compounds, which are found in UAOD system. High oxidation rates of OSCs in $H_2O_2$/diesel emulsion have been showed by the utilization of these three techniques. Ultra-low sulfur diesel fuel is achieved by solid adsorption, which results in removing of oxidized sulfur compounds that are found in the diesel fuel. In this regard, ambient temperature and atmospheric pressure is required during the whole process of UAOD (Etemadi, et al. 2007).

Until present, four generations have been developed for UAOD process. The identification of native surfactants in the crude oil has developed the first generation of UAOD. Long-chain carboxylic acids, long chain amines, and long chain mercaptans are consisted of these surfactants, and suitable pH levels can allow their release in this regard. A new type of surfactant has been developed by the caustic and acid flooding. At this stage, sulfur content of heavy oil is reduced by the application of 20 kHz ultrasound.

Various types of oxidants were studies and the transition metals were applied in the second generation of UAOD. The Venturella type of transition metal catalysts were utilized during the third generation of UAOD. Some bromo by-products were produced by the utilization of Tetraoctylammonium bromide as a phase transfer agent (Mei, et al. 2003).

Byproducts were removed in the fourth generation of UAOD. The oil/water emulsion was enhanced by using Tetraoctylammonium bromide as PTA and it molecular formula is $[CH_3(CH_2)_7]_4N(Br)$. 2-bro and 3-bromo compounds are produced after UAOD process, which is an anion of the quaternary ammonium salt. Sulfones are also produced in this process as byproducts. BTs are less reactive with this system, as compared to the DBTs that are more reactive in this regard.

The QAS was changed from its Keggin structure in the last generation of UAOD. The long carbon was used as quaternary cation, whereas, smaller anion was used as a fluoride during the process. No by-products were produced by using Tetraoctylammonium fluoride (TOAF) with fluoride, which was used as a smaller anion. In the result, OSC oxidation was yielded highly under the condition of ultrasound.

More than 95% organic sulfur compounds can be desulfurized in various types of diesel fuel in short time in a batch system of UAOD process. A custom, portable, continuous desulfurization unit has been optimized by the UAOD process. In UAOD process, oxidation reactions can be started by hydrogen peroxide concentration of 0.25%, which can also avoid the hydrogen peroxide's corrosive nature (Wan, et al. 2005).

Figure 2.1 depicts the conceptual model of oxidation as a catalytic cycle in UAOD process. In this regard, various steps have been established to explain the cycle. Firstly, the polyperoxometalate $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is produced by disaggregating and per-oxidizing the poly-oxometalates in the presence of excess $H_2O_2$. This production is also considered as one of the most effective species that are used for the epoxidation process. Secondly, an exchange is takes place during the aqueous phase between the solid and liquid anions. Thirdly, phase transfer agents are represented by the quaternary ammonium salts. Fourthly, peroxometal complex oxidizes the organic sulfur compounds to their analogous sulfones. This process is done very efficiently and with high mode of selectivity by the complex. Fifthly, PTA is dissociated by the already reduced peroxometal complex, which is then, returned to its aqueous phase. Lastly, the efficiencies of oxidation reactions are enhanced by the ultrasound.

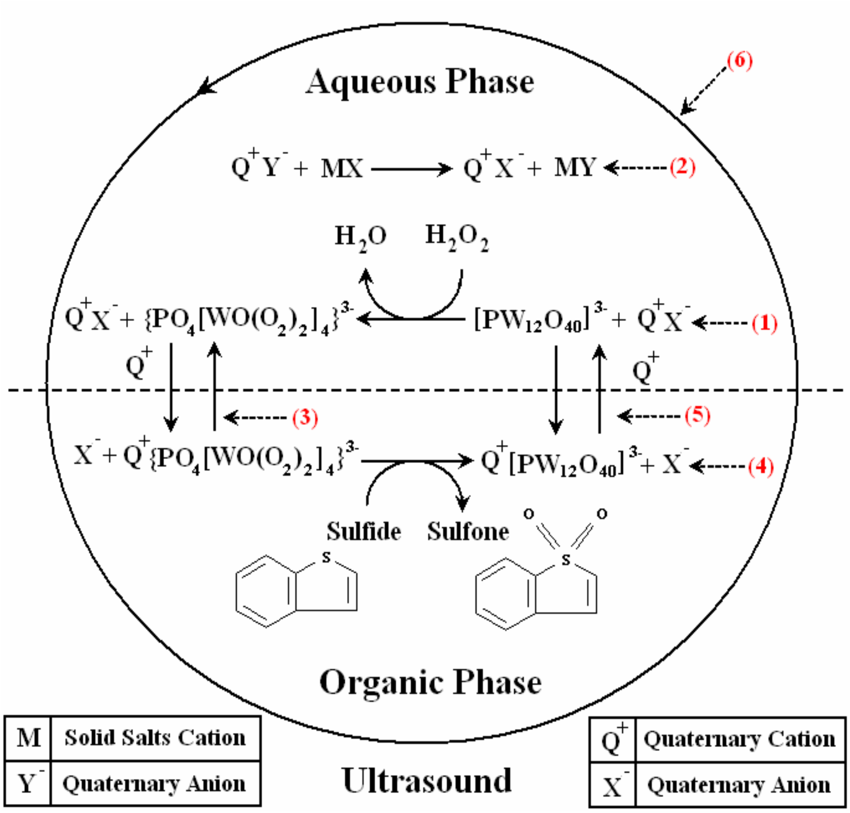


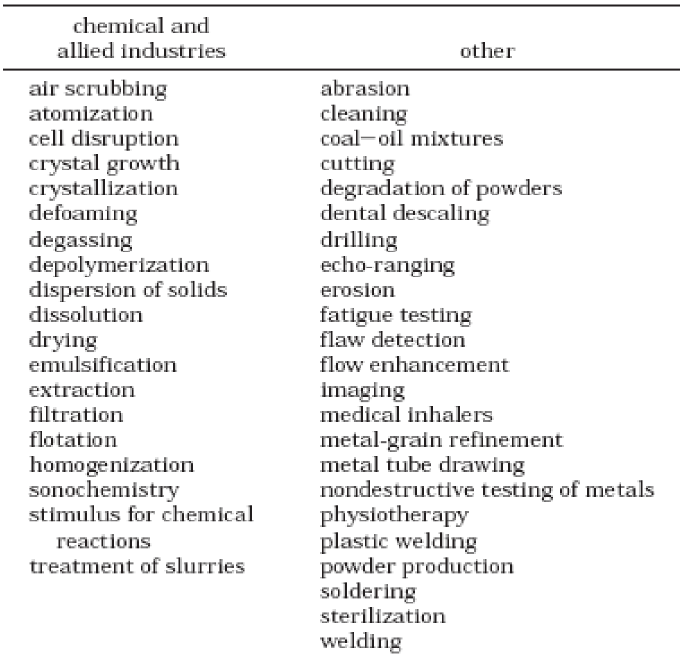
Figure 2.1 Conceptual model of UAOD process (Wan, et al. 2005)

## 2.3 Sonochemistry

### 2.3.1 Introduction of Ultrasound

Ultrasound is simply sound pitched above human hearing. Ultrasound is the part of the sonic spectrum which ranges from about 20 kHz to 10 MHz and can be roughly be subdivided into three main regions: (A) low frequency, high power ultrasound (20-100 kHz), (B) high frequency, medium power ultrasound (100 kHz-1 MHz), (C) and high frequency, low power ultrasound (1-10 MHz). The frequency level is inversely proportional to the power output. High power, low frequency ultrasound does alter the state of the medium and is the type of ultrasound typically used for sonochmical applications. Table 2.1 shows the application of ultrasound (Thompson, et al. 1999).

Table 2.1: Application of Ultrasound (Thompson, et al. 1999)



| chemical and allied industries | other |
|---|---|
| air scrubbing | abrasion |
| atomization | cleaning |
| cell disruption | coal—oil mixtures |
| crystal growth | cutting |
| crystallization | degradation of powders |
| defoaming | dental descaling |
| degassing | drilling |
| depolymerization | echo-ranging |
| dispersion of solids | erosion |
| dissolution | fatigue testing |
| drying | flaw detection |
| emulsification | flow enhancement |
| extraction | imaging |
| filtration | medical inhalers |
| flotation | metal-grain refinement |
| homogenization | metal tube drawing |
| sonochemistry | nondestructive testing of metals |
| stimulus for chemical reactions | physiotherapy |
|  | plastic welding |
| treatment of slurries | powder production |
|  | soldering |
|  | sterilization |
|  | welding |

### 2.3.2 Theory

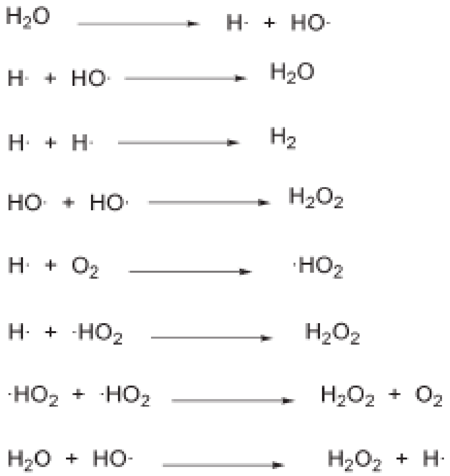
The chemical effects due to the cavitation have been explained by two theories, which exist as Hot-spot theory (Suslick, et al. 1986), and the Electrical theory (Margulis, et al. 1985, Cravotto, et al. 2006). The drastic conditions, which are created due to the cavitation collapse, have been experimentally shown by the Hot-spot theory. It has also been explained in the theory that these changes occur inside the medium, which takes an extremely short time and requires 2000-5000K of temperature, and up to 1800 atm of pressure inside the cavity that collapses, as mentioned previously in our discussion.

Under certain conditions, the emission of light is considered as a remarkable event, which occurs during the collapse of the cavitation. This phenomenon is known as sono-luminescence. Furthermore, a couple of strong physical effects are caused by the collapse outside the air bubbles in the liquid, resulting in the shock waves, shear forces, and jet waves. A postulation regarding the electrical charge has been given in the Electrical theory. The surface of a cavitation bubble has been shown as the place of creation of the electrical charge, which results in the formation of massive electrical field gradients. These bubbles are found to be across the bubble that may result in the breakage of the bond upon the collapse of the cavity.

### 2.3.3 Sonochemistry in Aqueous Solution

The reactive species formed during the sonolysis of water are similar to those observed radiolysis (Table 2.2). Among the most extensively studied species are OH radical and hydrogen peroxide ($H_2O_2$), produced by the thermolysis of water molecules in the gas phase of the bubble, and recombination of the resulting free radicals $H_2O_2$ is formed in the cooler interfacial area of the cavitation bubble (Henglein, et al. 1985).

Table 2.2 Sonolytic reaction of radical species (Cravotto, et al. 2006)



$$H_2O \longrightarrow H\cdot + HO\cdot$$
$$H\cdot + HO\cdot \longrightarrow H_2O$$
$$H\cdot + H\cdot \longrightarrow H_2$$
$$HO\cdot + HO\cdot \longrightarrow H_2O_2$$
$$H\cdot + O_2 \longrightarrow \cdot HO_2$$
$$H\cdot + \cdot HO_2 \longrightarrow H_2O_2$$
$$\cdot HO_2 + \cdot HO_2 \longrightarrow H_2O_2 + O_2$$
$$H_2O + HO\cdot \longrightarrow H_2O_2 + H\cdot$$

### 2.3.3.1 Kinetic Analysis

The chemical transformation that occurs during sonolysis may occur in several different regions of the cavitation bubble. Figure 2.2 shows three regions of sonochemical activity in sonicated systems (Riesz, et al. 1990). In Zone 1, it is gaseous region of cavitation bubble that contains reaction mixture in vaporized form. In Zone 2, so called gas-liquid transition region, the reaction mixtures are less volatile. In Zone 3, is the bulk phase.

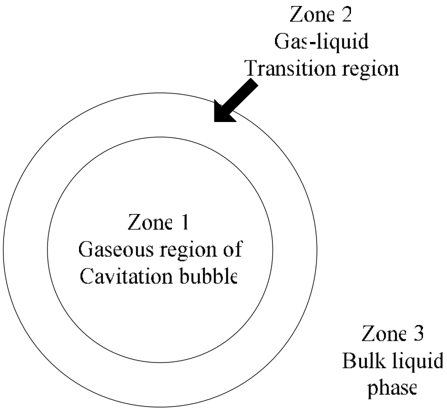


Figure 2.2 Three reaction zone of sonochemical reactions (Riesz, et al. 1990)

Attack by oxidizing species such as hydroxyl radical (OH) or oxygen atom or thermolysis of chemical bonds within the substrate can occur in either the gas phase or interfacial region. OH is most concentrated in the gas phase of the cavitation bubble. It is presumed that aromatic substrates are attacked by addition of OH whereas non-aromatic molecules are attach by hydrogen atom abstraction (Sawyer, et al. 1991) due to much stronger C-H bond in aromatic system.

### 2.3.4 Acoustic Cavitation

An interface of acoustic waves with the substance at a molecular or atomic stage does not result in the chemical consequences of high-intensity ultrasound. Instead, primary mechanism for sono-chemical effects is provided by the acoustic cavitation, that is, the cycle of the formation, development, and collapsing process of the bubbles (Hiller, et al. 1994), in the liquids that are irradiated with the high-intensity ultrasound as mentioned above.

The phenomenon of acoustic cavitation is the origin of sono-chemical effects in the liquids. A sinusoidal pressure variation is imposed by the ultrasonic waves that travel through a solution in the liquid, which results in the compression of liquid molecules by overcoming process of the intermolecular forces indirectly. For instance, the compression of the liquid molecules will take place in the ultrasonic frequency of 20 kHz obscuring each second. Therefore, the observations show varied results regarding the distance among the molecules, which occurs due to the oscillation of the molecules around their mean positions. However, the molecular structural intact is not supported and hold by the intra-molecular forces, if the increment is done in the intensity of ultrasound in the liquid.

Consequently, the formation of a cavity takes places due to the breakdown of the molecular structural intact. In this regard, 'Cavitation Bubble' is the term given to the cavity, whereas, the process is called 'Cavitation'. The cavitation threshold is the point, at which the cavitation process starts, resulting in the creation of the Cavitation Bubble. During the cavitation, the intense local heating, and high pressure is produced by the collapsing process of the bubbles in the liquid. It also shortens the lifetime of the fleeting and contained hot stops in the liquid, which are the reason of high-energy chemical reactions.

As earlier discussed in (Cravotto, et al. Henglein, et al. 1993, Greemspan, et al. 1993, Matula, et al. 1995), the temperature of these hot stops are found to be 5000°C, having about 1000 atm pressure in them. However, the cooling and heating rates are observed above $10^{10}$ K/s. Thus, the diffuse energy of sound is concentrated by the cavitation process to change into a set of conditions uniquely. These certain conditions are then used by the dissolved and usually, unstable precursors for the production of unusual materials in the liquid. In this regard, the collapse of both the stable and volatile cavitation events have been attributed to the chemical effects of ultrasound.

In a sound field, the formation and oscillation of bubbles are done for many acoustic cycles around a mean radius. These bubbles are known as ‘Stable Cavities’. In order to create and produce these steady cavities, there must be an equivalency between the growth rate and the contraction rate during the phase of the compression of these bubbles.

Unlike the ‘Stable Cavities’, there are other cavities, which are created for a few acoustic cycles, and are known as ‘Transient Cavities’ (Neppiras, et al. 1980). Extreme pressure and temperature are created within itself at the time of implosion of these cavities, which occurs during its existence, as several times larger difference is observed in the size of these cavities, as compared to their initial size before the implosion. The overall growth is contributed by a second effect, which is known as the ‘Shell Effect’. The diffusion rate of gas into bubble is a function of the concentration gradient. At the time of contraction of the bubbles, the expansion of the bubbles around the spherical shell occurs, which results in the reduction of the concentration of the gas that is found on outer side of the wall of bubbles. Thus, a greater difference is found in the rates of the diffusion of the bubble, before and after the placing of bubble at its equilibrium radius.

### 2.3.5 Sonoluminescence (SL)

During the acoustic cavitations, the emission of light was referred by the SL. During the underwater exposure of photographic plates, it was first observed, when these plates were irradiated with ultrasound in the solutions (Frenzel, et al. 1934). Generally, the Hot Spot theory explains the origin of the sono-luminescence and sono-chemistry, which is widely accepted by the scholars. It simplifies the expansion of potential energy of a bubble, when it is concentrated into the core of a heated gas, and which makes the implosion of that bubble.

Sono-luminescence has been divided into two forms; single-bubble SL (Crum, et al. 1994, Hiller, et al. 1994) and the multi-bubble SL (Henglein, et al. 1993), through which the information is gathered about the conditions during the implosion of the cavitation bubbles. Commonly, shock waves are the usually proposed mechanisms that are used in the SL during the implosion of the bubbles. Through this, the bubbles are converged at the center by these mechanisms (Greenspan, et al. 1993). Hydroxyl radical is another mechanism that is being used in SL, which produces the emission from the chemical species during their excited state (Matula, et al. 1995). However, small changes in bulk parameters can bring significant influences in the nature of the emissions.

The moment, at which the air bubbles glow in the water was observed by the first researchers and was then, known as the multiple-bubble sono-luminescence (MBSL). However, it is advised to observe this glowing condition in a darkened room due to the fainting characteristic of these bubbles. In 1990, two researchers; Crum and Gaitan observed the SBSL in its perfect conditions (Guitan, et al. 1992).

Placing of a single bubble of gas was done in the liquid, in order to create SBSL. In this regard, an air bubble was injected in the liquid, which created the SBSL. Normally, the bubble was arisen in the center of the cylindrical flask after its injection. However, the sound waves were bombarded that kept it in its place. Nowadays, experimental set up are available and practiced by the researchers in labs. Sono-luminescence requires around 100 decibels of sound waves, which can cause deafness in a normal person. Another factor that is imperative for the SL is the frequency of sound, which a human hearing cannot reach in its range.

### 2.3.6 Heterogeneous Systems: Liquid-Liquid Interface

Ultrasound forms very fine emulsions in systems with two immiscible liquids, which is very beneficial when working with biphasic systems or phase transfer catalyzed. When very fine emulsions are formed, the surface area available for reaction between the two phases is significantly increased, enhancing the mass transfer in the interfacial region, thus increasing the rate of the reaction. Ultrasound cavitation creates reactive intermediates that shorten the reaction time (Mei, et al. 2003).

## 2.4 Ionic Liquid

### 2.4.1 Overview of Ionic Liquid

Ions are the main constituents of the Ionic Liquids, which are also known as ILs. Normal salt can be resembled to the ILs. Molten Sodium Chloride is one of the examples of ILs, in which the nature of the dominant force is found to be columbic between the ions. In ILs, the ions are poorly coordinated and highly polar, which results less columbic attraction between them, this decrease in electrostatic attraction translates into lower melting points less than 100°C (Walton, et al. 1999).The reality is that ionic liquids can be liquid at temperatures as low as -96ºC. Because its low melting point, ionic liquids can act as solvents and reactions can be performed. Although, ionic liquid is made of ions (Jonathan, et al. 2001) rather than molecules, the reactions often give distinct selectivity and reactivity when compared with organic solvents. Additionally, some of the potentially possibilities are the $10^{18}$ ternary ionic liquids and the ionic liquids in a million binary quantity (Seddon, et al. 1999). Nowadays, approximately 600 molecular solvents are used for the comparison process of these reactions.

Ionic liquids lack a measurable vapor pressure at room temperature, near zero or no organic compounds will be create compare to the volatile organic solvent (Anastas, et al. 2003). The perceived benefit of substitution of the traditional industrial solvents is one of the primary driving forces that influence the research into ionic liquids. The volatile organic compounds and the nonvolatile ionic liquids are the usual solvents in this research, which are also known as VOCs and NILs respectively. The emission of VOCs might be prevented by the replacement of the conventional solvents by the ionic liquids. It can avoid many containment problems or handling issue, which is the idea of "green solvent" (Earle, et al. 2000). Intrinsically, ionic liquids are not found environmental, as observations show some of them as extremely toxic. However, the planning and designing can be done, in order to produce a benign of environmental loving, which might also result in the sustainable chemistry with large potential benefits (Earle, et al. 2000).

In order to avoid the utilization of the conventional organic solvents, four principal strategies are used by experts. Water, ionic liquids, heterogeneous catalysis, and supercritical fluids are these four approaches in this regard. However, the establishment of the solvent-less option is considered as the best one in the petrochemical industry, which is one of the chemical sectors with least pollution. It is very difficult to dissolve many compounds in water, although, it is very advantageous to make the use of the water. Additionally, it is also very expensive to dispose off the contaminated aqueous streams. Some of the highly versatile solvents that are used for the chemical synthesis are the supercritical fluids with the multi-properties of both gas and the liquid (Poliakoff, et al. 2002). In a chemical plant, the Thomas Swan & Co. Ltd. commercialized the technology recently, which was designed for the synthesis on a multi-purpose basis. A range of options is provided to the various industrialists by these alternative solvent strategies with ionic liquid (Rogers, et al. 2002, 2003) collectively. Through this, the chemical processes were designed to impact the environment on a very less extent.

Ionic liquids are non-flammable and non-explosive, this is because most of them have low flammability or no flash points (Seddon, et al. 1996). Ionic liquid are also applied in separation application, such as distillation or sublimation which is sometimes not possible using traditional organic solvents. Ionic liquids are immiscible with a number of organic solvents or aqueous solution, and it provide a non-aqueous, polar alternative for two or tri phase systems (Scurto, et al. 2006) for flexibility with reaction and separation schemes (Arce, et al. 2006), this has been used to effect total catalyst recovery in a number of transition metal catalysed reactions. Hydrophobic ionic liquids can also be used as immiscible polar phases with water (Huddleston, et al. 2001). With these unique properties of ionic liquids, ionic liquid will slowly replace traditional volatile organic solvent. Ionic liquids application can development of new reactions or processes that provide significant environmental, time and cost efficiency concerns compared to traditional chemical systems.

### 2.4.2 Room Temperature Ionic Liquid (RTIL)

#### 2.4.2.1 Introduction

Normally, an ionic liquid that contains nitrogen containing organic cation and inorganic anion, and the salts have melting temperature lower than room temperature is called room temperature ionic liquids (Endres. Et al. 2006), or RTILs. RTILs consist of bulky and asymmetric salt of organic cations (Endres. Et al. 2006), the most common were alkyl-imidazolium (RMIM), alkyl-pyridinium (RPY), tetra-alkylammonium (TAM) and tetra-alkylphosphonium (TAP). With anions, most of them are rely on halide based ions, which usually have high thermal stability and are water and air insensitive, the anion includes, tetrafluoroborate ($BF_4^-$) (Andersion, et al. 2002), hexafluorophosphate ($PF_6^-$) (Carda-Broch, et al. 2003), chloride ($Cl^-$)(Anderson, et al. 2002) and to large organic anions like Bis-(trifluoromethanesulfonyl)imide ($NTf_2$) (Anderson, et al. 2002), tri-fluoromethanesulfonate (Anderson, et al. 2002) or triflate (TfO) (Anderson, et al. 2002). Figure 2.3 shows common cations and anions for RTILs.

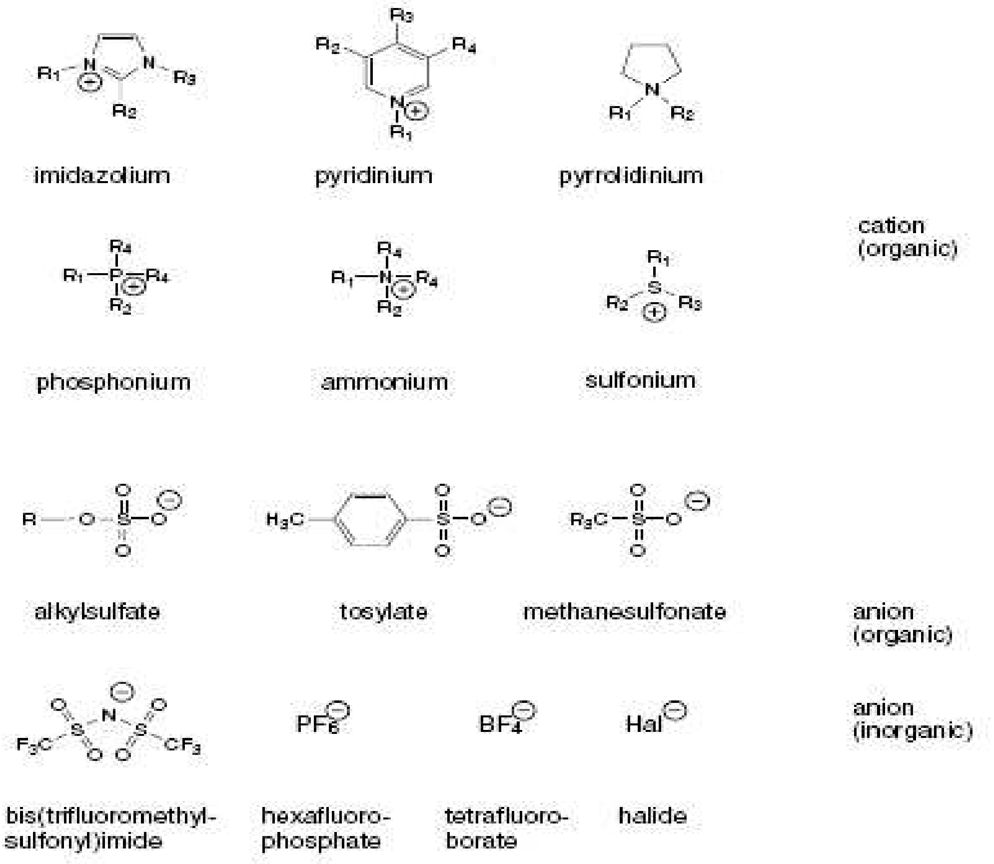
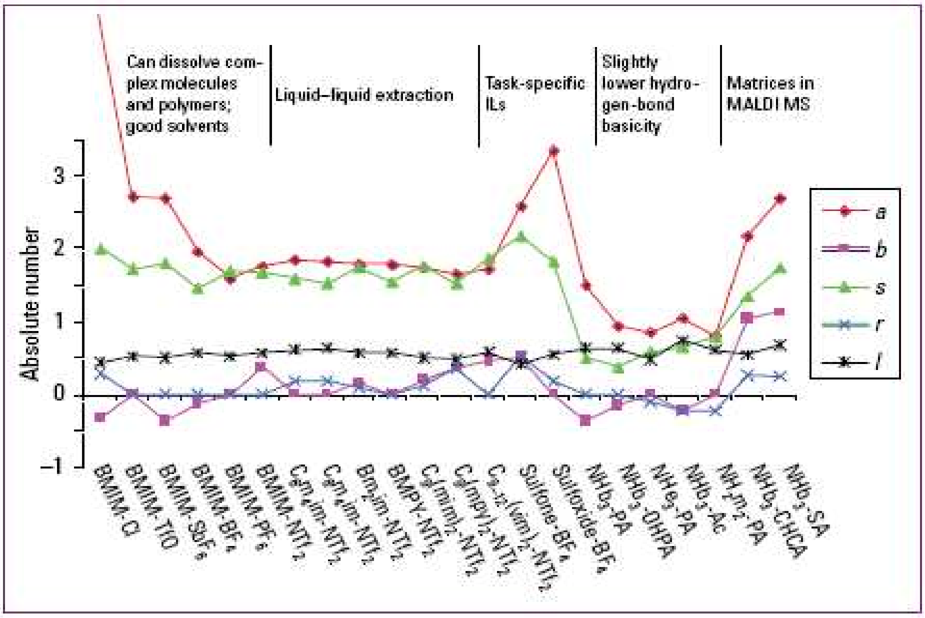


Figure 2.3: Common cations and anions for RTILs (ChemFiles)

RTIL has been described as custom synthesis or designer solvents (Earle, et al. 2000). Through a broad choice of cation and anion combination, a variety of unique properties such as hydrophobicity, viscosity, density and solvation can be achieved. RTILs will dissolve a wide range of organic molecules to an appreciable extent. The viscosities were controlled by the nature of the anion, with same class of anions, the viscosities increase as alkyl group is lengthened. Figure 2.4 shows the common RTILs that have been uses recently and its application (Anderson, et al. 2006).



*a*, hydrogen-bond basicity; *b*, hydrogen-bond acidity; *r*, interaction via nonbonding and π-electrons; *s*, dipolarity or polarizability; and *l*, dispersion forces. BMIM, 1-butyl-3-methylimidazolium; TfO, triflate; $NTf_2$, bis[(trifluoromethyl)sulfonyl]imide; sulfone-$BF_4$, butyl ethylsulfonylmethylimidazolium-$BF_4$; sulfoxide-$BF_4$, butyl ethylsulfinylmethylimidazolium-$BF_4$; $NHb_3$, tributylammonium; $NHe_3$, triethylammonium; $NH_2m_2$, dimethylammonium; PA, picolinate; OHPA, 2-hydroxypicolinate; Ac, acetate; CHCA, α-cyano-4-hydroxycinnamate; SA, sinapinate; vim, vinyl imidazolium; mim, methylimidazolium; mpy, methyl pyrrolidinium. Some data from Ref. 3 were used to construct this plot.

Figure 2.4 Various ILs used in different applications (Anderson, et al. 2006)

RTILs can be used as clean solvent for catalytic purposes, for example, Diels-Alder reactions (Fischer, et al. 1999), hydrogenation (Suarez, et al. 1996), hydrodimerisation of dienes (Dullius, et al. 1998), alkylation of olefins (Chauvin, et al. 1995), Dimersol process (Einloft, et al. 1996), Friedel-Craft acylation (Adams, et al. 1998).

RTILs can be used as electrolytes in electrochemistry, normally, ionic liquid consist of good electrical conductivities, wide electrochemical windows and low volatility (Lu, et al. 2002), [BMIM][$PF_6$] is an example of ionic liquid type electrolyte (Li, et al. 2005).

### 2.4.2.2 Extractions of Organic Molecules

It was possible to separate Hydrocarbons through the extraction of ILs. There are several steps that are involved in the method for separation of olefins, for example, propylene, butanes, and ethylene, etc. from the paraffin. In these steps, the formation of complex olefins was done by using salts, such as, silver, etc. the IL or salt solution extracted the olefin-containing mixture, which in result, absorbed the olefins. The absorption process separated the olefins after the removal of paraffin (Munson, et al. 2002).

The separation of $C_{6-9}$ aromatic hydrocarbons, and higher hydrocarbons from the streams of the benzene-rich petroleum was done by the development of a continuous process of extraction with the help of ILs. Alternative ‘green’ methods for separating hydrocarbon molecules were presented by the results. Considerably, the petroleum industry and polymer-processing industry has a very valuable significance of the above mentioned separation methods.

The hydrophilic [BMIM][Cl], and concentrated $K_3PO_4$ solutions were contacted for the formation of an aqueous biphasic system, which is also known as ABS. The separation technology has a very high importance of controlling the aqueous miscibility of hydrophilic ILs, which became possible through the above mentioned finding. The reason of this significance is that the hydrophilic ILs are recycled by this enabling process. Sufficient chemical potentials are provided by these aqueous biphasic systems, by which the organic molecules are allowed to be separated in two phases (Gutowski, et al. 2003).

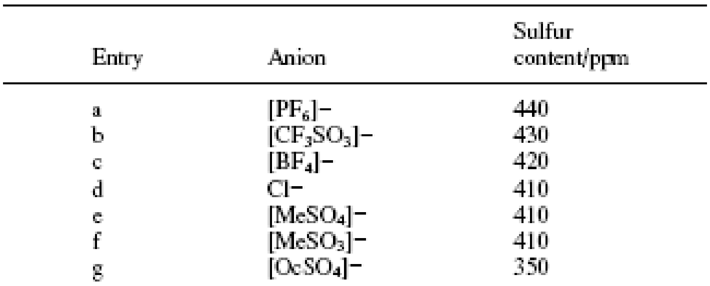
#### 2.4.2.3 Extractions of OSCs

Potential solutions for the sulfur-free clean fuels are being provided by the alternative technologies, which is of very particular interest. Chapter 1 has discussed varies of the desulphurization in this regard. An attractive alternative process is the extractive desulfurization process. Additionally, ambient conditions can allow the application of this process without requiring the special equipments. Besides, the elimination is also done to the hydrogen, and the low-energy consumption in this regard. Higher concentration can recover the organic-sulfur components, which leads to the process of extracting the solvents. Therefore, the olefin contents will not be affected by the absorption of sulfur compounds at the high capacity.

In extraction process, custom synthesized RTILs can be immiscible with aqueous or organic phases, and it allows liquid-liquid extraction. The choice of the anion (and in some cases, the structure and functionality of the cation) controls the water solubility of the RTIL. Most water-immiscible RTILs contain either $PF_6^-$ or bis[(trifluoromethyl)sulfonyl]imide anion. For example, the melting point of 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][$PF_6$] (Carda-Broch, et al. 2003) with an imidazole structure is -8°C (Carda-Broch, et al. 2003), and it is a colorless liquid with high viscosity at room temperature, [Bmim][PF] did not dissolve in either organic or aqueous phase, it can act as solvent to extract the reaction product and catalyst to improve reaction.

ILs that also acted as Lewis and Bronsted acids or bases were used as extraction media in the deep desulfurization of diesel fuels. ILs that had larger anions demonstrated significantly better extraction of dibenzothiophene than smaller anions, regardless of the cation used (Bosmann, et al. 2001). Table 2.3 shows the different anions in desulfurization process of model diesel oil by extraction with ILs of [BMIM][anion].

Table 2.3 Different anions in extractive desulfurization process with [BMIM][anion] type ILs (Bosmann, et al. 2001)



| Entry | Anion | Sulfur content/ppm |
|---|---|---|
| a | $[PF_6]-$ | 440 |
| b | $[CF_3SO_3]-$ | 430 |
| c | $[BF_4]-$ | 420 |
| d | Cl− | 410 |
| e | $[MeSO_4]-$ | 410 |
| f | $[MeSO_3]-$ | 410 |
| g | $[OcSO_4]-$ | 350 |

Several types of ILs: [EMIM][$BF_4$], [BMIM][$PF_6$], [BMIM][$BF_4$] and Tri-methylammonium chloroaluminate ($AlCl_3$-TMAC) have been studied for EDS process. Results show high selectivity for the adsorption of aromatics and aromatic S- and N- containing molecules from fuels. Especially, Lewis acidic $AlCl_3$-TMAC ILs was found have high efficiency adsorption capacities for aromatics, particularly sulfur containing aromatic compounds, but regeneration for further use is problematic (Ahang, et al. 2004).

From literature**,** [BMIM][$BF_4$] and [BMIM][$PF_6$] were used to remove sulfur containing compounds from light oils with a combination of chemical oxidation and solvent extraction**.** Because, the main partition of the sulfones are oxidized by the high polarity to the phase of IL. In the result, the sulfur compounds are extracted from the oil continuously. This leads to the higher yield of these compounds, as compared to the process without the above mentioned technique (Wei, et al. 2003). Figure 2.5 shows the result of combination of oxidation and extraction of light oil. The used or saturated ILs can be regenerated by distillation or by dissolution in water. At low temperature and non-corrosiveness, the stability of the ILs are very steady in the air and water. Therefore, the sulfur containing compounds can be removed through the multiple cycles by the utilization of the ILs from fuels.

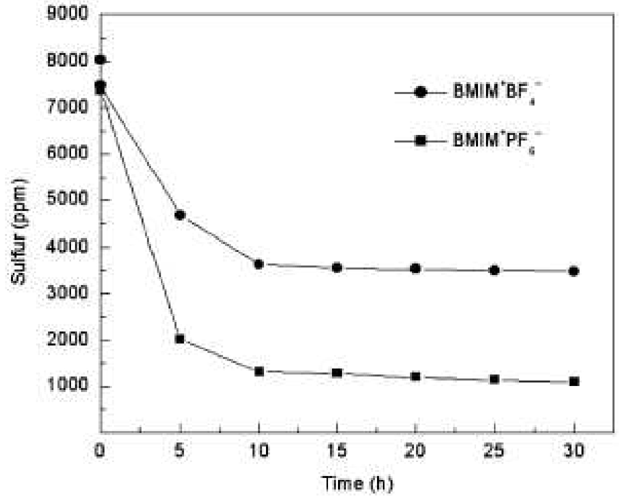


Figure 2.5 Desulfurization of light oil by combination of oxidation and extraction process with different ILs (Wei, et al. 2003)

An electrochemical process is directed to an embodiment of the instant invention, which is used for the removal of sulfur from the hydrocarbon and polymerizable sulfur compound streams. This process comprises of feed of hydrocarbons, which contains the compounds of polymerizable sulfur with an IL. Secondly, in an electrochemical reactor, the above mentioned step is combined with the electrochemically oxidize. This step is possible under certain conditions, which allows the polymerizable sulfur compounds to produce the sulfur oligomers. A first fraction of sulfur oligomers, entrained hydrocarbon, and ionic liquid is obtained by this step. Subsequently, a second fraction is also obtained that comprises of de-sulfuric hydrocarbons. This leads to the recovering of the above mentioned fractions.

One possible configuration is depicted by Figure 2.6, which carries out the instant invention. Hydrocarbons and sulfur compounds are comprised by the feed, which is also known as Stream. In this regard, an electrochemical reactor is fed by this stream. The ionic liquid comprises of this stream. In the result, a de-sulfuric hydrocarbon is formed under the electrochemical reaction results. This formation is done from the reactor's top and the later fraction of the above mentioned steps. This comprises of sulfur oligomers, ionic liquid, and entrained hydrocarbon, which results from the reactor's bottom. Optionally, the distillation column might receive the second fraction. Subsequently, the top of the distillation column recovers the entrained de-sulfuric hydrocarbon, which then leads to the combination of the counterpart that created from the electrochemical reactor. The recovering of the remaining mixture of ionic liquid and sulfur oligomers is done by the electrochemical reactor. The recycling process is also done, in order to utilize it for the further use (Munson, et al. 2002).

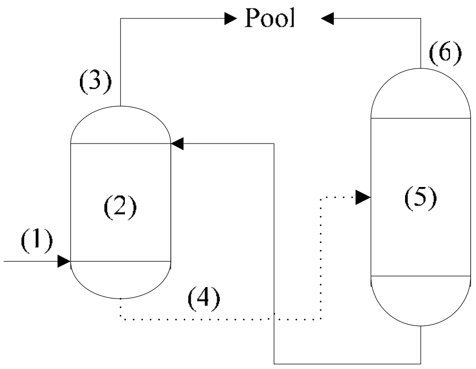


Figure 2.6 Block diagram of separation hydrocarbon by ILs. (Munson, et al. 2002)

## 2.5 Oxidant: Hydrogen Peroxide

In this research, the main object is to oxidize sulfur compounds from a fuel sample to its relative sulfides or sulfones. Therefore, an oxidant is necessary to apply to the oxidation reaction. The oxidant is a chemical compound that converts OSCs to much more polar oxidized species. From the literature, a large variety of oxidants have been studied; the common oxidants include hypohalite compounds, chlorite, permanganate salts, ammonium cerium (IV) nitrate, hexavalent chromium compounds, peroxide compounds, Tollen's Reagent, sulfoxides, persulfuric acid, oxygen and ozone. These oxidants enable donate oxygen atoms to the sulfur in mercaptans (thiols), sulfides, disulfides and thiophenes to form sulfoxides or sulfones.

To select the optimum oxidant for research purposes, oxidants must have the following considerations: (1) amount of active oxygen content, (2) selective ability in its application, (3) by product of the reaction, (4) price. As Table 2.4 indicated, it is clear that hydrogen peroxide ($H_2O_2$) gives the highest percentage of active oxygen. The percentage of active oxygen is calculated as the ratio between the weight of oxygen that can be transferred to a suitable substrate and the molecular weight of the oxidant (Strukul, et al. 1992).

Table 2.4 Single oxygen atoms donor (Strukul, et al. 1992. & Bregeault, et al. 2003 )

| **Donor** | **Active Oxygen (wt%)** | **By-product** |
|---|---|---|
| $H_2O_2$ | 47.0[a] | $H_2O$ |
| $O_3$ | 33.3 | $O_2$ |
| *t*-BuOOH | 17.8 | *t*-BuOH |
| $N_2O$ | 36.4 | $N_2$ |
| $NaClO_2$ | 35.6 | NaCl |
| NaClO | 21.6 | NaCl |
| NaBrO | 13.4 | NaBr |
| $C_5H_{11}NO_2$[d] | 13.7 | $C_5H_{11}NO$ |
| $HNO_3$ | 25.4 | $NO_x$ |
| $KHSO_5$ | 10.5[c] | $KHSO_4$ |
| $NaIO_4$ | 7.2[b] | $NaIO_3$ |
| PhIO | 7.3 | PhI |

[a]: Calculated in 100% $H_2O_2$, [b]: Assuming only one oxygen atom is utilized, [c]: Stabilized and commercialized as the "triple salt": $2KHSO_5.KHSO_4.K_2SO_4$ (oxone), [d]: *N*-Methylmorpholine *N*-oxide (NMO).

With catalyst (TS-1), oxidation of sulfur compounds with $H_2O_2$ at ambient conditions provide sulfones. The reaction is promoted by titanosilicate catalyst, and other hydrocarbon would not be oxidized. Unlike other oxidants, the most remarkable feature for $H_2O_2$ is its tendency to decompose readily into water and oxygen after the reaction, the decomposition of $H_2O_2$ is shown below:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The by-product of water would not be considered as the environmental issue, therefore, $H_2O_2$ can be considered a "green oxidant". Today, $H_2O_2$ has been commercially synthesized worldwide, therefore, the cost for $H_2O_2$ would not be considered. With these advantages, $H_2O_2$ will be chosen as an oxidant and used through out the entire research process.

Anhydrous $H_2O_2$ is a clear, colorless liquid, of nearly the same viscosity and dielectric constant as water, but of greater density. Table 2.5 shows the physical properties of $H_2O_2$ with a different concentration grade that has been commercially available.

Table 2.5 Physical properties of commercial $H_2O_2$ solutions (Strukul, et al. 1992)

| | **$H_2O_2$ strength (wt%)** | | |
|---|---|---|---|
| **Property** | 35 | 50 | 70 |
| Density at 20°C (g/cm$^3$) | 1.1312 | 1.1953 | 1.2886 |
| Viscosity at 20°C (mPa s) | 1.11 | 1.17 | 1.23 |
| Freezing point (°C) | -33 | -52.2 | -40.3 |
| Boiling point (°C) | 107.9 | 113.8 | 125.5 |

## 2.6 Phase Transfer Catalysis (PTC)

### 2.6.1 Introduction

Phase transfer catalysts (PTC) increases the calibration of reactions between nonelectrolyste substrates found in organic phases and increase catalyst rates of ionic reagents in the aqueous phase (Gordon, et al. 1977 and Starks, et al. 1994). Onium cations and neutral complexants are the primary catalysts which accelerate interface transfer for inorganic cations (Sasson, et al. 1997). PTC's serve an important function, extracting the anion or neutral compound from the aqueous phase, stimulating transfer to the organic reaction phase and enabling the anion or neutral compound to respond without limitations. Reactivity increases due to the PTC stimulation, allowing hydration and solubility, which significantly reduces the energy of activation (Halpern, et al.).

PTC can also be used in the oxidation process for desulfurization, especially in diesel oils. An important sulfur component of diesel oil is dibenzothiophene which reaches oxidation using 0.5 wt% Aliquatâ 336, 0.3 wt% phosphotungstic acid and 11% aq. $H_2O_2$ at 60°C (Collins, et al. 1997). $H_2O_2$ costs are typically high, and an alternative to this is Hydrodesulfurization (HDS). Obtaining HDS of gas oils to be less than 0.5wt% sulfur is a painstaking process but also more cost effective. Sequential HDS followed by PTC ODS is used to achieve 0.005 wt% sulfur, which is lower than US and European requirements. This is a significant component in guiding commercial processes, and adhering to environmental EPA and United Nations standards.

### 2.6.2 Kinetics and Mechanism of PTC

Kinetic behavior for PTC is governed by specific reactants. The catalyst is often a quaternary ammonium salt (QAS's), such as tetrabutyl ammonium, $[C_4H_9]_4N^+$. In layman terms, this is known as the "quat" and symbolized by $Q^+$. The benefits of QAS's is due to its loose ionic nature, enabling high reaction rates and dispersal of elements, and subsequently allowing for increased productivity in numerous processes (Collins, et al. 1997 and Starks, et al 1994). The "Starks' extraction mechanism" (Starks, et al. 1971) shown by Figure 2.7., includes two significant stages: (1) a rapid ion exchange between the catalyst and the salt during the aqueous phase and (2) the rate-determination in the organic phase. This kinetic process is demonstrative of PTC's loose composition and more specifically important in creating the stasis necessary for the PTC process in general.

The phase transfer catalyzed nucleophilic substitution reaction, $RX + Y^- \rightarrow RY + X^-$, allows nucleophile $Y^-$ to make the transition to the organic phase. The nucleophile creates an ion pair with the release of anion $X^-$ and calibration of $[Q^+Y^-]$ inducing a cyclical process, until the nuclephiles and substrates are fully absorbed in the kinetic process.

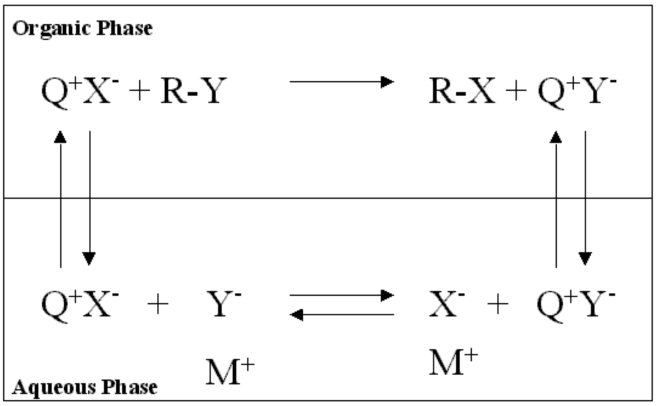


Figure 2.7 Starks' extraction mechanism

Gordon and Kutina discuss the kinetics of this reaction in great detail (Gordon, et al. 1977), proposing a mathematical model of PTC reaction that includes the ion exchange selectivity coefficient ($K_{Y/X}^{\ sel}$):

$$RX + Y^- \qquad RY + X^-$$

Assuming that $[X^-]_{aq \cdot P} + K_{Y/X}^{sel} * [Y^-]_{aq \cdot P} = \text{constant}$

The equation: $kt = \text{Constant} * \ln [Y^-]_{aq \cdot P} / [RX]$

The equation holds only at that $K_{Y/X}^{sel} = 1$.

### 2.6.3 Choice of PTA

Appropriate PTA is important for creating the best relationship for catalytic reaction conditions. Analysis of effective catalysts encompass two aspects: (a) the ability of quaternary ammonium cation to transfer the reactive nucleophilic anion across the phase interface, and (b) the enhanced reactivity of the anion in the organic phase.

In the UAOD process, the quanternary ammonium salt, tetraoctylammonium fluoride (TOAF), was utilized and provided the best results given factors of stability and its removal from the organic phase. TOAF also does not produce any byproducts (Wan, et al. 2005). In oil/water mixtures, TOAF decreases the surface tension in addition to enabling the transfer of oxygen from aqueous to organic phases, subsequently creating sulfone through oxidization processes.

Utilizing ultrasound enables for increased reaction effectiveness for phase transfer agents (Thompson, et al. 1999). Due to the significant nature of surface activity of phase transfer agents, ultrasound serves as a co-agent in the deterioration of surface tension and facilitates the production of micro-bubbles. This Ultrasound as a catalyst provides an environment that promotes emulsification, which improves liquid to liquid interfacial area. This may be important when dealing with gas-filled and cavitation bubbles which harbor viscous films. The unstable nature of viscous films may cause reaction deficiency and skew the results provided by the phase transfer agent. The gas-filled bubbles within the films show increased activity due to the ultrasound process while simultaneously, cavitational bubbles burst and increase liquid surface area, subsequently stabilizing the viscous film and catalyzing the emulsification process.

## 2.7 Mechanical Stir

When two immiscible liquids, such as aqueous phase (RTIL, or $H_2O_2$) and Organic phase (diesel fuel), often of low viscosity, are agitated a system is created having dispersed liquid droplets in a continuous liquid phase. Such a situation is often created in solvent extraction units where a high interfacial area between the two immiscible liquid phases is necessary to achieve inter phase transfer. Thus mechanical stir is used to create conditions favorable for mass transfer and if stirred is stopped the two phases will separate, leading to a greatly reduced interfacial area (Kodas, et al. 1987).

Another very common mixing process involving immiscible liquid is emulsification. An emulsion is a phenomenon with mixture of two immiscible (unblendable) substances (Hildebrand, et al. 1941). One substance so called dispersed phase, is dispersed in the continuous phase. It is customary to classify emulsions into two types: the oil-in-water (O/W) type consisting of droplets of oil dispersed in water, and the water-in-oil (W/O) type in which the phases are reversed. The continuous liquid is referred to as the dispersion medium, and the liquid which is in the form of droplets is called the disperse phase. Normally, when emulsions forms, it tend to have a cloudy appearance, this is because so many phase interfaces (the boundary between the phases is called the interface) scatter light that passes through the emulsion (Stamm, et al. 1926). Emulsions are unstable and thus do not form spontaneously. Energy input through shaking, stirring, homogenizers, or spray processes are needed to form an emulsion. When time passed, emulsions slowly revert to the stable state of oil separated from water. PTA can increase the kinetic stability of emulsions greatly so that, once formed, the emulsion does not change significantly over time. Whether an emulsion turns into a water-in-oil emulsion or an oil-in-water emulsion depends on the volume fraction of both phases and on the type of PTA. According to the Bancroft rule: the emulsifiers and emulsifying particles tend to promote dispersion of the phase in which they do not dissolve very well; for example, proteins dissolve better in water than in oil and so tend to form oil-in-water emulsions

## 2.8 Acid Catalyst

Organic acid and Polyoxometalates are the two main catalysts that are used for the desulfurization selectively. (Zhao, et al. 2004). Organic acids include formic acid, acetic acid (Shiraishi, et al. 2002). In this regard, the chemical oxidation of sulfur containing compounds was taken as a base during the investigation. During desulfurization, hydrogen peroxide and acetic acid was taken as an oxidizing agent. The resulting compounds followed the previously mentioned by the extraction with acetonitrile. From the corresponding sulfones, it was observed that oxidizing agent was able to oxidize DBT and model sulfur compound BT, as shown in the results. During the experiment, the extraction of solvent was successfully able to remove these corresponding sulfones.

With light oil (Shiraishi, et at. 2002), the results shows accumulation of the sulfones compounds that are found to be producing during the reaction, it is quite impossible, and therefore, the desulfurization of the light oils will be unsuccessful in this regard. However, it has been observed by the studies that the solvent extraction is capable of removing these compounds easily and successfully during the reaction. Finally, the oil recovery can also be improved and was obtained during the reaction. A reduction of less than 0.05% can be observed by this desulfurization method, which is able to concentrate the sulfur during the reaction.

## 2.9 Adsorption

### 2.9.1 Background

With the purpose of arriving at particularly low sulfur in diesel petroleum, adsorbents can be employed to specifically eliminate organic sulfur compounds (OSCs) and abandon the soaked and pungent complexes in the fuel. This entire procedure requires towering competence adsorbents to do away with sulfur from the mass of diesel fuel and, conversely, for scale-up concerns; huge quantities of adsorbents are required. The scheme at the back of expanding UAOD procedure is to zoom onto the specificity state in the oxidation pace by oxidizing OSCs. Selective adsorption after UAOD course is a positive advance for attaining ultra-low sulfur which not only is according to the stringent fuel requirements but can also be employed for fuel units. After elevated alteration capitulation, the sulfur mixes in oxidized form can be adsorbed by solid adsorbents like alumina. The most is made out of the adsorbent’s competence. Aromatic framed arrangements of pungent complexes in diesel fuel are alike to the parallel sulfur complexes; yet, by employing the UAOD method, OSCs have more empathy to oxidize than the non-sulfur aromatics. Acquiring benefit of the OSCs after oxidation clears the way for utmost sulfur deduction by careful adsorption after UAOD procedure (Etemadi, et al. 2007 & Lu, et al. 2000).

Division of sulfur complexes from hydrocarbons in diesel fuels is obtained through solid adsorbents. Sulfur complexes in fluid remnant fuels are more polar than the hydrocarbons of parallel arrangements and oxidation of OSCs are much quicker than the oxidation of the majority of hydrocarbons (Bortolini, et al. 1985 & Ballisteri, et al. 1992). Studies have demonstrated the efficiency of intermetallic adsorption and ultrasonic oxidation in desulfurizing upstream rudimentary oil (Lu, et al. 2000). After the oxidation, the OSCs are oxidized to sulfoxide or sulfones that are more polar than sulfides.

In powder form, Alumina is an adsorbent which bears relevance in refinement business. Alumina is very receptive to the quantity of water that is tied to it: the more elevated its water content, the less polar sites it has to attach natural complexes (Gerstenmaier, et al. 2002). This action is mentioned as I, II, or III, (I is the most dynamic). Alumina is accessible in three types: acidic, neutral, and basic. Acidic alumina helps nonaligned and anionic groups; whereas, basic alumina helps action exchange; and neutral alumina has similarity for adsorbing electronegative complexes. The nature of the adsorption sites in these dissimilar grades of alumina is a utility of pre-handling and the establishment circumstances (Etemadi, et al. 2007).

Calcining is thermal conduct procedure employed to ores and other hard supplies in order to carry under a thermal treatment, stage change, or taking away of a volatile portion. The calcination temperature development usually occurs below the melting point of the materials. For alumina, the calcining temperature was 550$^{o}$C (Gilchrist, 1989).

### 2.9.2 Fluidized Bed Reactor (FBR)

Fluidized bed reactor is extensively employed in business for stirring hard elements with gases or liquids. In most manufacturing applications, a fluidized bed comprises an uprightly-oriented column full of granular matter, and a fluid (gas or liquid) is pushed up through a dispenser at the floor of the bed. When the pull energy of running fluid surpasses gravity, particles are raised and fluidization takes place. This becomes the outcomes in the standard then holding a number of imprints and features of usual fluids, for instance the aptitude to free-flow under gravity, or to push by application of the fluid-based equipment. It diminishes the density of the medium; without upsetting its rudimentary properties. The consequential occurrence is tagged thus as fluidization (Howard, 1989 & Tavoulareas, 1991). Fluidized beds are employed for catalytic responses, power production, desulfurization of flue gases, and calcination.

In this dissertation, a fluidized-bed reactor has been devised with arrangement of the two components: packed-bed and stirred tank, nonstop flow reactors. A packed bed usually is a vacuumed tube, pipe, or container which is brimmed with a packing material. The purpose of a packed bed is used for improve surface contact area between two phase, such as oxidized organic sulfur and adsorbent. The fluidized-bed reactor can be seen below with Figure 2.8:

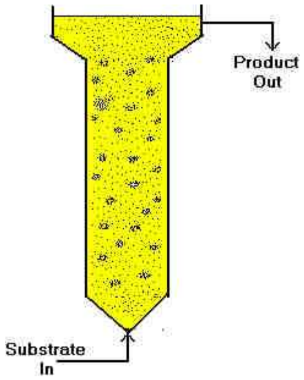


Figure 2.8 Fluidized bed reactor (Howard, 1989)

### 2.9.3 Advantages

The amplification in fluidized bed reactor employed in the present commercial system is mainly because of the intrinsic rewards of the machinery.

Uniform Particle Mixing: Because of the internal fluid-like properties of the hard fabric, fluidized beds do not go through the meager assimilation as in packed beds. This total stirring permits for a consistent produce which can be difficult to obtain time and again in other reactor structures. The removal of radial and axial absorption gradients also lets go for improved fluid-solid contact: indispensable for response competence and value (Howard, 1989 & Tavoulareas, 1991).

Uniform Temperature Gradients: A good deal of compound reactions generate or need the accumulation of high temperature. Local hot or cold points in the reaction bed usually stand to be a difficulty in packed beds; they are shunned in a fluidized condition like that of a FBR. In other reactor kinds, these limited heat dissimilarities, particularly hot-points, can affect product deficiency. Thus FBRs go well with the exothermic reactions. Investigators have also experienced that the bed-to-surface heat transmission coefficients for FBRs are great (Howard, 1989 & Tavoulareas, 1991).

Capacity to Operate Reactor in Continuous System: The fluidized bed feature of these reactors permits for the capacity to constantly take out the product and bring in new reactants into the reaction container. Functioning at a constant progression condition permits producers to manufacture their different products more competently because of the elimination of startup situations in batch processes (Howard, 1989 & Tavoulareas, 1991).

## 2.10 Microporous Crystalline Titanium Silicates

Zeolite is a crystalline aluminosilicate with a cage structure. They are aluminosilicate framework structures made from corner sharing $SiO_4$ and $AlO_4$ tetrahedra. Figure 2.9 shows the how the zeolite are form by cage structures. The success of zeolites in numerous industrial catalytic processes simulated the search for catalyst that containing elements different from $Al^{3+}$ in a silica lattice. The reason of introducing foreign atoms into solids to change their catalytic properties is the heart of heterogenous catalysis.

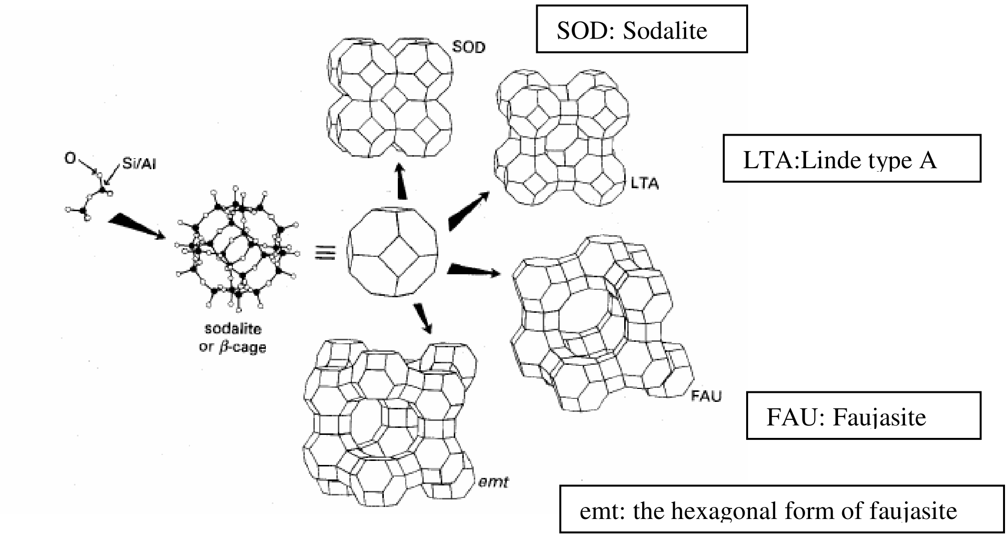


Figure 2.9 Formation of different zeolites by cage structure

In 1980, the first titanium silicates (TS-1) were synthesized by Taramasson et al (Taramasson, et al. 1983), with a crystalline structure of silicate-1 with Ti(IV) in framework position (tetrahedral coordination in substituting for Si(IV) in framework positions of crystalline silica). After the discovery of TS-1, in oxidation reactions with hydrogen peroxide as the oxidant, many organic compounds could be oxidized selectively and efficiently. In oxidation processes, one goal to achieve high yields is the fast removal of the initially formed oxidation products in order to minimize their further oxidation into less valuable products. For example, in heterogeneous oxidation, the goal is done by using low surface area larger pore catalyst that allows rapid diffusion of products out of the particles. For titanium-based catalysts, despite their high surface area and microporous structures, the selectivities can achieve 80% and sometimes even 95%. Another advantage of titanium based catalyst is regenerability and ease of separation from products that characterize any solid catalyst.

TS-1 are highly efficient catalysts for oxidation of a large number of organic substrates such alkenes, alcohols, aromatics using $H_2O_2$ as oxidant under mild condition, but the reaction will slow down when molecule have more than ten carbon ring, such as aromatic ring (DBT) corresponding to the linear chain. Therefore, a new type of titanium containing large pore zeolites with Ti were synthesized, such as Ti-beta, Ti-HMS (Hexagonal Mesoporous silica). TS-1/$H_2O_2$ was used to oxidize this at 333K with good conversion results (Kong, et al. 2004).

Much research activity was devoted to the study of catalytic materials having:

- Titanium ions in the framework positions of different zeolites structures with larger pore size (Ti-beta) or mesoporous materials (MCM-41), with selectively oxidizing larger molecules than TS-1.
- Different transition metal ions, in pentasyl-type zeolites (structure similar to TS-1) or different types of zeolite structures, or mesoporous materials.

# CHAPTER 3

# MODIFIED DESULFURIZATION METHOD ON MODEL SULFUR COMPOUND STUDY

## 3.1 Introduction

The kinetics and selectivity of the oxidation supports the scheme regarding the application of an oxidation desulfurization scheme, which is related to the organic sulfide to sulfones. From the previous UAOD process that has been developed, organic substrate oxidations in particular have been studied by the system of POM/$H_2O_2$. (Mei, et al. 2003 and Wan, et al. 2005). In the presence of $H_2O_2$, polyoxoperoxo species are formed from the tungsten and molybdenum POMs that have a uniquely Keggin structure. Mai, et al. 2003 and Wan, et al. 2005 have already demonstrated BT and DBT and their families by UAOD process under mild conditions. It has also been noted that the oxidation process of sulfur compounds having even low nucleophilicity can form sulfoxide or sulfones; moreover, these results can be achieved in high yields. However, with current UAOD processes, results show low desulfurization efficiency on thiophene's and benzothiophenes.

The development of an oxidative desulfurization process has been the aim of this study. High reaction rate and high selectivity conditions have been considered during this process. Six complementary techniques were designed in this process. Acid catalyst, phase transfer agent (PTA), oxidant, sonication, mechanical stir and room temperature ionic liquids (RTILs) are the six techniques that have been mentioned earlier Chapter 2.

The modified desulfurization method includes two parts. The first part involves desulfurization of OSCs with the above mentioned six complementary techniques. In the second part, desulfurization of thiophene occurs via solid catalyst with microporous crystalline titanium silicates. Titanium Beta (Ti-B) has been chosen as the catalyst.

In this chapter, a series of experiments were developed to work out efficient protocol reaction conditions based on DBT model sulfur compound. This includes amount of catalyst, types of catalyst, type and amount of ionic liquid, hydrogen peroxide usage, phase transfer agent, and treatment methods. Finally, the qualitative and quantitative results were analyzed by instruments.

## 3.2 Materials and Experimental Procedures

### 3.2.1 Materials

#### 3.2.1.1 Chemical Preparation

Sulfur model compounds that has been used for the UAOD and extraction process are listed as follows: Thiophene (T), 2-methyl thiophene (2MT), 2-ethyl thiophene (2ET), benzothiophene (BT), 2-methyl benzothiophene (2MBT), dibenzothiophene (DBT), 4,6-dimethyl dibenzothiophene (4,6-DMDBT), benzothiophene sulfone (BTO) and dibenzothiophene sulfone (DBTO), were obtained from Aldrich Chemical. Tetraoctylammonium fluoride used as phase transfer agent (PTA) were synthesized from literature (Dermeik, et al. 1989).

Solvents for preparing model sulfur compounds solution and gas chromatography analysis, i.e., toluene (HPLC grade), were obtained from VWR Inc. Acetic acid and tri-fluoro acetic acid (TFA) with glacial grade used as catalyst were obtained from Aldrich Chemical. 30% hydrogen peroxide ($H_2O_2$) used as oxidant were obtained from VWR Inc. 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][$PF_6$], 1-butyl-3-methylimidazolium octyl sulfate [BMIM][$OcSO_4$] and 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][$EtSO_4$], 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][$EtSO_4$], 1-ethyl-2,3-di-methylimidazolium ethyl sulfate [EDMIM][$EtSO_4$], Tri-butyl methyl ammonium methyl sulfate [$TBMNH_4$][$MeSO_4$] and Tri-butyl methyl phosphonium methyl sulfate [TBMP][$MeSO_4$] as ionic liquid were obtained Aldrich Chemical.

#### 3.2.1.2 Synthesis of Ti-B Solid Catalyst

Ti-B was synthesized according to Xia, et al. For solution A, 0.58 gram of TBOT is first added to 4 gram of deionzed water and mixed for 1 hour. Next, 2 gram of $H_2O_2$ to the mixture. The mixture is stirred at room temperature for 1 hour, to form a solution containing peroxide titanate. For solution B, 0.0124 gram of anhydrous $NaAlO_2$ and 0.015 gram of NaOH are dissolved in 8g of TEAOH at room temperature and stirred for 1 hour. Solution B is added to solution A and stirred for 1.5 hours. A homogenous solution (Figure 3.1) appears after 2 hours and is heated to 353K and dried while stirring (Figure 3.2). When the gel is completely dry, it is ground into fine powder (Figure 3.3).

Figure 3.1 Homogeneous solution of mixture of solution A and B after stirring

Figure 3.2 Dry gel formation

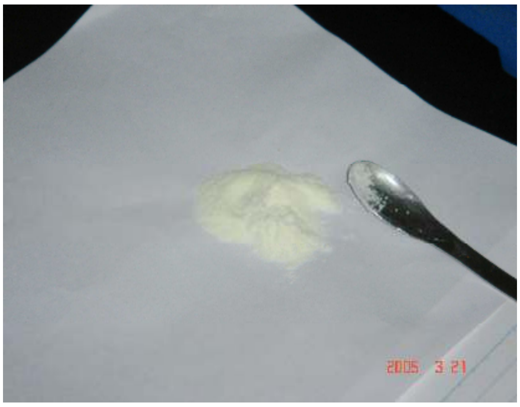


Figure 3.3 Powder after grinding

The fine powder is transferred into a Teflon beaker situated in a Teflon inner (Figure 3.4) of an autoclave, and 5 gram of water is added to the bottom of autoclave, this is the source of steam (VPT), the crystallization was carried out in steam first at 403K for 96 hours, and 448K for 18 hours (Xia, et al. 1998). The product was washed with distilled water, dried at 308K for 10 hours and calcined at 793K for 10 hours in the flow of air. The Ti-Beta product was treated with 1M $H_2SO_4$ at room temperature for 12 hours and then washed with distilled water, dried at 308K for 10 hours, and calcined at 793K for 5 hours in the flow of air.

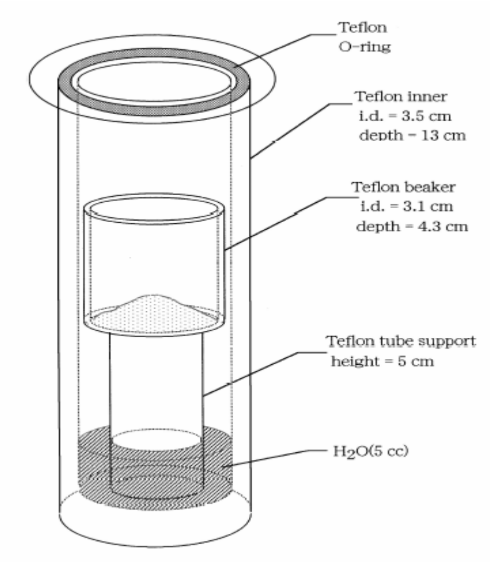


Figure 3.4 Apparatus for synthesis of Ti-Beta by DGC method (Xia, et al. 1998)

### 3.2.2 Ultrasonic Reactor

In all UAOD process, a probe type ultrasound reactor has been used. The probe type reactor were purchased and manufactured by Sonic & Materials Inc. (Newtown, CT) and the reactor model is VCX-750. The advantages of this model include energy set-point, remote process capability, variable power out put control and independent on/off pulser. The detail specifications are shown in Table 3.1.

Table 3.1 Specification of probe type ultrasound: VCX-750

| Item | Description |
|---|---|
| Dimensions | (H x W x D) 235 x 190 x 340 mm |
| Weight | 15 Ibs |
| Power Supply | 750 Watts, 20 KHz |
| Sealed Converter | Piezoelectric lead zircinate tutanate crystals (PZT) |
| Standard Probe | 0.5" solid or with threaded end and replaceable tip |
| Intensity | 10 watts/cm$^2$ to 100 watts/cm$^2$ |

Probe type ultrasound reactor can produce high intensity ultrasound irradiation at “point”, it produces an ultra-fine emulsion for the mixture with ultrasonic intensities at 100 watts/cm$^2$. With the experiment, the probe tip was immersed into the layer of organic phase and aqueous phase and the tip is placed 1 to 2 mm above the aqueous phase. The schematic diagram of set up is shown in Figure 3.5.

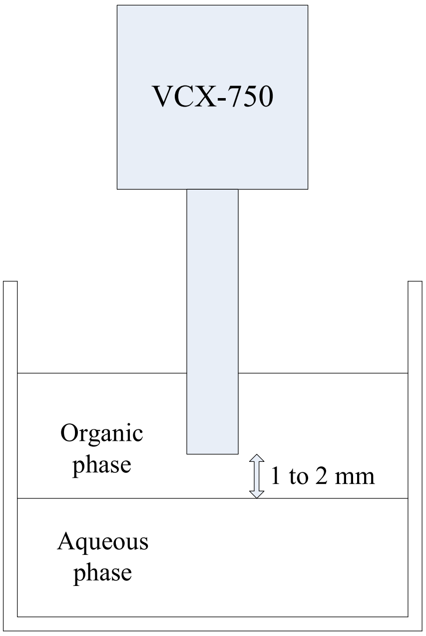


Figure 3.5 Schematic diagram of UAOD set up

### 3.2.3 Sulfur Analytical Methods

**Total Sulfur Analyzer:** Total sulfur concentration of unknown sample can be quantitatively determined by Sulfur-in-Oil Analyzer (SLFA-20) manufactured by Horiba Inc. The analyzer complies with ASTM D4294 and ISO 8754. ASTM D4294 is described as follows: an unknown concentration liquid sample is placed in the beam emitted from a non-dispersive X-ray fluresence (NDXRF). The resultant excited characteristic radiation is measured and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulfur concentration in parts per million (ppm). The sulfur analyzer can detect range of 0 to 4 wt% of total sulfur, with a lower detection limit of 20 ppm.

**Identification and Quantification of OSCs:** HP-6890 Series gas chromatograph (GC) equipped with a Sulfur Chemiluminescence Detector (SCD)-

Sievers model 355B. The chromatograph was fitted with a 60-m DB-5 fused-silica column that was directly installed into the discharge tube. The column temperature was first maintained at 80$^{o}$C for 1 minute, the column temperature was then raised to 290$^{o}$C at the rate of 6$^{o}$C/minute and then maintained at 290$^{o}$C for 2 minutes to let remaining hydrocarbon burn out. For carrier gas, ultra high purity grade helium and ultra hydrogen were used at a constant pressure of 50 psi. The injected sample volume was 1μL. With SCD, the operation conditions were as follows: burner temperature set at 800$^{o}$C, 5.8 ml/min of air, 100 ml/min of hydrogen. With ozone generator: 60 ml/min at 60 psig and 25$^{o}$C.

GC-SCD can identify a series of sulfur components, including, thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and other alky-substituted organic sulfur that exists in various gasoline or diesel sample. SCD detector can detect a range of 0.1 to 1 wt% of sulfur. Figure 3.6 shows the schematic diagram of the major components of GC-SCD set up.

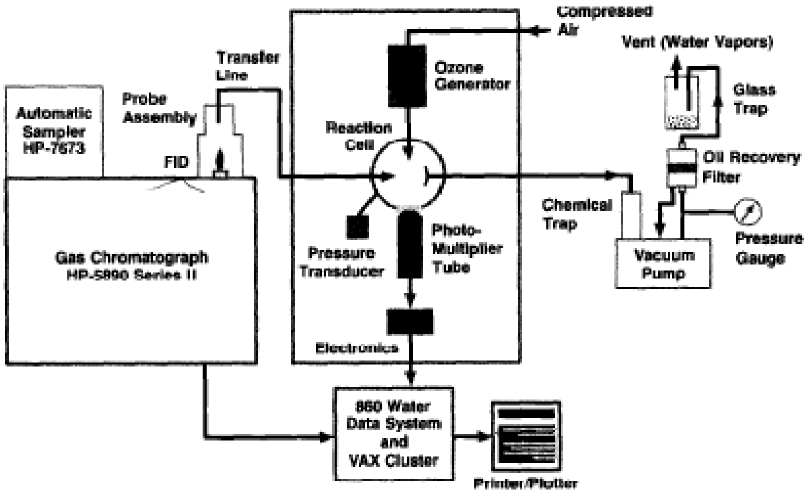


Figure 3.6 Block diagram of GC-SCD set up

Sulfur Chemiluminescence detector (SCD) has been used to detect sulfur compounds in liquid and gas with both qualitative and quantitative determination. Basically, two stages of detection method are involved, such as reaction furnace and SCD reaction cell. Initially, the sample with air/hydrogen mixture was passed through a high temperature furnace (>1,800°C) with vacuum condition, the sample was reduced into sulfur monoxide. Sulfur monoxide then reacts with ozone forming sulfur dioxide and emit 340-nm (Benner, et al. 1990) UV light, the UV light can be detect by photomultiplier tube, and intensity of the light is proportional to the concentration of sulfur. Therefore, qualitative and quantitative determination can be achieved. Figure 3.7 shows the reaction mechanism of SCD (GAS Inc. 2004).

Previously, pulse flame photometric detector (PFPD), flame ionization detector (FID) and mass spectroscopy detector (MS) were used to determine sulfur compounds. The advantages of SCD to overcome these detectors are list as follows: (1) it gives high sensitivity of any sulfur compounds and its detection limit can range from few hundred ppm to ppb level, (2) no interference (only detect sulfur compounds), (3) no hydrocarbon quenching (4) ASTM methods approval.

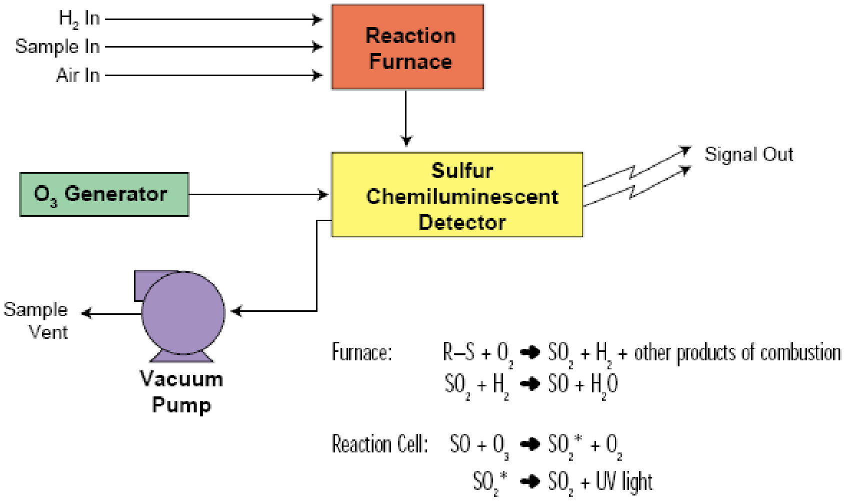


Figure 3.7 Reaction mechanism of SCD (GAS Inc. 2004)

## 3.3 Results and Discussion (Modification Desulfurization Method with RTIL)

### 3.3.1 Effect of the Quaternary Ammonium Salts (QAS) as Phase Transfer Agents (PTA)

#### 3.3.1.1 Previous Work Review and PTA Selection

As discussed in Chapter 2, two or more reagents are used in the conduction of different reactions, which takes place in two or more phases. In this case, these reactions utilize PTA, in order to accelerate the reactions, as reactions are usually found to be inhibiting due to their incapability of attracting the reagents during the process. Organic phase or interfacial region receives the delivery of anion, which is done by the QAS that works as a PTA during the reaction. Thus, the oxidation of organic sulfur compounds is facilitated by the QAS. The previous work (Mei, et al 2003 and Wan, et al 2005), shows that the oxidation of DBT to DBTO and BT to BTO does not occur or proceeds at a very low reaction rate in presence of surface-active agents other than QASs or cationic surfactants. In the reaction system, it has been found that the effective oxidant is indicated by means of its form of peroxo metal anion, and especially, cationic surfactants inclusively. Table 3.2 shows the effect of different types of surfactants on UAOD.

Table 3.2 Effect of different types of surfactants on UAOD process (Wan, et al. 2005)

| **Type** | **Surfactant** | **Desulfurization** |
|---|---|---|
| Cationic | Tetraoctylammonium Bromide (TOAB) | + |
| | Tetrabutylammonium Bromide (TBAB) | + |
| | Methyltributylammonium Chloride (MBAC) | + |
| | Methyltributylammonium Hydroxide (MBAH) | + |
| | Tetramethylammonium Fluoride (TMAF) | + |
| Anionic | 1-Octanesulfonic Acid, Sodium Salt | – |
| Nonionic | Tween 80 | – |
| Control | No Surfactant | – |

Note: + indicates that there is reaction occurring under reaction conditions.
– indicates that there is no reaction occurring under reaction conditions.

Choosing a phase transfer agent is usually the most important stop in design and development of the UAOD process. From previous work, tetraoctylammonium floride (TOAF) gives the best catalytic activities with large lipophilic cation that can easily oxidize OSCs into its relative sulfone. Therefore, TOAF has been chosen as PTA for entire UAOD process.

### 3.3.1.2 Experimental Procedure

DBT 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 DBT 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 DBT were prepared. $H_2O_2$ and 3 gram of acetic 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 DBT model sulfur compound stock solution that mix with 0.3g of TOAF. 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 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. A series of different amounts of PTA were also examined to see if the desulfurization efficiency will be affected.

### 3.3.1.3 Results and Discussion

Table 3.3 shows the oxidation of DBT sulfur model compound with and without PTA under 10 minutes UAOD process.

Table 3.3 Effect of amount of PTA on UAOD

| **Catalyst** | **PTA** | **Ionic liquid** | **Initial conc.** | **Final conc.** | **Desulfurization** |
|---|---|---|---|---|---|
| (gram) | (gram) | (gram) | (ppm) | (ppm) | (%) |
| 3 | 0 | 5 | 512 | 395 | 22.9 |
| 3 | 0.3 | 5 | 512 | 271 | 47.1 |
| 3 | 0.6 | 5 | 512 | 265 | 48.2 |
| 3 | 0.9 | 5 | 512 | 262 | 48.8 |

Table 3.3 has been prepared for the better understanding of the effect of amount that PTA implies on UAOD. These studies have shown that the efficiency of the desulfurization can be improved with the help of PTA from 22.9% to almost 47.1%. Similarly, results have shown that when PTA was used in higher quantity, the results showed a high percentage of desulfurization. For instance, the percentage of desulfurization went up from 48.2% to 48.8%. In this case, PTA was used about 0.6 grams, which resulted in 48.2% of desulfurization. However, when the amount of PTA was increased from 0.6 grams to 0.9 grams, the desulfurization increased to 48.8% in same conditions, that is, the catalyst was used 3 grams, and the ionic liquid was kept at 5 grams. It can be seen from the Table 3.3 that initial concentration was also same at 512 ppm. However, final concentration decreased from 265 ppm to 262

ppm in result of the increment in the grams of PTA. From the Table 3.3, we can say that the desulfurization efficiency improved, and can be improved practically. However, it can be seen from these results, the percentage only went up in small distances.

Figure 3.8 shows the GC-SCD chromatogram of DBT model sulfur compound before and after the reaction. At 16.4 minute, the peak indicates the retention time for DBT compound. The concentration of DBT decreases after UAOD process, the absence of DBT is oxidized into DBTO and is extract into IL phase. To confirm this hypothesis, the IL phase is mix with toluene for 10 minutes, the mixture was than separated by centrifuge, this extraction process enable DBTO from IL phase extract into organic solvent phase that allow GC-SCD analysis. Figure 3.9 shows the GC-SCD chromatogram of the DBTO that has been extract from IL. From the chromatogram, it clearly shows after 10 minute UAOD, DBT is oxidized into sulfone and extract into IL phase, only small amount of DBT extracted into IL phase.

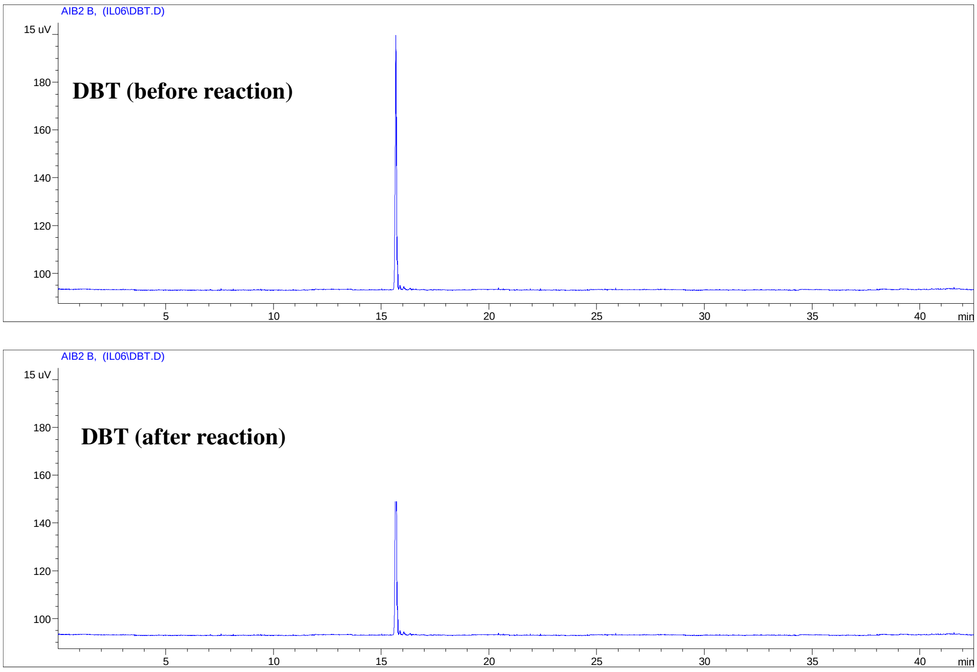


Figure 3.8 GC-SCD chromatogram of DBT before and after UAOD process

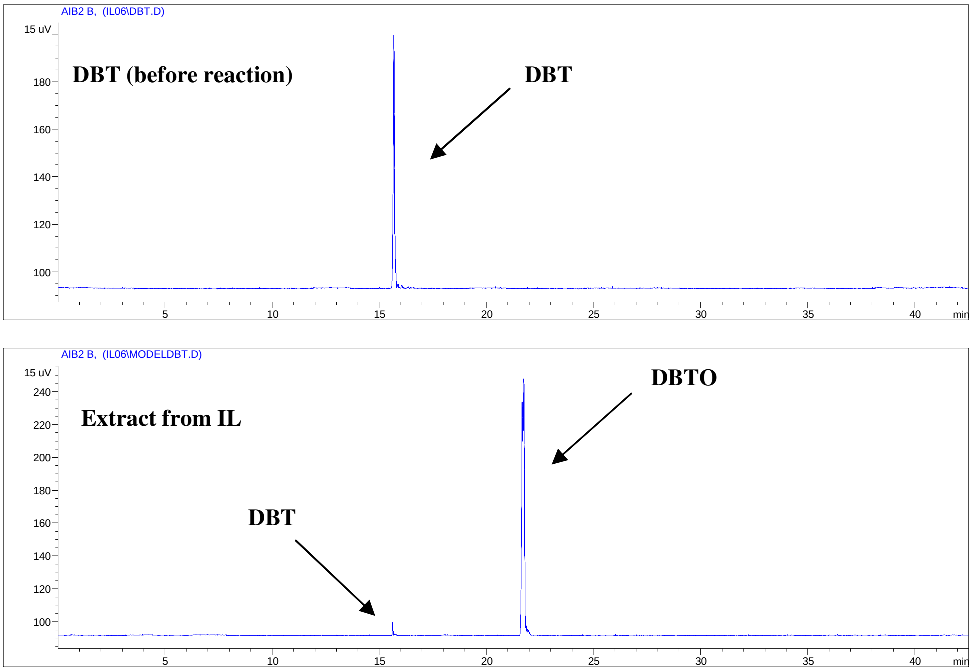


Figure 3.9 GC-SCD chromatogram of DBT and DBTO from IL phase

### 3.3.2. Effect of the Desulfurization Method with Combination of Mechanical Stir and UAOD

#### 3.3.2.1 Effect of UAOD

In this section, we will discuss the effects of the desulfurization methods that might be combined with the UAOD system and mechanical stir during the process. From the results in section 3.3.1, it has been shown that desulfurization efficiency was achieved 47.1% after the utilization of only UAOD in the process. There are different reasons that are associated with the provision of only this percent of desulfurization. One of the primary reasons is that more time is required by the UAOD during the process of oxidation of sulfur partition, which converts during the ionic liquid phase, as discuss earlier in the literature. However, other studies have shown that utilization of more sonication time will improve the results at a higher extent. However, the greater usage of sonication time may increase the cost, but comes out to be low desulfurization efficiency in this case, as sonication time requires electricity, and an increment in the sonication time will increase the electricity, which will increase the cost of the total process. Therefore, in order to improve the efficiency of the desulfurization and to get better and fast results, it is necessary to combine the stirred method and sonication time collectively. This will enhance the process and will improve the results from the previous ones.

### 3.3.2.2 Experimental Procedure

DBT 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 DBT 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 DBT were prepared. $H_2O_2$ and 3 gram of acetic 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 DBT model sulfur compound stock solution that mix with 0.3g of TOAF. 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.

With the same experimental procedure, a series of experiments on different sonication time and stir time have been conducted.

### 3.3.2.3 Results and Discussion

According to Table 3.4, the results show different reaction or sonication times that were used in the experiment, in order to increase the efficiency of desulfurization. However, it can be observed from these results that when the reaction time was taken as 10 minutes with UAOD, the initial concentration was 512 ppm, and final concentration came out to be 271 ppm. During this sonication time of 10 minutes, the desulfurization percentage was 47.1. In order to increase the efficiency, the reaction time was increased to 20 minutes, which showed an increment from 47.1 to 50.2%, which is not a great amount of increment in the efficiency. Similarly, when reaction time was taken as 40 minutes with UAOD, the efficiency of desulfurization came out to be 55.5%. We can observe that there is little difference between 55.5 and 47.1%. Therefore, it can be concluded an increment in the sonication time does not bring any prominent change and improvement in the efficiency. Thus, it is advisable to keep 10 minutes of sonication time, which will also be at lower cost, as compared to 40 minutes of reaction time.

Table 3.4 Effect of sonication time on desulfurization efficiency with DBT

| **Reaction time** | **Initial conc.** | **Final conc.** | **Desulfurization** |
|---|---|---|---|
| (minute & hour) | (ppm) | (ppm) | (%) |
| 10 min UAOD | 512 | 271 | 47.1 |
| 20 min UAOD | 512 | 255 | 50.2 |
| 30 min UAOD | 512 | 241 | 52.9 |
| 40 min UAOD | 512 | 228 | 55.5 |

Table 3.5 shows the desulfurization efficiency with different stirred time and combination with sonication on DBT model sulfur compound. From the results

gathered in Tablet 3.5, we can observe that 93.4% of DBT was oxidized into DBTO after passing almost six hours, while using only stirred method during the reaction. This has shown remarkable results; however, the desulfurization process has taken a very long time in these conditions.

As advised earlier in our study, a combination of stirred method and sonication will give improved results. Therefore, we can observe that 89.3% of desulfurization efficiency has been achieved by the combination process of sonication and stirred method during the reaction. In this regard, treatment time was found to be reduced from 6 hours that were taken in the earlier experiment with only stirred method, to only 3 hours at the time of combination of stirred method and sonication.

From the results that are gathered in the Table 3.5, we have seen that the efficiency of desulfurization has been enhanced by the application of combination of sonication and stirred method. Therefore, in the literature that was studied earlier, and results shown in the Table 3.5, sonication time of ten minutes and 170 minutes for stirred method will be applied during the study of rest of model sulfur compounds. This condition will be taken as the standard desulfurization treatment method in our future studies.

Table 3.5 Effect of different mixing method on DBT

| **Reaction time** | **Initial conc.** | **Final conc.** | **Desulfurization** |
|---|---|---|---|
| (minute) | (ppm) | (ppm) | (%) |
| Stir 1 hour | 512 | 314 | 38.7 |
| Stir 3 hour | 512 | 187 | 63.5 |
| Stir 6 hour | 512 | 34 | 93.4 |
| 10 min UAOD & 50 min stir | 512 | 178 | 65.2 |
| 10 min UAOD & 170 min stir | 512 | 55 | 89.3 |
| 10 min UAOD & 350 min stir | 512 | 17 | 96.7 |

### 3.3.3 Effect of Type and Amount of Catalyst

#### 3.3.3.1 Better Catalyst Selection

Currently, the catalyst that has been selected for the process of desulfurization is acetic acid. However, 89.3% of desulfurization has been achieved with regard to the final concentration of 55 ppm and initial concentration of 512 ppm in the DBT model sulfur compound, which is unacceptable by the new EPA standard, which requires 15 ppm. Therefore, in order to enhance the efficiency of desulfurization, it is necessary and important to use any other catalyst, which should be stronger than the acetic acid, and must bring improved results.

In this case, a new catalyst has been selected, in order to replace the previous acetic acid for the better and improved outcome. In this regard, tri-fluoro acetic acid has been selected for this purpose. Tri-fluoro acetic acid is also known as TFA and is part of the same group catalyst that is belonged by the acetic acid. And it allows much stronger catalytic activity during the reaction.

### 3.3.3.2 Experimental Procedure

DBT 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 DBT 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 DBT were prepared. $H_2O_2$ and 3 gram of mixture catalyst of acetic acid and TFA were add into the beaker, the mixture was stirred at room temperature for 5 minutes, leading to solution A. Solution B was prepared with DBT model sulfur compound stock solution that mix with 0.3g of TOAF. 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 $50^oC$ water bath and then 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 3 hours with 50oC water bath, 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 extracted with polar solvent for further analysis.

With the same experimental procedure, a series of experiments on different concentration and amount usage of catalyst with 10%, 20%, 30% and 40% TFA has been examined.

#### 3.3.3.3 Results and Discussion

Table 3.6 shows the desulfurization of DBT model sulfur compound on different concentration of catalyst.

Table 3.6 Effect of different concentration catalyst on DBT

| **Catalyst** | **Initial conc.** | **Final conc.** | **Desulfurization** |
|---|---|---|---|
| (gram) | (ppm) | (ppm) | (%) |
| Acetic acid (3g) | 512 | 55 | 89.3 |
| 10% TFA (3g) | 512 | 26 | 94.9 |
| 20% TFA (3g) | 512 | 14 | 98.6 |
| 30% TFA (3g) | 512 | 0 | 100.0 |
| 40% TFA (3g) | 512 | 0 | 100.0 |

From the Table 3.6, effect of different concentration catalysts have been tried to studied that are found on DBT. In this regard, experiments showed that the efficiency of desulfurization have been found to improve and enhance with the help of tri-fluoro acetic acid, also known as TFA. In the earlier studies, it was decided to use TFA was used instead of acetic acid, and the studies showed positive results in this regard. During the reactions, the reduction of the DBT concentration was found to be less than 15 ppm, which was required by the new EPA standard, and thus, it fulfilled the requirement. In this case, only 20% TPA was used during the reaction.

In conclusion, TFA enhances the efficiency of desulfurization, so, better results will be achieved, if more TFA is utilized during the reaction. However, like sonication time, TFA also has higher cost, as compared to the acetic acid. Therefore, it is advisable to select only 20% TFA instead of an increment in it. Thus, the standard catalyst concentration will be only 20% TFA.

However, in order to observe and examine the utilization capacity of 100% TFA, it was used during the experiment. When 100% TFA was used, the reaction accelerated vigorously during the sonication time. In just about five-minute's sonication, the glass container exploded out the reaction mixture. Therefore, it is not possible and not advisable to use 100% TFA for this process. Therefore, it was decided by mixed the TFA with acetic acid during the process. In the result, the chances of having an explosion were lowered by the mixing of TFA and acetic acid in the process. It was also observed that instead of concentrated TFA, the combination of TFA with the acetic acid gives better and positive results, as well as, no explosion is occurred during the experiment.

Table 3.7 shows the desulfurization of DBT model sulfur compound on different weight of 20% TFA usage.

Table 3.7 Effect of different weight of catalyst usage on DBT

| **Catalyst** (gram) | **Initial conc.** (ppm) | **Final conc.** (ppm) | **Desulfurization** (%) |
|---|---|---|---|
| 20% TFA (0.5g) | 512 | 78 | 84.8 |
| 20% TFA (1.0g) | 512 | 35 | 93.2 |
| 20% TFA (1.5g) | 512 | 14 | 97.9 |
| 20% TFA (2.5g) | 512 | 7 | 98.6 |
| 20% TFA (3.0g) | 512 | 7 | 98.6 |

The Table 3.7 has been formulated, in order to gather and present the effect of different weight of catalyst usage on DBT during the experiment. From the experiment, we analyze different and various characteristics of the subject, and it was found out that the efficiency of the desulfurization is enhanced and improved by an increment in the usage of catalyst, and its enhancement was quite obvious during the process.

During the experiment, try to consider the cost, in order to get the best possible benefits while also keeping the cost as low as possible. In this case, it was observed and decided that 1.5 grams of usage of the optimal catalyst, that is, 20% TFA, should be used during the process. This amount is only half, if we compare it with the previous usage described in the earlier sections of 3.3.1 and 3.3.2. The half amount comes out to be only 3 grams of acetic acid during the process. In this regard, it can be conclude that not only catalyst cost is saved by the optimal use of TFA, but better, enhanced, and improved efficiency is given by this step during the process. Therefore, it is advisable to keep the optimal catalyst usage of 1.5 grams, rather than going for an increment in it.

### 3.3.4 Effect of the type of RTILs

#### 3.3.4.1 ILs are not always Green: Alternative RTIL Selection

During the ODS process of the hydrophobic [BMIM][$PF_6$] ionic liquid, a decomposition product of 1-butyl-3-methylimidazolium hydrate is created that has been identified crystallographically, as found out from previous literature, as well as, from the results of experiments. It has been observed that the [BMIM][$PF_6$] ionic liquid extracts white fumes during the process of UAOD. Observations have also been gathered regarding the toxic and corrosive properties of these white fumes that contains hydrogen floride (HF).

For a combination of reasons, many researches have used [BMIM][$PF_6$] ionic liquid during their studies. Lack of organic vapor pressure, hydrophobicity, etc. are some of the reasons that tends the researchers for the utilization of this liquid. However, despite the well established instability of the [$PF_6$] anion, it has received wide spread interest. During the contact of the above mentioned anion with the moisture (Swatloski, et al. 2003), this instability has been found at a higher extent. In the result of this instability, volatiles, such as, HF, $POF_3$, etc. are formed, by which, glassware can be dissolved, and ultrasound probe can be damaged during the reaction. In this regard, handling of HF-containing compounds should be done very carefully, which is very important, and one should emphasize repeatedly considerably.

The guidelines for the development of new ionic liquids should be provided by the utilization of non-toxic pharmaceutically acceptable ions, as well as, GRAS materials. The establishment of the toxicological and environmental hazards for the individual ions have been done for new ionic liquids that are developed by the provision of the above mentioned guidelines, as taken from the literature. (Carda-Broch, et al. 2003). In this regard, it should also be considered that acceptability should be done low during the process. The list of non-toxic pharmaceutically suitable anions includes inorganic anions such as $Cl^-$, $Br^-$, $SO_4^{2-}$, $PO_4^{3-}$, $NO_3^-$, and organic anions such as acetate, succinate, glycolate, and methane-sulfonate.

Halogen-free ionic liquids are concentrated completely by the present, in order to avoid these stability and corrosion problems during the extraction process of oxidized sulfur compounds. Solid and liquid type of sulfate anion based IL have been chosen in this research as the alternative RTIL source. Liquid type IL were 1-butyl-3-methylimidazolium octyl sulfate [BMIM][$OcSO_4$] and 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][$EtSO_4$]. Solid type IL were 1-ethyl-2,3-di-methylimidazolium ethyl sulfate [EDMIM][$EtSO_4$], Tri-butyl methyl ammonium methyl sulfate [$TBMNH_4$][$MeSO_4$] and Tri-butyl methyl phosphonium methyl sulfate [TBMP][$MeSO_4$]. From literature (Eber, et al. 2004), sulfate anion based IL is stable under mild condition, no toxic by-product and good extractability with OSCs. Figure 3.10 shows all the chemical structure of various IL that has been used.

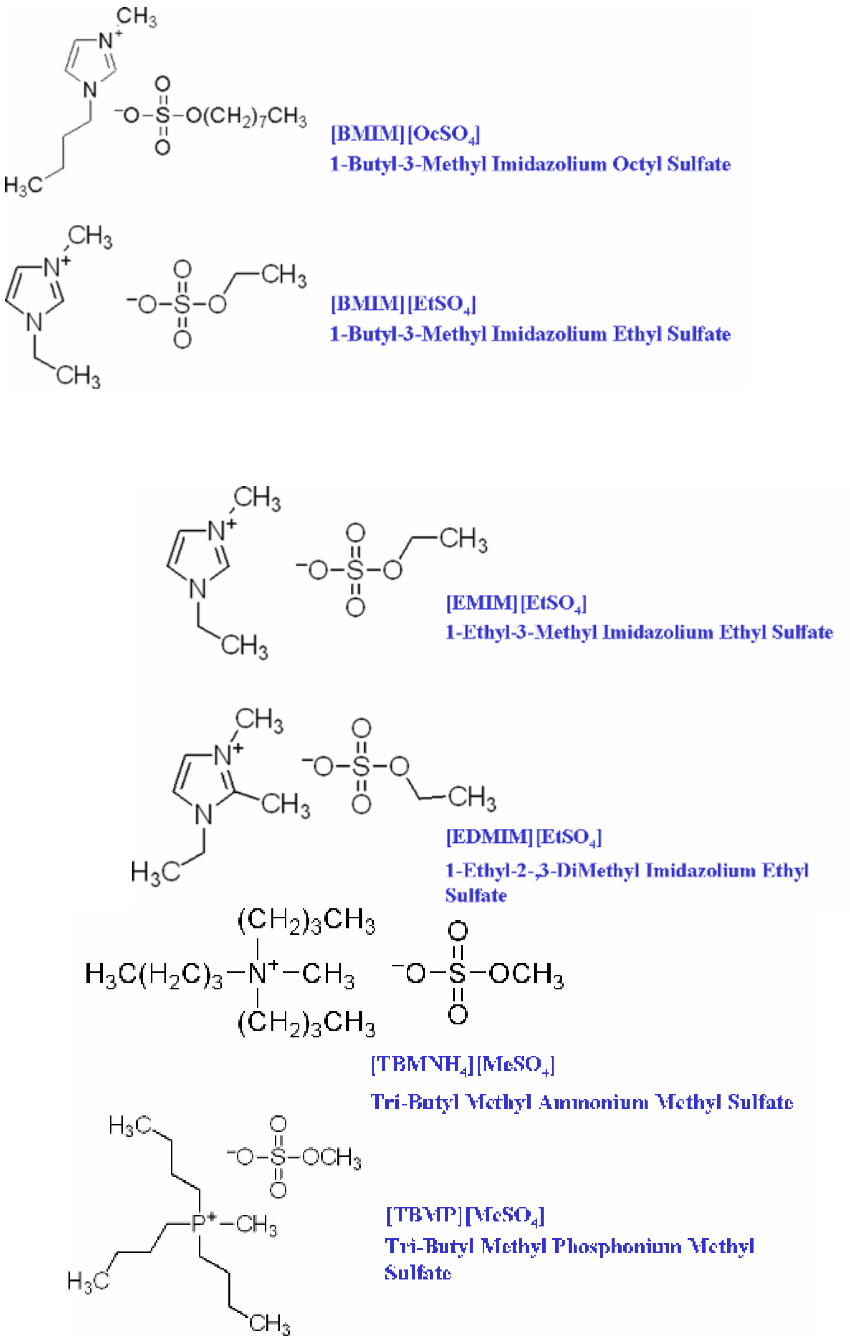


Figure 3.10 Sulfate anion based ILs

### 3.3.4.2 Experimental Procedure

DBT 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 DBT sulfur model compounds is described as follows. An equal weight ratio of 5 gram of hydrogen peroxide ($H_2O_2$), 1-butyl-3-methylimidazolium octyl sulfate [EMIM][$EtSO_4$] and DBT were prepared. $H_2O_2$ and 1.5 gram of 20% TFA 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 DBT model sulfur compound stock solution that mix with 0.3g of TOAF. Solution B was added to solution A. Finally, [EMIM][$EtSO_4$] ionic liquid was slowly added into the mixture. The mixture was first heated to $50^oC$ 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 $50^oC$ water bath for 3 hours, than the phase was separated by centrifuge and the top organic phase was used for quantitative and qualitative analysis. The bottom aqueous phase of ionic liquid was extract with polar solvent for further analysis.

With the same experimental procedure describe above. 1-ethyl-3-methylimidazolium ethyl sulfate [BMIM][$OcSO_4$], 1-ethyl-2,3-di-methylimidazolium ethyl sulfate [EDMIM][$EtSO_4$], Tri-butyl methyl ammonium methyl sulfate [$TBMNH_4$][$MeSO_4$] and Tri-butyl methyl phosphonium methyl sulfate [TBMP][$MeSO_4$] as another alternative IL source that also been examined.

With solid type IL, it is heat with water bath and melt the solid IL into liquid form in order to mixing with aqueous phase.

### 3.3.4.3 Results and Discussion

Table 3.8 shows the desulfurization efficiency of DBT model sulfur compound by using different types of RTILs.

Table 3.8 Desulfurization efficiency with different types of ILs on DBT

| **Ionic liquid type** (Liquid IL) | **Initial conc.** (ppm) | **Final conc.** (ppm) | **Desulfurization** (%) |
|---|---|---|---|
| [BMIM][$PF_6$] | 512 | 14 | 97.3 |
| [EMIM][$EtSO_4$] | 512 | 7 | 98.6 |
| [BMIM][$OcSO_4$] | 512 | 15 | 97.1 |

| **Ionic liquid type** (Solid IL) | **Initial conc.** (ppm) | **Final conc.** (ppm) | **Desulfurization** (%) |
|---|---|---|---|
| [EDMIM][$EtSO_4$] | 512 | 14 | 97.3 |
| [$TBMNH_4$][$MeSO_4$] | 512 | 11 | 97.9 |
| [TBMP][$MeSO_4$] | 512 | 12 | 97.7 |

From the above-given table 3.8, it ahs been tried to achieve the efficiency of desulfurization with the help of different types of ILs on DBT. During the experiment, promising and significant results with average 97.9% desulfurization efficiency were showed by sulfate anion based IL regarding their ability of desulfurization. Although, no by-product is given by the sulfate based anion IL during the process, and during the reaction, it does not produce any kind of corrosive fumes, which is a positive sign of this halogen-free starting and cheap materials. During the experiment, it shows better efficiency of the desulfurization is given by the [EMIM][$EtSO_4$] that comes out to be almost 98.6%, which is a significant percentage of the efficiency. Therefore, it is advisable and preferable to use the right ionic liquid during the process.

On a large scale, the cheap starting materials are available that allow the accessibility of halogen-free [BMIM][$OcSO_4$] and [EMIM][$EtSO_4$]. On a large scale, the detergent is taken as sodium octylsulfate, whereas, alkylating agent is considered dialkylsulfates (Eber, et. al. 2004). The utilization of sulfur-containing ionic liquids for the process of desulfurization might look inconsistent at first glance. However, it is unwanted to leach any ionic liquid into the oil phase, and therefore, it is not important to select a suitable ionic liquid through a critical criterion for the composition of the extracting agent.

### 3.3.5 Effect of the Concentration of Hydrogen Peroxide

#### 3.3.5.1 Introduction

The entire process uses hydrogen peroxide ($H_2O_2$) as its primary oxidant. An important variable in process design is the concentration of aqueous $H_2O_2$ concerning the rate of oxidation, non-productive decomposition, cost, and safety. In this section, the effects on the oxidation efficiency of DBTs and DBTOs have been studied by employing $H_2O_2$ with four different concentrations.

### 3.3.5.2 Experimental Procedure

DBT 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 DBT sulfur model compounds is described as follows. An equal weight ratio of 5 gram of hydrogen peroxide ($H_2O_2$), 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][EtSO$_4$] and DBT were prepared. $H_2O_2$ and 1.5 gram of 20% TFA 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 DBT model sulfur compound stock solution that mix with 0.3g of TOAF. Solution B was added to solution A. Finally, [EMIM][EtSO$_4$] ionic liquid was slowly added into the mixture. The mixture was first heated to $50^oC$ 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 $70^oC$ water bath for 3 hours, than the phase was separated by centrifuge and the top organic phase was used for quantitative and qualitative analysis.

### 3.3.5.3 Results and Discussion

Figure 3.11 shows the direct proportional relationship of the oxidation rate of DBT to DBTO with the concentration of $H_2O_2$ has been tried to shown, even in the presence of excess amount of the utilization of $H_2O_2$. However, there is little difference between 30% and 50% $H_2O_2$. With 10 minutes sonication, the conversion of DBT to DBTO can achieve more than 50% with 50% $H_2O_2$. DBT can be completely oxidized by addition 3 hours stir with 30% and 50% $H_2O_2$. In terms of both efficiency and selectivity, the oxidative desulfurization methods that are being used today have been preceded by the above mentioned results.

With very dilute solution of $H_2O_2$ (3% and 10%), only 19% and 31% of DBT is oxidized into DBTO upon 10 minute sonication. In addition, only 80%, and 83% of DBT is oxidized into DBT upon 3 hours stir. Great importance has been given to these results. The flexible design of UAPD process with respect to a wide range of selection of residence by the control of $H_2O_2$'s concentration has been indicated in these results.

The optimal concentration of the oxidant was selected to be the 30% $H_2O_2$, as careful handling was needed in case of 50%, and no significant changes have been observed in the results that came from the 50% $H_2O_2$, as compared to the results shown with 30% $H_2O_2$.

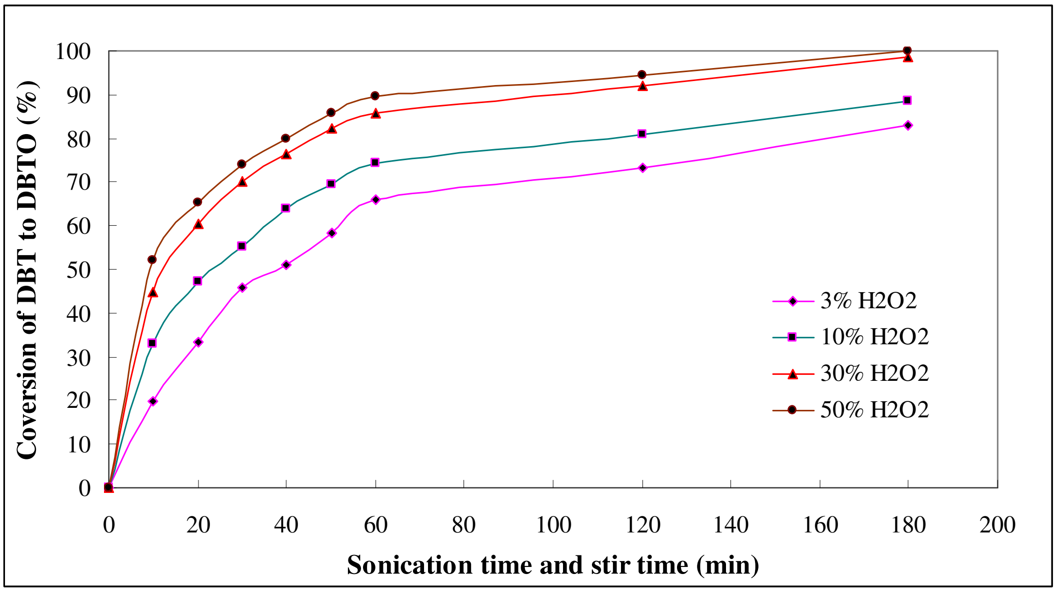


Figure 3.11 Effect of the concentration of $H_2O_2$ on conversion of DBT to DBTO

### 3.3.6 Desulfurization Efficiency on Various Model Sulfur Compounds Under Efficient Protocol Condition (Modified UAOD Process)

#### 3.3.6.1 Introduction

From Chapter 1, thiophenes (Ts), benzothiophenes (BTs) and dibenzothiophenes (DBTs) are the main kinds of OSCs in diesel fuels. Further, due to steric hindrance, alkyl-DBTs especially 4,6-DMDBT were the most refractory compounds in current HDS technology (Ma, et al. 1994; Song, et al. 2000).

In order to study the relative reactivity of OSCs under new desulfurization method that involve RTILs and UAOD conditions, with model sulfur compounds, namely T, 2MT, 2ET, BT, 2MBT, DBT and 4,6-DMDBT was carried out under efficient protocol condition (Table 3.9), also named as "modified UAOD process" that has been done with DBT model sulfur compound studies.

Table 3.9 Efficient protocol condition of UAOD on model sulfur compounds

| | |
|---|---|
| OSCs/toluene solution | 5 gram |
| 30% $H_2O_2$ | 5 gram |
| 20% TFA | 1.5 gram |
| TAOF | 0.3 gram |
| [EMIM][$EtSO_4$] | 5 gram |
| Reaction temperature | 50°C |
| UAOD time | 10 min |
| Stir time | 170 min |

### 3.3.6.2 Results and Discussion

Table 3.10 and Figure 3.12 shows the summary results of various model sulfur compounds into their corresponding sulfones under efficient protocol conditions. Results shows the oxidation activity of these model sulfur compounds decrease in the order of DBT > 4,6-DMDBT > T > 2ET > 2MT > BT > 2MBT. The desulfurization efficiency of DBT and 4,6-DMDBT reach over 96% while the desulfurization efficiency of BT and 2-MBT is barely above 40%.

By using modified desulfurization method, much better result has been achieve compare with the literature (Lu, et al. 2006), more than 96% has been approached by the conversion of DBT and 4,6-DMDBT with the help of UAOD and stir time of 170 minutes. From the literature (Lu, et al. 2006), and it has been found that after six hours of reaction time, DBT has achieved only 65% conversion. A remarkable improvement has been indicated by this reference that has increased the efficiency of the oxidation, as compare to the systems that are similar, and are not equipped with the facility of the ultrasound.

Table 3.10 Summery of model sulfur compound under optimized condition

| **Model Compound** | **Initial conc.** | **Final conc.** | **Desulfurization** |
|---|---|---|---|
| | (ppm) | (ppm) | (%) |
| T | 524 | 88 | 89.5 |
| 2MT | 500 | 79 | 84.2 |
| 2ET | 500 | 67 | 86.6 |
| BT | 500 | 298 | 40.4 |
| 2MBT | 518 | 318 | 38.6 |
| DBT | 512 | 7 | 98.6 |
| 4,6-DMDBT | 521 | 17 | 96.0 |

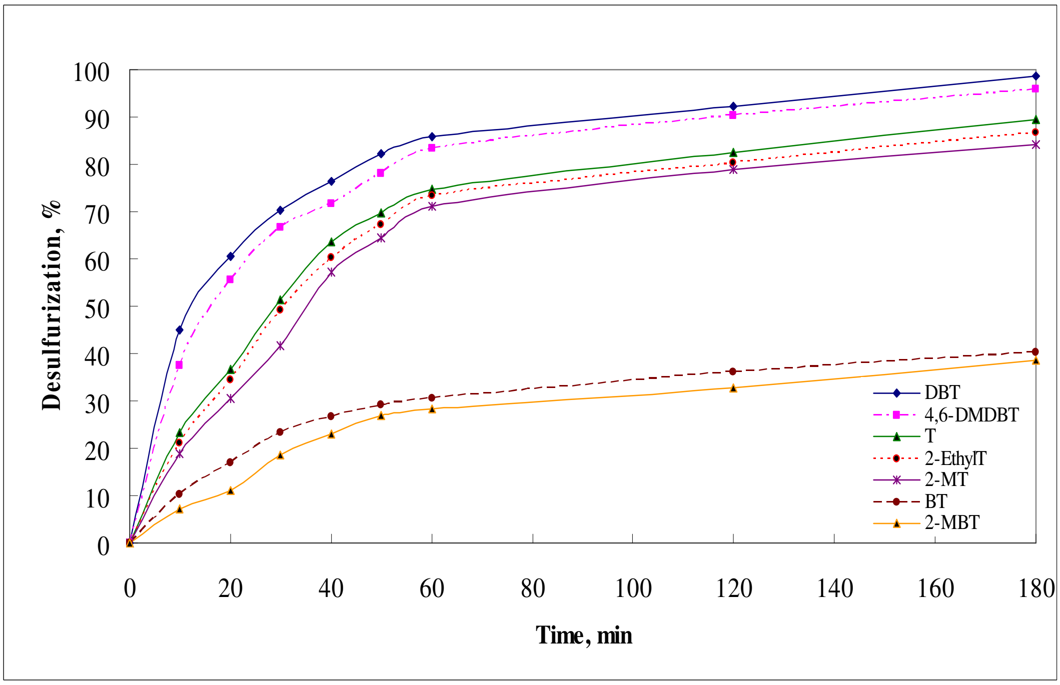


Figure 3.12 Desulfurization efficiency on various model sulfur compounds with toluene as the solvent

### 3.3.7 Desulfurization Efficiency on Various Model Sulfur Compounds by “Sulfur” free Valley Oil as the Solvent

#### 3.3.7.1 Introduction

In section 3.3.6, model compounds studies using toluene as solvent to dissolve various sulfur model compound have been discussed at length. The results show average desulfurization efficiency with thiophene is 86% and 39% for benzothiophene. However, referring to Chapter 4, under protocol condition, various types of diesel, from low to high sulfur content, can reduce to less than 15 ppm. One possible reason for this observation is that that low desulfurization on T’s and BT’s is due to competitive oxidation of toluene and sulfur compound, although oxidation of toluene forming benzaldehyde with benzoic acid as a by-product. A similar experiment has also been done by Chandalla, et al; according to him, toluene is dissolved in acetic acid and is oxidized air and using sodium bromide as the catalyst. Besides, he confirms the by-product as benzaldehyde and benzoic acid by argentometric method (Chandalla, et al., 1984).

The initial pH of Valley Oil is 6.6 which is slightly acidic, after desulfurization, the pH for “Sulfur” free Valley Oil is 5.8, this indicate that partial of acid catalyst has been penetrate into oil phase. Before dissolve model sulfur compound, the “Sulfur” free Valley Oil is neutralize to pH 6.6 with 0.1N of NaOH to remove acidity.

### 3.3.7.2 Result and Discussion

Table 3.11 and Figure 3.13 illustrate the results summary of various model sulfur compounds into their corresponding sulfones under efficient protocol conditions. By using “Sulfur free Valley Oil”, all the model sulfur compounds can achieve average 98.2% sulfur reduction. From section 3.3.6, BTs only achieve 40% conversion by using toluene as solvent. These remarkable results fairy manifest that “sulfur” free diesel can be used as solvent to dissolve model sulfur compound under modified UAOD process. Overall, three major types of organic sulfur compounds can all reduce to less than 15 ppm under modified UAOD process.

A plot of ln (Co/Ci) versus reaction time should be linear, the slope of plot represent the rate constant (k). Table 3.11 and Figure 3.13 exhibit the results of rate constant of model sulfur compounds. In the present experiment, the oxidation of model sulfur compounds were carried out under pseudo first order conditions with excess of $H_2O_2$.

Table 3.11 Summery of model sulfur compound under optimized condition with “Sulfur” free Valley Oil as solvent

| **Model Compound** | **Initial conc.** | **Final conc.** | **Desulfurization** |
|---|---|---|---|
| | (ppm) | (ppm) | (%) |
| T | 511 | 12 | 97.7 |
| 2MT | 537 | 14 | 97.4 |
| 2ET | 504 | 12 | 97.6 |
| BT | 524 | 5 | 99.4 |
| 2MBT | 504 | 9 | 98.2 |
| DBT | 530 | 6 | 98.9 |
| 4,6-DMDBT | 533 | 8 | 98.5 |

In a multifaceted substance as diesel petroleum, there subsists viable corrosion surrounded by natural sulfur mixes and other entrenched ingredients such as olefinic mixes. The outcomes obtained by judging against the pace steadiness of DBT in toluene and “sulfur free Valley Oil” were 0.021 $\text{min}^{-1}$ and 0.0228 $\text{min}^{-1}$ correspondingly. Both these cases present very alike rate steadiness. Therefore, it can be summarized that by making use of m UAOD procedure, oxidation of DBTs will not influence either natural solvent as mold oil or “sulfur free diesel.

Outcomes manifest that the oxidation movement of these replica sulfur amalgams diminish in the arrangement of: BT > 4, 6-DMDBT > DBT > 2MBT > 2ET > 2MT > T. By means of utilizing “Sulfur free Valley Oil”, all the replica sulfur mixes can pull off a standard 98.2% sulfur decrease. From section 3.3.6, BTs reach only 40% change by utilizing toluene as in the chips. However, if “sulfur” free Valley Oil is exploited as the solvent, it can accomplish a standard 99% alteration. These off-the-mark outcomes signify that “sulfur” free diesel can be made use of as solvent in place of making use of toluene. In general, three main types of natural sulfur mixes can all be diminished to not as much as 15 ppm beneath the modified UAOD procedure.

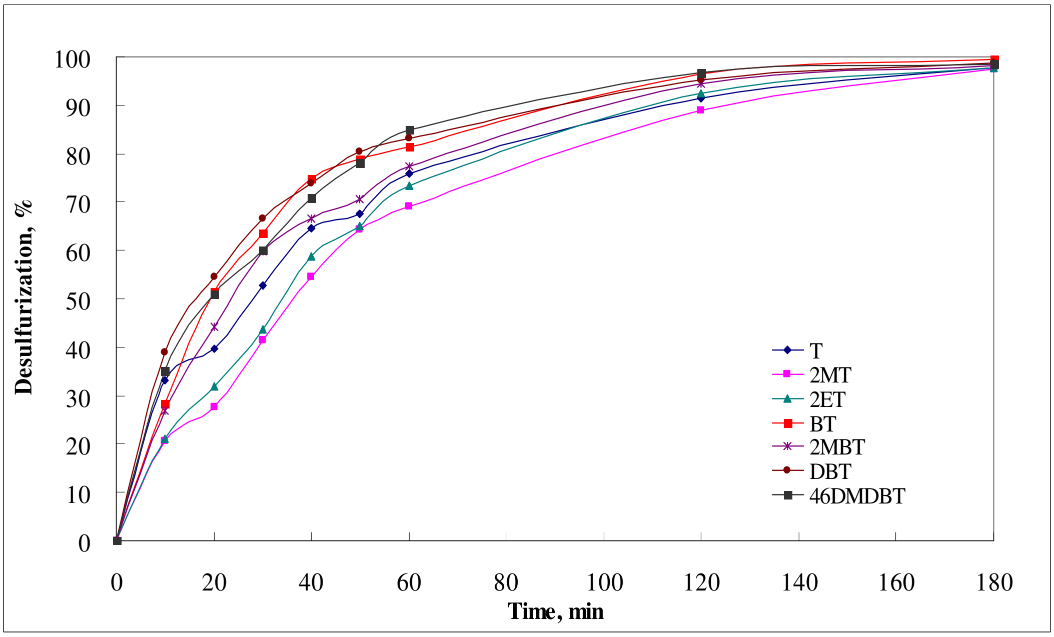


Figure 3.13 Desulfurization efficiency on various model sulfur compounds with "Sulfur" free Valley Oil as solvent

### 3.3.8 Kinetic Studies of Model Sulfur Compound

According to Te, et al. 2001; Collins, et al. 1997, a great many empirical investigations manifest that when an above-limit quantity of hydrogen peroxide is present; the oxidation of macrobiotic sulfur compounds chases the artificial first arrangement kinetics in carboxylic acid / $H_2O_2$ and polyoxometalate / $H_2O_2$ schemes. In such test conductions, adaptation of sulfur mixes was gauged keeping in focus their primary absorption ($C_o$) and after t min result ($C_i$). Conversion X is illustrated in Equation 3.1:

$$X = \frac{C_0 - C_t}{C_0} \qquad \text{(Eq. 3.1)}$$

Keeping in practice the assumption that the quantity and accumulation of the response combination stayed at a steady level; just minute quantity of fluid taster were taken out while the response of going on. If BT and DBT oxidation goes after simulated primary arrangement response kinetic, the rate steadiness and response time t can be explained with the equation given below Equation 3.2:

$$\ln(\frac{C_t}{C_0}) = -kt \qquad \text{(Eq. 3.2)}$$

For the purpose of studying the relative reactivity of organic sulfur compounds, under modified UAOD process, the oxidation of sulfur compounds, namely T, 2MT, 2ET, BT, 2MBT, DBT and 4,6-DMDBT, (each with sulfur concentration 500 ppm) was carried out under protocol condition (using “Sulfur” free diesel as solvent) which is discussed in the section 3.3.7.

Due to the fact that $H_2O_2$ was there in abundant quantity, a plot of ln ($C_i/C_o$) in apposition to t should be linear; and the value of the slope represent the rate constant, *k*. Figure 3.14 illustrates a plot of ln ($C_i/C_o$) in opposition to response time. The consequence displayed a linear relationship that corroborates the pseudo-first-order response kinetics. Table 3.12 manifests the summery of rate constant (*k*).

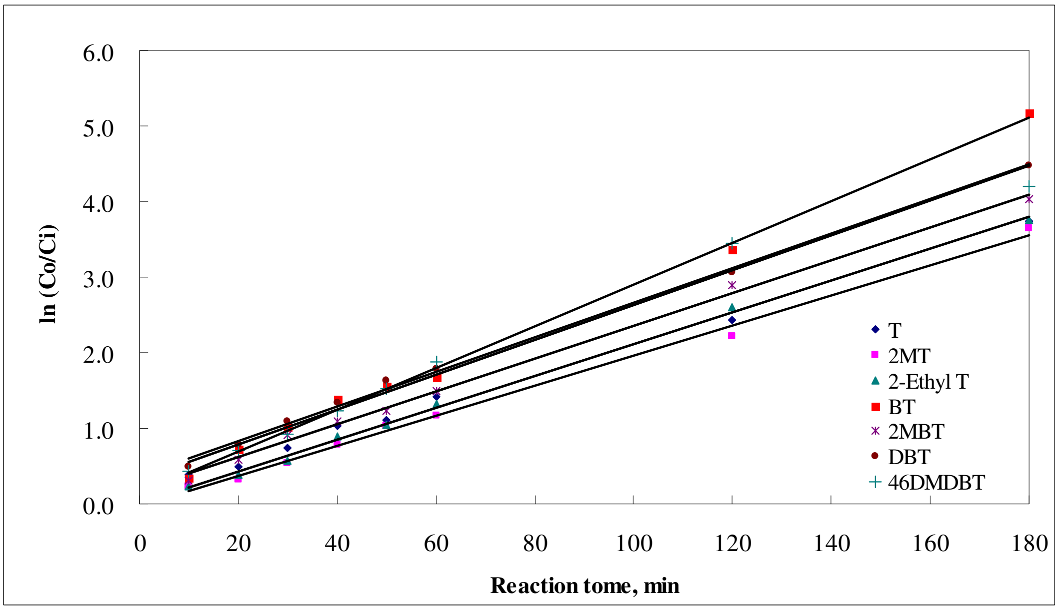


Figure 3.14 Plot of ln(Co/Ci) vs time for oxidation model sulfur compound under pseudo first order reaction

For the above illustration, it is clearly noticeable that the oxidation reactivities of these organic sulfur compounds decrease in the following order: BT > 4,6-DMDBT > DBT > 2MBT > 2ET > 2MT > T. For example, after 200 minutes of reaction process, the conversion of BT reacted over 99% while the conversion of the Ts climbed only to an average of 97%. Overall, for all the sulfur compounds, under protocol condition, it can all come to a reduced level which is below 15 ppm.

In a multifaceted substance as diesel petroleum, there subsists viable corrosion surrounded by natural sulfur mixes and other entrenched ingredients such as olefinic mixes. The outcomes obtained by judging against the pace steadiness of DBT in toluene and “sulfur free Valley Oil” were 0.021 $\text{min}^{-1}$ and 0.0228 $\text{min}^{-1}$ correspondingly. Both these cases present very alike rate steadiness. Therefore, it can be summarized that by making use of m UAOD procedure, oxidation of DBTs will not influence either natural solvent as mold oil or “sulfur free diesel.

Outcomes manifest that the oxidation movement of these replica sulfur amalgams diminish in the arrangement of: BT > 4, 6-DMDBT > DBT > 2MBT > 2ET > 2MT > T. By means of utilizing “Sulfur free Valley Oil”, all the replica sulfur mixes can pull off a standard 98.2% sulfur decrease. From section 3.3.6, BTs reach only 40% change by utilizing toluene as in the chips. However, if “sulfur” free Valley Oil is exploited as the solvent, it can accomplish a standard 99% alteration. These off-the-mark outcomes signify that “sulfur” free diesel can be made use of as solvent in place of making use of toluene. In general, three main types of natural sulfur mixes can all be diminished to not as much as 15 ppm beneath the modified UAOD procedure.

Table 3.12 illustrates the velocity steadiness with inaccuracy with seven dissimilar type of sulfur representation mix. Because the oxidant was over the required quantity, a scheme of ln (Ci/Co) in opposition to response time outcomes a sequential association that endorses the artificial primary arrangement response kinetics.

Table 3.12 Summery of model sulfur compound under optimized condition with "Sulfur" free Valley Oil as solvent

| **Model Sulfur Compound** | **Rate Constant ($min^{-1}$)** | **$R^2$** |
|---|---|---|
| T | 0.0196 +/- 0.0003 | 0.9972 |
| 2MT | 0.0199 +/- 0.0006 | 0.9954 |
| 2ET | 0.0210 +/- 0.0003 | 0.9984 |
| BT | 0.0276 +/- 0.0006 | 0.9971 |
| 2MBT | 0.0218 +/- 0.0005 | 0.9970 |
| DBT | 0.0228 +/- 0.0003 | 0.9970 |
| 46DMDBT | 0.023 +/- 0.001 | 0.9792 |

## 3.4 Results and Discussion (Modification Desulfurization Method with Solid Catalyst)

### 3.4.1 Introduction

For current UAOD process, one of the most promising non-HDS processes, is very efficient in oxidizing thioethers, mercaptans and BTs, but, thiophene and its derivatives were found difficult be oxidized from previous literature. In this section, selective oxidation of 2MT, 3MT and 2,5-DMT has been studied under UAOD and stir condition. The desulfurization process was carried under Ti-B with $H_2O_2$ at mild condition. 2MT, 3MT and 2,5-DMT can be oxidized over Ti-B in toluene solvent.

### 3.4.2 Experimental Procedure

2MT, 3MT and 2,5-DMT sulfur model compound was dissolved into toluene to make a stock solution with given sulfur content approximately 500 ppm. The oxidation and sulfur model compounds are described as follows. An equal weight ratio of 5 gram of hydrogen peroxide ($H_2O_2$), and model sulfur compound were prepared and mixed for 5 minutes. 0.3 gram TOAF was added into the mixture. The mixture was first heated to 70$^{o}$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.

Another set of experiments were conducted with mechanical stirring and the results are compared and discussed.

### 3.4.3 Results and Discussion

#### 3.4.3.1 Effect of UAOD

According to the Table 3.13, the results shows desulfurization efficiency of model sulfur compounds with two different types of catalyst under 10 minute UAOD. From the results, it has been shown that desulfurization efficiency by using transition metal catalyst (TMC) was less than 5% after the utilization of only UAOD in the process. With Solid catalyst (Ti-B), more than 25% of desulfurization efficiency can be achieved.

Table 3.13 Summery of various model sulfur compound under optimized condition

| ***2MT*** | **Before UAOD** | **After UAOD** | **Desulfurization** |
|---|---|---|---|
| **Catalyst** | (ppm) | (ppm) | (%) |
| **Liquid (TMC)** | 503 | 478 | 4.9 |
| **Solid (Ti-B)** | 503 | 375 | 25.4 |

| ***3MT*** | **Before UAOD** | **After UAOD** | **Desulfurization** |
|---|---|---|---|
| **Catalyst** | (ppm) | (ppm) | (%) |
| **Liquid (TMC)** | 543 | 530 | 2.4 |
| **Solid (Ti-B)** | 543 | 405 | 25.4 |

| ***2,5-DMT*** | **Before UAOD** | **After UAOD** | **Desulfurization** |
|---|---|---|---|
| **Catalyst** | (ppm) | (ppm) | (%) |
| **Liquid (TMC)** | 503 | 483 | 3.9 |
| **Solid (Ti-B)** | 503 | 354 | 29.4 |

### 3.4.3.2 Effect of Stir

According to the Table 3.14, the results shows desulfurization efficiency of model sulfur compounds under stir condition for three hours. From the results, it has been shown that desulfurization efficiency for all thiophene model sulfur compounds can achieve more than 90%. In the case of sulfoxidation of various thiophene, which can penetrate the pore of Ti-B, the activity of this catalyst is higher than the activity of Ti-mesoporous material, Ti-HMS.

Table 3.14 Desulfurization efficiency based on stir method

| **Sulfur Compound** | **Initial conc. (ppm)** | **Final conc. (ppm)** | **Desulfurization (%)** |
|---|---|---|---|
| **2MT** | 503 | 45 | 91.1 |
| **3MT** | 543 | 52 | 90.4 |
| **2,5-DMT** | 512 | 33 | 93.6 |

### 3.5 Summary

In the biphasic reaction system, the reaction is facilitated between organic and aqueous phase by a barrier that is bridged by the PTA during the reaction. However, it is not sufficient to get an organic phase with the simple transfer of $H_2O_2$, in order to initiate the reaction. High selectivity and conversion are the results of oxidation process that occurs selectively during the reaction. In this regard, it has been observed that $H_2O_2$ is found to be reacting with the catalyst precursor, that is, pre-acid, such as, acetic acid and tri-fluoro acetic acid (TFA). Various studies have been carried out on the various capabilities and characteristics of TFA. In this regard, it has been observed that better catalytic reactivity can be given by the TFA. Acetic acid is found to be providing lower reactivity, as compared to the former one during the different reactions. However, sometimes, TFA may give extreme results, such as possible explosion, which might be a deteriorating effect in the reaction. Therefore, it has been suggested to change the usage of catalyst with safe reaction conditions can be given by the combination of acetic acid and TFA, which will give better reactivity and results during the reaction with 20% TFA.

In another study, results showed that corrosive by-product is not formed with the utilization of sulfate anion based ionic liquid during the reaction. However, [BMIM][$PF_6$] ionic liquid has shown contrary results and was able to form corrosive by-product, as compared to the previously mentioned compound. It was also observed during different reactions that the sonication tip would be corroded by some of the corrosive by-products, such as, HF, etc. Although, during the reaction, [BMIM][$PF_6$] were degraded into white solid as by product named as [BMIM]F.$H_2O$. It has been observed that [BMIM][$PF_6$] ionic liquid is found to be expensive than other ionic liquids. Therefore, the cheaper and alternative ionic liquid source came out to be the sulfate anion based ionic liquid, as compared to the [BMIM][$PF_6$] ionic liquid. Additionally, similar and even better desulfurization efficiency was achieved by the cheaper one, that is, the sulfate anion based ionic liquid, as compared to its counterpart, $PF_6$ anion based ionic liquid. Five different sulfate anion based ionic liquid has been used for testing the desulfurization efficiency with DBT model sulfur compound. From the results, [EMIM][$EtSO_4$] ionic liquid gives the best result with 98.6% sulfur reduction, therefore, it [EMIM][$EtSO_4$] ionic liquid has been selected as the ionic liquid source for entire modified UAOD process.

The production of fine emulsions is one of the capabilities of the ultrasound, which it forms between some of the liquid-liquid phases, thereby providing the reaction with increased interfacial area. The structure of the catalyst might also be modified by it. In addition, more active-intermediates can also be created by it. In the result, short time and mild conditions are provided to the reaction. Different studies have shown results that have indicated that low partition rate is found in the ionic liquid. Therefore, in order to carry out the removal of oxidized sulfur compounds, stirring and sonication are required by the ionic liquid, which can allow the partition or extraction of the above mentioned compounds from the organic phase.

With modified UAOD process, various model sulfur compounds have shown significant results with toluene as the solvent. Thiophenes (T's) can achieve average 87% and dibenzothiophenes (DBT's) can achieve 97% as the desulfurization efficiency. Model sulfur compounds have shown considerable results in these experiments during different studies related to this subject. However, Benzothiophenes (BT's) is the only model sulfur compound that has showed exceptional and contrary results during the reaction. This is because due to competitive oxidation and selectivity between toluene and BT's, under modified UAOD process. Therefore, instead using toluene as the solvent, "Sulfur" free diesel has been used as solvent to dissolve the model sulfur compound in order to testify the desulfurization efficiency under the new process.

By using "Sulfur" free diesel as the solvent for model sulfur compound study, under modified UAOD process. In this regards, it has been observed that a remarkable result of average 98.8% sulfur reduction for all sulfur model compounds. Another advantage by using "sulfur" free diesel as solvent, is because it can representative the real reaction environment when modified UAOD process is apply on real diesel sample. Although, from kinetic study, plot of ln (Ci/Co) versus reaction time gives a linear relationship that confirmed the pseudo first order reaction. The kinetic constant ranking are shown as follow: BT > 4,6-DMDBT > DBT > 2MBT > 2ET > 2MT > T.

With alternative desulfurization method, titanium ions in the framework positions of different zeolites structures with larger pore size (Ti-B) has been used as solid catalyst. According to the previous work (Wan, et al. 2005), under 10 minutes UAOD process with TMC (transition metal catalyst), it only shows the desulfurization efficiency 4% for thiophene’s. However, by using solid catalyst, the desulfurization efficiency for thiophene’s increased to average 26%. This is because it still require more time to oxidize the sulfur compound, therefore, stir method has been applied instead ultrasound. From the results, desulfurization efficiency for all the thiophene’s can achieve to average 94%.

# CHAPTER 4

# MODIFIED DESULFURIZATION METHOD ON DIESEL FUEL

## 4.1 Introduction

Different studies have shown that alky-benzothiophenes (BTs) and alkyl-dibenzothiophenes (DBTs) are mostly found as the sulfur compounds in diesel fuels. It has been observed from the studies of chapter 1 that the DBTs having alkyl substituents at 4- and/or 6-position are the major sulfur compounds that are found to be remaining in diesel fuels containing less than 0.1% sulfur content.

Mei, et al. 2003 and Wan, et al. 2005 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 ULSD. 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 4.1 shows the refractory organic sulfur compounds that have been left under current UAOD process that has been used since 2003 with MGO diesel sample.

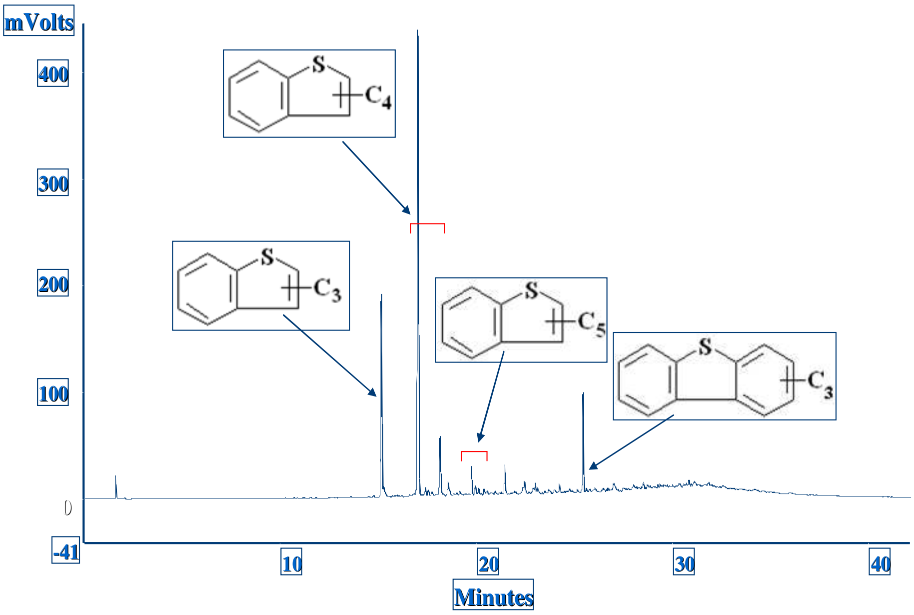


Figure 4.1 OSCs remaining after current UAOD process (Wan, et al. 2003)

Even though, the modified desulfurization method that development from Chapter 3 is capable of oxidizing model sulfur compounds such as Ts, BTs and DBTs into sulfones with high desulfurization efficiency. The evaluation of the effectiveness of this new process is essential, which is found on commercial diesel fuels.

In this study, modified desulfurization method on commercial diesel fuels was developed to consist of following steps: Stirring, UAOD and solvent extraction. The desulfurization efficiency was also enhanced by using RTILs, PTA and organic acid catalyst

Modified UAOD process consists of two steps. One of the two steps is the oxidation process of organic sulfur compounds that is done selectively, whereas, in the second step, the oxidized sulfur compounds are separated from the diesel fuels.

Distillation, solid adsorption, and solvent extraction are the available methods that can be utilized for the various separation methods during the new process of desulfurization. Solvent extraction includes organic solvent extraction and RTIL extraction during the UAOD and stir condition.

In this chapter, a modified UAOD process, operating at mild condition for a given time was executed. Marine logistic fuels and transportation fuels are some of the types of commercial diesel fuels, which are evaluated regarding their effect from the new process by the evaluation of above mentioned diesel fuels, such as, JP-5, Treated Valley Oil, F-76 and Valley Oil respectively.

With the modified UAOD process, remarkably, more than 99.9% desulfurization efficiency is achieved for both low and high sulfur content diesel sample. Also, it can be used for fuel cell application, because it requires ppb level of sulfur to avoid poisoning the fuel cell reactor.

### 4.2 Materials

Three diesel fuels were used as the feedstock in this study. (1) Diesel fuels with sulfur content of 8,100 ppm (Valley Oil) were received from Golden Eagle Oil Refinery, INC. (2) Marine logistic fuels with sulfur content of 740 ppm (JP-5) were received from Long Beach, Navy. (3) Diesel fuels with sulfur content of 560 ppm (Treated Valley Oil) were produce by using Wan, et al method.

From previous UAOD process and studies related to this process, the sulfur content was found to be reducing from 8,100 ppm to 550 ppm only with the utilization of Treated Valley Oil. In order to reduce higher amount of sulfur content, more catalyst, and phase transfer agent will be required, which will of course, increased the cost of the reaction. In addition, more sonication time will also be required for lowering the sulfur content during the process, which will once again be responsible for the increment in the cost of the process. Therefore, the current UAOD process was not able to deal with the remaining sulfur content, which as the refractory compounds during the process. In the result, in order to study one of the feedstock, this Treated Valley Oil has been selected, as it will be more economical and will be also be able to enhance the efficiency of desulphurization during the reaction.

Tetraoctylammonium fluoride used as phase transfer agent (PTA) was synthesized from (Dermeik, et al. 1989). Acetic acid and tri-fluoro acetic acid (TFA) with glacial grade used as catalyst were obtained from Aldrich Chemical. 30% hydrogen peroxide ($H_2O_2$) used as oxidant were obtained from VWR Inc. 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][$PF_6$], 1-butyl-3-methylimidazolium octyl sulfate [BMIM][$OcSO_4$] and 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][$EtSO_4$] as ionic liquid that has been used for the extraction were obtained Aldrich Chemical.

## 4.3 Experimental Procedure

### 4.3.1 Sample Preparation (Treated Valley Oil)

In UAOD process, 20 gram Valley Oil is mixed with 25 gram hydrogen peroxide (30%), 0.2 gram transition metal catalyst (TMC) and 1.37 ml phase transfer agent (PTA). Sonication is applied to the mixture for 20 minutes so as to enhance oxidation. Then, oil phase is separated and passed through a column of alumina to remove sulfones by solid adsorption.

### 4.3.2 Desulfurization of Commercial Diesel Fuel

The oxidation and extraction procedure of commercial diesel fuel is described as follows. An equal weight ratio of 5 gram of hydrogen peroxide ($H_2O_2$), ionic liquid and diesel fuel sample were prepared. $H_2O_2$ and 1.5 gram of 20% TFA 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 diesel fuel sample that mix with 0.3 gram of TOAF. Solution B was added to solution A. Finally, ionic liquid was slowly added into the mixture. The mixture was first heated to $70^oC$ 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 $70^oC$ water bath for certain time, then the phase was separated by centrifuge and the top organic phase was used for quantitative and qualitative analysis.

## 4.4 Experimental Procedure Modification

### 4.4.1 Modified UAOD Process

More time for the process of oxidation and extraction of ionic liquid was allowed by the introduction of an increment in the stir time, which increased from three hours to six hours. In addition, the high sulfur content of Valley Oil was used, as described in the above mentioned method. However, the optimization methods can be followed by the low sulfur content diesel fuel, that is, JP-5 and Treated Valley Oil, as earlier mentioned in chapter3, which took three hours for the stir time. In this regard, ten minutes of UAOD was able to start the different methods of desulfurization, as given in chapter three. In this case, the stir time was followed after the above mentioned ten minutes of UAOD during the reaction. However, the reaction method was inverted with the introduction of new method of desulfurization, which required the stir to apply first during the reaction, and followed by 10 minutes of UAOD. This introduction of the new method was done, in order to achieve and compare results for the better and effective efficiency of desulfurization during the reaction.

### 4.4.2 Addition of New Phase Transfer Agent (PTA)

The desulfurization can be increased and enhanced by acetonitrile ($CH_3CN$), which can act as the second type of PTA during the process. Mei, et al has indicated different characteristics of acetone in this regard. It has been observed by the above mentioned experts that high polarity is found to be in acetone, as compared to its counterparts, that are, saturated hydrocarbons and benzenes. These counterparts tend to be making a partition into polar solvents. However, acetone is able to remove alkylnaphthalenes, as well as, performing the process of extracting oxidized organic sulfur compounds that remain during the oxidation process. As the removal of alkylnaphthalenes is not required, therefore, only a small amount of acetonitrile is used during the reaction, in order to avoid this removal. Therefore, only 0.3 gram of acetonitrile was used and added in 5 grams of diesel fuel sample in order to minimize this effect during the reaction.

## 4.5 Analytical Methods

**Total Sulfur Analyzer:** Total sulfur concentration of unknown sample can be quantitatively determined by Sulfur-in-Oil Analyzer (SLFA-20) that is manufactured by Horiba Inc. The analyzer complies with ASTM D4294 and ISO 8754. ASTM D4294 is described as follows; an unknown concentration liquid sample is placed in the beam which emitted from a non-dispersive X-ray flurescence (NDXRF). The resultant excited characteristic radiation is measured and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulfur concentration in parts per million (ppm). The sulfur analyzer can detect range of 0 to 4 wt% of total sulfur, with a lower detection limit of 20 ppm.

**Identification and Quantification of OSCs from Diesel Fuel:** HP-6890 Series Gas Chromatograph (GC) equipped with a Sulfur Chemiluminescence Detector (SCD)-Sievers model 355B. The chromatograph was fitted with a 60-m

DB-5 fused-silica column that was directly installed into the discharge tube. The column temperature was first maintained at 80°C for 1 minute, the column temperature was then raised to 290°C at the rate of 6°C/minute and then maintained at 290°C for 2 minutes to let the remaining hydrocarbon to burn out. For carrier gas, ultra high purity grade helium and ultra high purity grade hydrogen were used at a constant pressure of 50 psi. The injected sample volume was 1μL. With SCD, the operation conditions were as follows: burner temperature set at 800°C, 5.8 ml/min of air, 100 ml/min of hydrogen. With ozone generator: 60 ml/min at 60 psig and 25°C.

GC-SCD can identify a series of sulfur components, including, thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and other alky-substituted organic sulfur that exist in various gasoline or diesel sample. SCD detector can detect range of 0.1 to 1 wt% of sulfur.

## 4.6 Results and Discussion

### 4.6.1 Characterization of Diesel Fuels

Some common model sulfur compounds have been identified, before the qualitative identification process of organic sulfur compounds, which are found in the Valley Oil. In addition, retention time for each of these already-identified common model sulfur compounds has also been recognized during the experiment. This identification process is very important, as the various types of organic sulfur compounds that are found in the diesel fuel sample can be identified very easily, if the retention time of model sulfur compound will be already known during the experiment. Therefore, the identification step of common model sulfur compounds helped in recognizing the later ones, in order to achieve better, effective, and fast results.

Fig.4.2 shows GC-SCD chromatogram of various model sulfur markers with BT, 2-MBT, 3,5-DMBT, DBT, 4-MDBT and 4,6-DMDBT. From the chromatograph, BT appear at 6.3 minute, 2-MBT appear at 7.5 min, 3,5-DMBT appear at 9.6 minute, DBT appear at 15.8 min, 4-MDBT appear at 17.6 min, and 4,6-DMDBT appear at 19.2 minute.

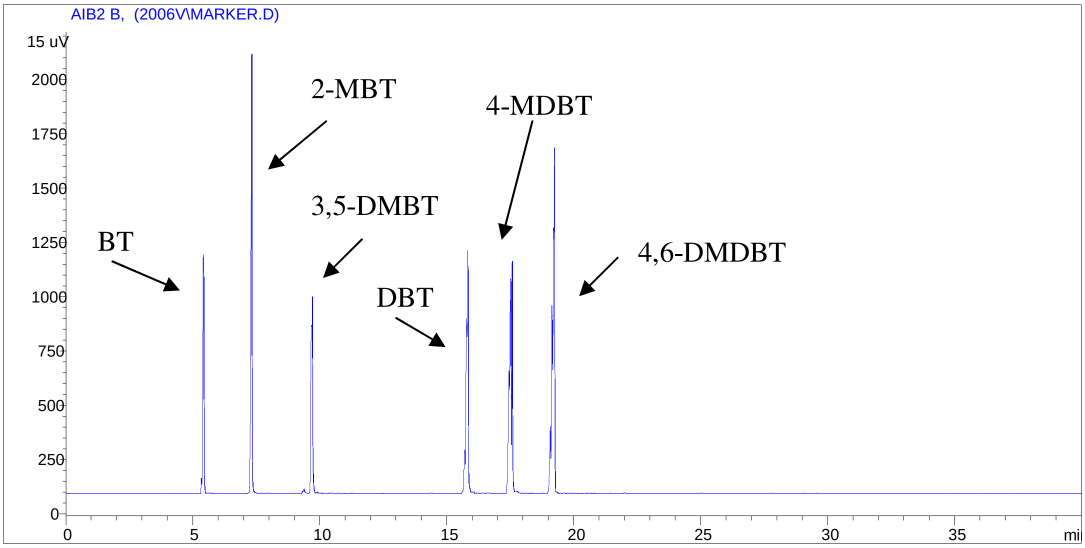


Figure 4.2 GC-SCD chromatogram of various model sulfur marker

The different basic compositions of different diesel fuels have been differentiated by showing of GC-SCD chromatogram of Valley Oil, Treated Valley Oil, and JP-5 in Figure 4.3.

According to various studies, it has been estimated that approximately 5% thiophene (Ts), 45% benzothiophene (BTs) and 50% dibenzothiophene (DBTs) are contained in the Valley Oil. It has also been estimated by a number of experts that approximately, 40% benzothiophene (BTs) and 60% dibenzothiophene (DBTs) are contained in the Treated Valley Oil. However, almost 95% of BTs and 5% of DBTs have been estimated in the JP-5.

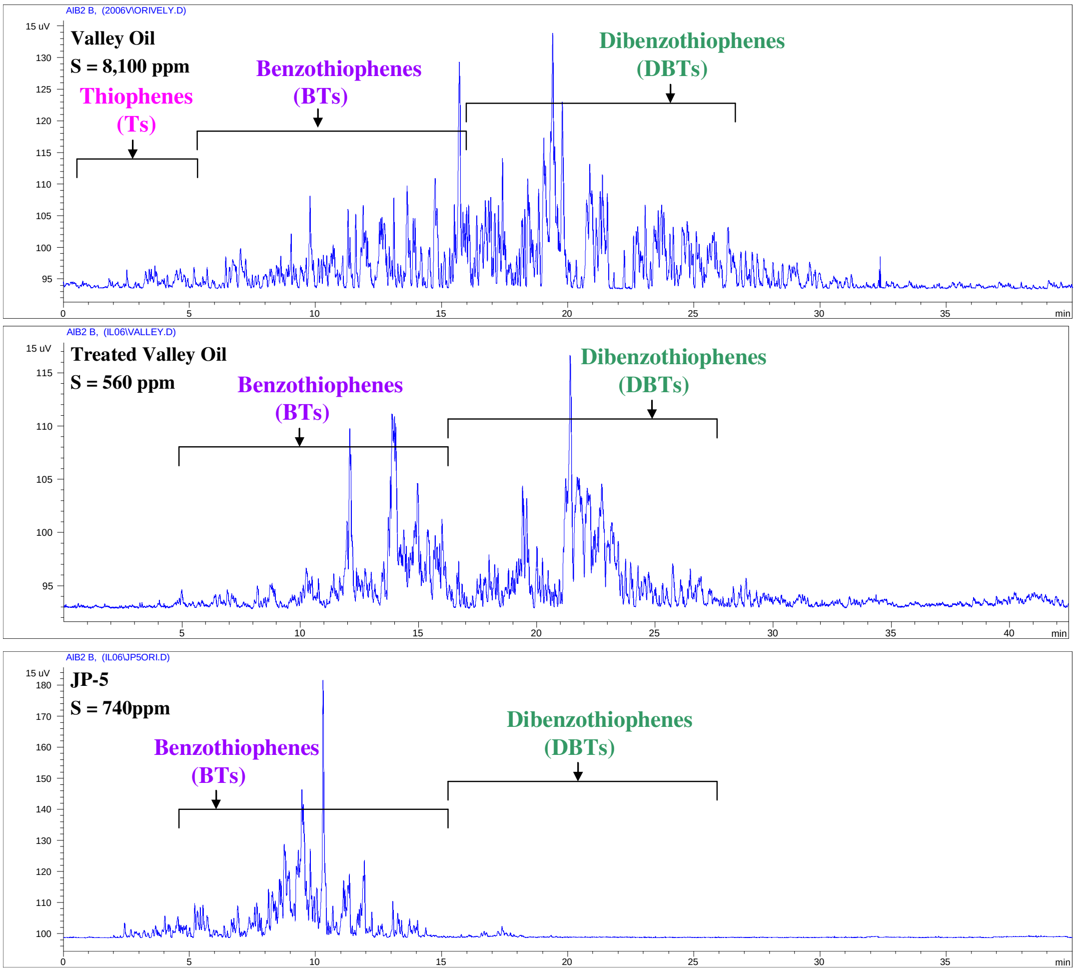


Fig 4.3 Composition and distribution of OSCs in different diesel sample with GC-SCD chromatogram

### 4.6.2 Modified UAOD process on Low-Sulfur Diesel (Treated Valley Oil: 560 ppm)

With different desulfurization methods shown in Table 4.1, Different studies and experiments have shown results that better and effective results of increment in the efficiency of desulfurization by more than 10% has been observed by the introduction of new alternative method, which requires the stirring method to be done first, and then the UAOD to follow it. On the other hand, better ability regarding the extraction has been showed by the [EMIM][EtSO$_4$], as shown earlier in the experiments. However, model sulfur compounds have been joined by real commercial diesel fuel that have also been extracted by [EMIM][EtSO$_4$] during this new alternative method of desulfurization. This enables us to give it more importance, and therefore, great significance has been received by the [EMIM][EtSO$_4$] in this regard.

Table 4.1 Effect of desulfurization efficiency based on combination of mixing methods

*UAOD 10 minutes & Stirred 3 hours*

| **Ionic liquid** | **UAOD** | **Desulfurization** | **Stir 3 hours** | **Desulfurization** |
|---|---|---|---|---|
| | (ppm) | (%) | (ppm) | (%) |
| [BMIM][$PF_6$] | 350 | 37.5 | 237 | 57.7 |
| [EMIM][$EtSO_4$] | 312 | 44.3 | 204 | 63.6 |
| [BMIM][$OcSO_4$] | 344 | 38.6 | 241 | 57.0 |

*Stirred 3 hours and UAOD 10 minutes*

| **Ionic liquid** | **Stir 3 hours** | **Desulfurization** | **UAOD** | **Desulfurization** |
|---|---|---|---|---|
| | (ppm) | (%) | (ppm) | (%) |
| [BMIM][$PF_6$] | 232 | 58.6 | 178 | 68.2 |
| [EMIM][$EtSO_4$] | 188 | 66.4 | 141 | 74.8 |
| [BMIM][$OcSO_4$] | 219 | 60.9 | 164 | 70.7 |

Table 4.2 shows the effect of addition of acetonitrile on the efficiency of desulfurization. In this regard, we can observe that another remarkable increase of 10% was made by the efficiency of desulfurization. This occurs by the addition of second type of PTA, which allowed the above mentioned significant amplification in the desulfurization efficiency. Therefore, we can say that the reaction process will enhance, and can be enhanced by the utilization of acetone and TOAF in a combined way. In this regard, it was also observed that the enhancement will required only small amount of usage to be made during the reaction process. Table 4.2 shows the proper combination usage and the effect on efficiency of the desulfurization in a very

proper manner, in order to understand the changes that arise by the addition of acetone during the process of reaction.

Table 4.2 Effect of adding acetonitrile on desulfurization efficiency

| **Ionic liquid** | **Stir 3 hours** (ppm) | **Desulfurization** (%) | **UAOD** (ppm) | **Desulfurization** (%) |
|---|---|---|---|---|
| ***Without $CH_3CN$*** | | | | |
| [EMIM][EtSO$_4$] | 188 | 66.4 | 141 | 74.8 |
| ***With $CH_3CN$*** | | | | |
| [EMIM][EtSO$_4$] | 131 | 76.6 | 84 | 85.0 |

The total sulfur concentration of the Treated Valley was 560 ppm that analyzed by total sulfur analyzer. As shown in Figure 4.4, based on the [EMIM][EtSO$_4$] ionic liquid and modified UAOD procee that describe before. Most of organic sulfur compounds in the Treated Valley Oil were completely oxidized into corresponding sulfones under efficient protocol condition.

The oxidation process of alkyl-BTs and alkyl-DBTs has been clearly shown in the chromatogram. In the result, corresponding alkyl-BTOs and alkyl DBTs have been the resulted oxidized form of the above mentioned respectively. In this regard, the results showed that the shifting of the peaks was done from left to right, which occurred after the process of desulfurization.

[EMIM][EtSO$_4$] ionic liquid and hydrogen peroxide were contained in the aqueous phase that was extracted from 85% of the total organic sulfur compounds. This resulted in the reduction that was observed to be reduced from 560 ppm to 84 ppm, which is a huge amount of reduction. A number of reasons have been given and observed by the previous literature. However, some of them are possible for the incapability of the remaining oxidized sulfur, which was not able to extract into the phase of ionic liquid. In this regard, one of the reasons is that longer time is required by this oxidized sulfur, in order to allow their partitioning into the phase of ionic liquid.

Therefore, the findings have shown that it is possible to extract 100% of this oxidized sulfur into their ionic phase. However, it will increase the cost and will not be economical anymore, as the stir time will have to be increase to for example, twenty hours, which will be enough for the partitioning of oxidized sulfur into the ionic phase theoretically. Therefore, in order to keep the cost economical and in the budget, the sample fuel is used for the process of extraction with the organic solvent. In this case, one of the examples of organic solvent is acetonitrile, which allows the removal of the remaining of oxidized sulfur that was not extracted into the ionic liquid phase.

In this regard, 1:5 came out to be the ratio of the extraction weight of the acetonitrile, which was taken as the diesel fuel sample, as mentioned above earlier. In the result, a diesel fuel is produced that is found to be having sulfur content of 0 ppm. This production occurs after the extraction of the remaining oxidized sulfur that was done by acetonitrile, which is followed by the partitioning of sulfones into solvent that is found in oxidized diesel fuels. The results have shown that no sulfur peak cannot be detected during the entire process, as shown in the chromatogram. Therefore, 100% will be the overall efficiency of the desulfurization.

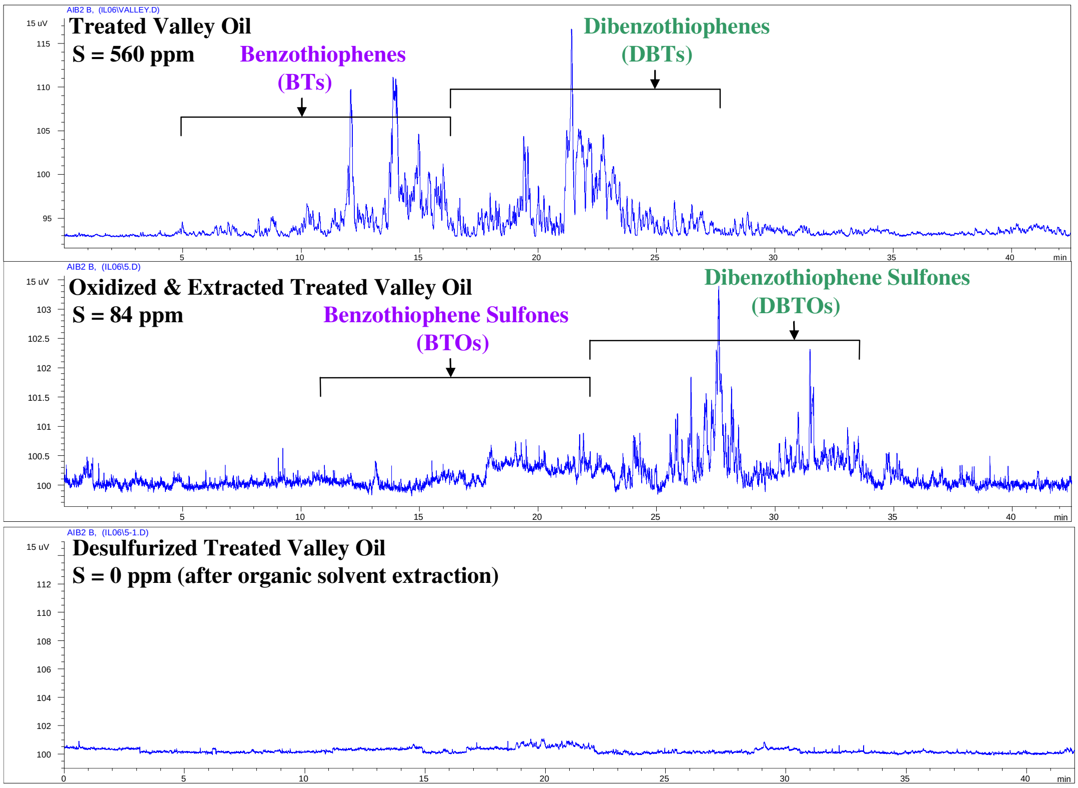


Figure 4.4 GC-SCD chromatograms of Treated Valley Oil under modification UAOD process based in the [EMIM][EtSO$_4$] ionic liquid

### 4.6.3 Modified UAOD Process on Low-Sulfur Diesel Fuel (JP-5: 740 ppm)

Nowadays, military uses JP-5 as fuels for aircrafts, which are also counted among the Jet fuels. In addition, the most widespread aviation fuel considered by the Navy is the JP-5. Hydrocarbons and non-hydrocarbon components are found to be in a complex mixture in this kerosene-type fuel. Hundreds of different major hydrocarbon components and their anti-counterparts are found to be in trace concentrations, as well as, in the additives. However, the refinery process, specification of the product, and the crude source are found to be responsible for the actual composition of these jet fuels.

Sulfur analyzer shown that 740 ppm is the total sulfur content that is found in the JP-5. In this regard, 9.8 is the estimated retention time for dimethyl-BTs from the sulfur market, even though, BTs are the major types of organic sulfur compounds. Methyl-BT is found to be contained in 50% of BT, whereas, dimethyl-BTs or tri-methyl-BTs are contained in the remaining percentage of BT, as observed in the GC-SCD chromatogram.

A new method of modification is being used, in order to desulfurize JP-5 during the process. The development of the Treated Valley Oil has been sourced for this new method that is predicted to achieve effective and better results.

Figure 4.5 has been illustrated, in order to represent the change that has been done in JP-5 by oxidation and extraction process of organic sulfur compounds by ionic liquid, as well the solvent extraction. Oxidation process and the forming of corresponding BTs have been shown in the Figure 4.5. 83.8% (740 ppm reduce to 120 ppm) oxidized sulfur has been extracted into ionic liquid, and remaining BTOs will remove by solvent extraction by acetonitrile. As the result, the desulfurized JP-5 has been produced, having 0 ppm of total sulfur concentration. The overall desulfurization efficiency is 100%.

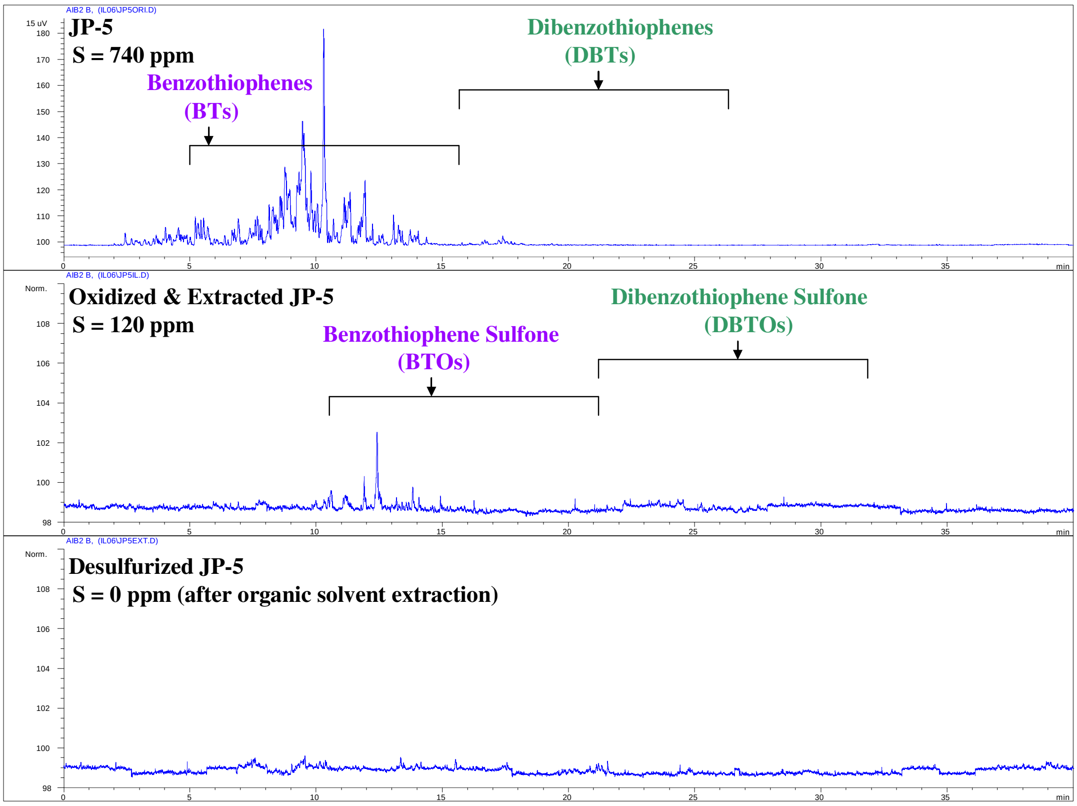


Figure 4.5 GC-SCD chromatograms of JP-5 under modification UAOD process based in the [EMIM][EtSO$_4$] ionic liquid

### 4.6.4 Modified UAOD Process on Medium-Sulfur Diesel Fuel (F-76: 4,220 ppm)

Mainly, combat, as well as, applications related to undersea has considered the research of fuel cells. In addition, the utilization of NATO F-76 diesel fuel by the fuel cell commercial systems is being studied for proving it, in order to implement the same in the future ships by a ship service fuel cell system, which has been referred as SSFC by the experts. One of the kinds of MIL-SPEC distillate fuel is the F-76 diesel fuel, which has been preferred for many purposes, such as, boilers, turbines, shipboard, etc. A number of characteristics have been observed in the F-76, such as, quality control, tight arrangement and specification, and a number of other features. In this regard, naval facilities and oilers are usually considered for the sourcing of this fuel. Moreover, 60°C has been noted as its minimum flash point.

The total sulfur content of F-76 is 4,220 ppm. In this regard, the original F-76 has been considered for the distribution of OSCs, as been shown by GC-SCD chromatogram in the Figure 4.6. Although the BTs and DBTs constitute of major portion of F-76, high and significant concentration has been noted in the DBTs, as compared with the BTs. However, trimethyl-BTs become the dominant species among BTs.

Moreover, Figure 4.6 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%.

Again, complete removal of the OSCs has been indicated in Figure 4.6, which has previously been studied in the paper. In this respect, previous works of the experts have also been related accordingly (Mei et al, 2003). It has been observed that UAOD process of F-76 results in four remaining sulfur compounds. In the result, $C_3$-BTs, $C_4$-BTs, $C_5$-BTs and $C_3$-DBTs groups have been formed for the categorization of sulfur compounds in the process.

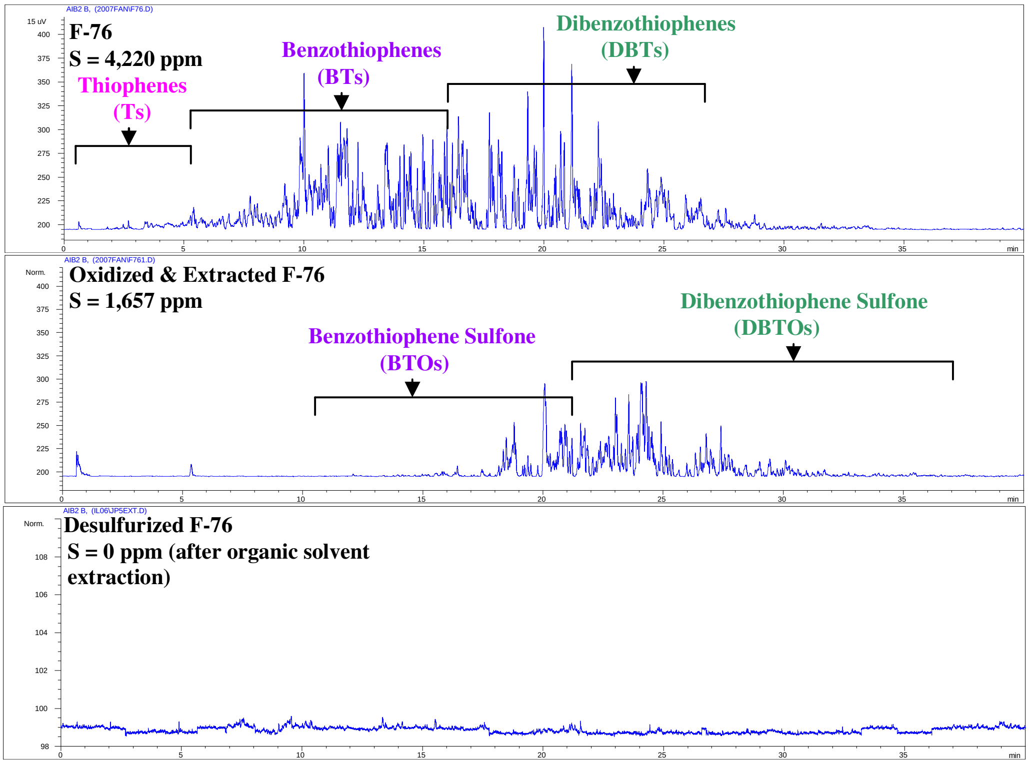


Figure 4.6 GC-SCD chromatograms of F-76 under modification UAOD process based in the [EMIM][EtSO$_4$] ionic liquid

### 4.6.5 Modified UAOD Process on High-Sulfur Diesel Fuel (Valley Oil: 8,100 ppm)

The total sulfur concentration pf Valley Oil is 8,100 ppm. Valley Oil contains three types of organic sulfur compounds with in original high sulfur diesel that have different aromatic skeletons in it. Alkyl-BTs are the first type that has alkyl carbon atom from the range of 0 to 5. Alkyl-DBTs are the second type that is having alkyl carbon from the range of 0 to 6. In this regard, Ts have been found in only small portion.

Table 4.3 has been given below for the presentation of the ability of ionic liquid for the removal of sulfones. In this regard, different and various ionic liquids were examined and experimented during the process. The results showed that the highest extraction partition ability was given by the [EMIM][EtSO$_4$] that removed the sulfones in the stir time of six hours. During this course, the removal of more than 50% of organic sulfur was done, which is a very remarkable result. The findings showed that UAOD and PTA were also responsible for the enhancement of efficiency of desulfurization during the process.

Table 4.3 Effect of RTILs on desulfurization efficiency on Valley Oil (one time treatment)

| **Ionic liquid** | **Stir 6 hours** | **Desulfurization** | **UAOD** | **Desulfurization** |
|---|---|---|---|---|
| | (ppm) | (%) | (ppm) | (%) |
| [BMIM][PF$_6$] | 5,715 | 29.4 | 4012 | 50.5 |
| [EMIM][EtSO$_4$] | 3,883 | 52.1 | 2,400 | 70.4 |
| [BMIM][OcSO$_4$] | 6,288 | 22.4 | 4622 | 42.9 |

The change of organic sulfur compounds in Valley Oil due to the oxidation, extraction by ionic liquid and solvent extraction have been shown in Figure 4.7.

As we know different reactivity in oxidation have been found in the organic sulfur compounds, and therefore, studies have shown results that their capability of extracting the oxidized products also vary from time to time during the extraction of the solvent material.

In this regard, un-reacted DBTs were mixed with those peaks that were having the retention time, which came out to be 20.8 in the results that were achieved after the examination of the process. In addition, un-extracted DBTOs were also included in the complex mixture with those peaks.

Findings have shown results that the un-reacted DBTs were one of the remaining ones after the extraction process of organic solvents. Trimethyl-DBTs and tetra-methyl-DBTs are the classification of these remaining DBTs that are un-reacted, as shown in the results. In the result, 97.7% was the overall efficiency of the desulfurization of Valley Oil, which was achieved from 8,100 ppm to 187 ppm.

However, this 97.7% was still not enough to fulfill the needs and requirements of the EPA regulations, as 15 ppm was required according to its new regulation for on-road diesel fuel. In this regard, a need for further treatment was felt and required, in order to meet the EPA new regulations as mentioned above.

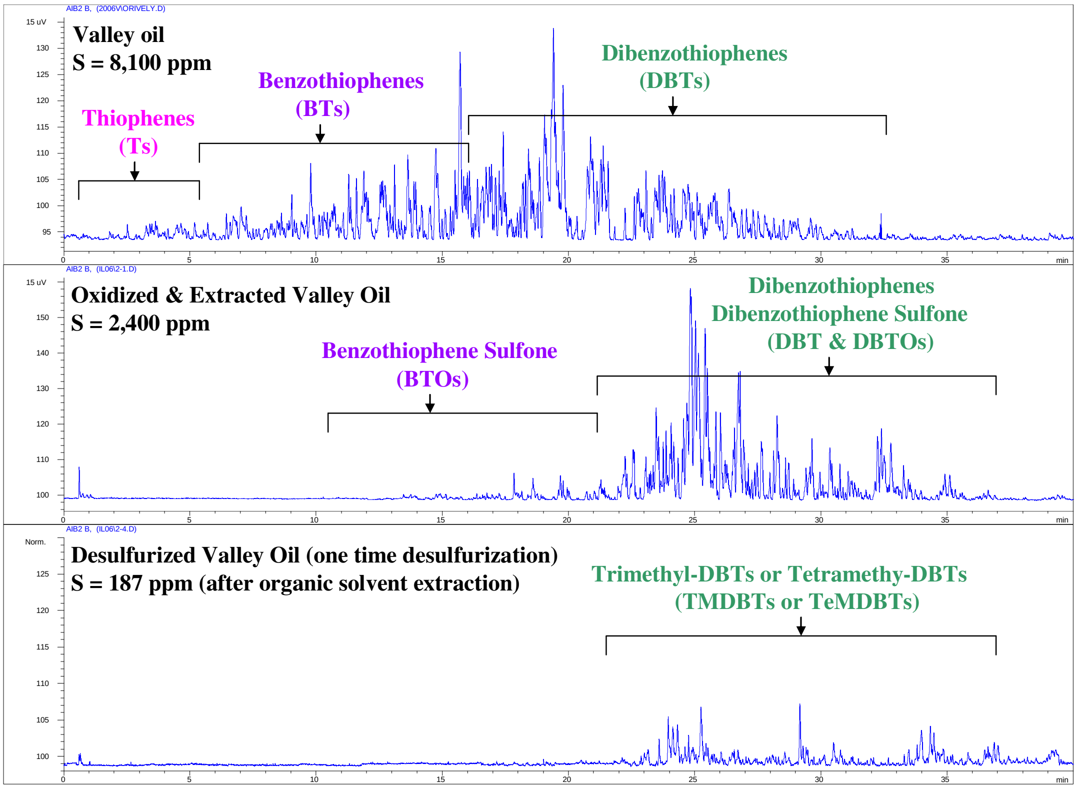


Figure 4.7 GC-SCD chromatograms of Valley Oil with one time desulfurization

There are different and various reasons regarding the incapability of extraction of ionic liquids that have been observed and examined by a number of experts. Due to high sulfur content of Valley Oil, the saturation has already been done in the ionic liquid phase. This is one of the reasons that ionic liquids cannot be extracted by the oxidation process of sulfur compounds. Therefore, it is necessary to perform the treatment second time.

The experimental procedures are consistent during the entire process that have been utilized during the first time. However, new and fresh RTILs, PTA, and catalyst are used during the second time. In this regard, the second time treatment utilizes the diesel fuel samples that were achieved from the first time treatment.

During the second time of desulfurization process, a reduction is observed in the concentration of sulfur, which reduces from 2,400 ppm to 1,372 ppm, which is a huge amount of reduction of the sulfur concentration. However, this shows that ionic liquid phase has been able to extract more sulfones in it, as shown in the Figure 4.8.

Studies have shown that the remaining concentration of the sulfur comes out to be 6 ppm after the extraction of the organic solvent during the treatment. In addition, corresponding sulfones have been achieved by the oxidation process of most of the un-oxidized sulfur that was done during the first time treatment, as shown in the chromatogram. In the result, 99.9% efficiency of the desulfurization is achieved remarkably and which, met the regulations that have been given by the EPA.

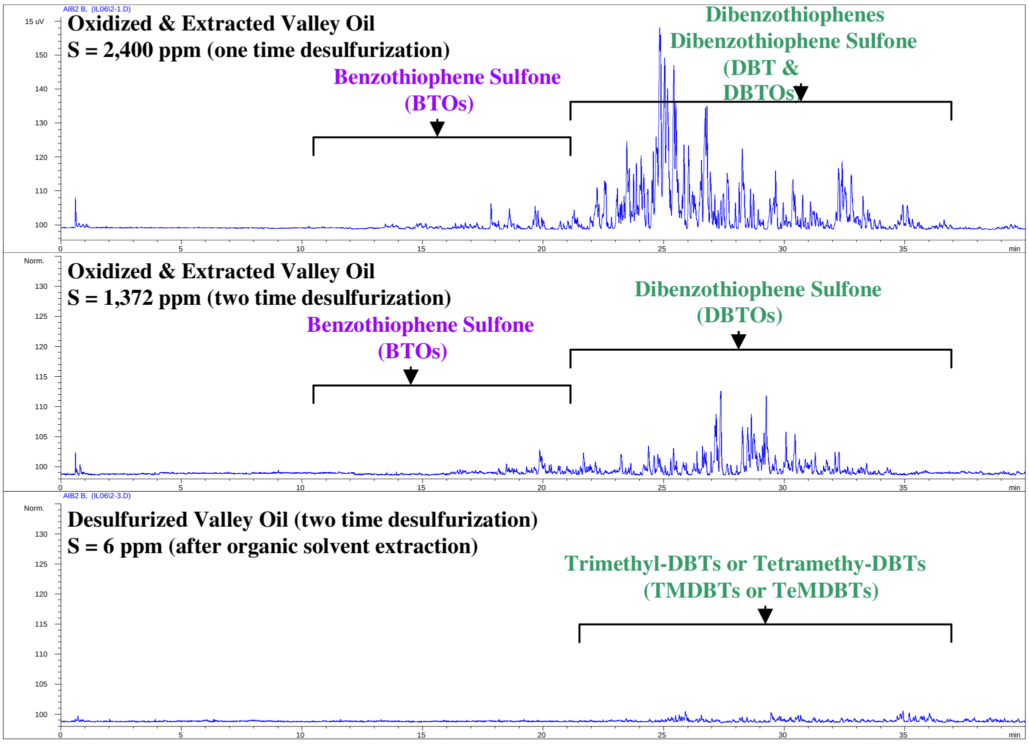


Figure 4.8 GC-SCD chromatograms of Valley Oil with two time desulfurization

Figure 4.9 shows the summery of GC-SCD chromatogram of Valley Oil at various stage of treatment.

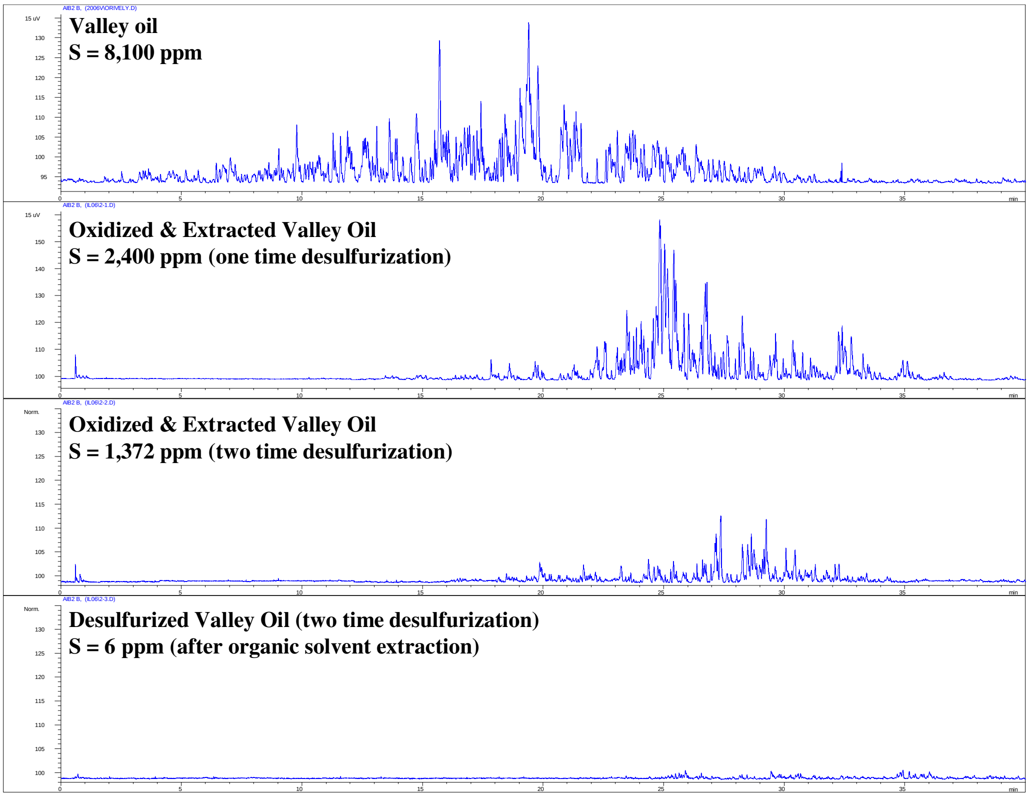


Figure 4.9 GC-SCD chromatograms of Valley Oil in different stages of treatment

### 4.6.6 Desulfurization of Diesel Fuel with Different Sulfate Anion Based ILs

Table 4.4 shows the desulfurization efficiency of different sulfur content diesel fuels by using different types of sulfate anion based ILs with protocol method that has been discuss in Chapter 3. The results clearly indicate that by using sulfate anion based ILs, all kind of diesel fuels can achieve more than 99.9% of sulfur reduction. Again, [EMIM][EtSO$_4$] IL shows slight better desulfurization efficiency on diesel fuels that same as the model sulfur compound.

Table 4.4 Summery of desulfurization efficiency of various diesel fuels with sulfate anion based IL

| **Valley Oil**<br>**RTIL** | **Initial conc. (ppm)** | **Final conc. (ppm)** | **Desulfurization (%)** |
|---|---|---|---|
| [EMIM][EtSO$_4$] | 8,100 | 6 | >99.9 |
| [EDMIM][EtSO$_4$] | 8,100 | 8 | >99.9 |
| [TBMNH$_4$][MeSO$_4$] | 8,100 | 11 | >99.8 |
| [TBMP][MeSO$_4$] | 8,100 | 9 | >99.9 |

| **F-76**<br>**RTIL** | **Initial conc. (ppm)** | **Final conc. (ppm)** | **Desulfurization (%)** |
|---|---|---|---|
| [EMIM][EtSO$_4$] | 4,220 | 2 | >99.9 |
| [EDMIM][EtSO$_4$] | 4,220 | 5 | >99.9 |
| [TBMNH$_4$][MeSO$_4$] | 4,220 | 5 | >99.9 |
| [TBMP][MeSO$_4$] | 4,220 | 8 | >99.8 |

| **JP-5**<br>**RTIL** | **Initial conc. (ppm)** | **Final conc. (ppm)** | **Desulfurization (%)** |
|---|---|---|---|
| [EMIM][EtSO$_4$] | 740 | 0 | 100 |
| [EDMIM][EtSO$_4$] | 740 | 4 | >99.4 |
| [TBMNH$_4$][MeSO$_4$] | 740 | 3 | >99.4 |
| [TBMP][MeSO$_4$] | 740 | 2 | >99.4 |

### 4.6.7 Desulfurization of Valley Oil with Different $H_2O_2$ Concentration

A highly insipid blue fluid is hydrogen peroxide ($H_2O_2$), which emerges colorless in a thin resolution, somewhat stickier than water. It has strong corroding properties and is deficient in poisonous derivative ingredients. While clean hydrogen peroxide is rather steady, it crumbles into water and oxygen when its temperature is taken above about 80°C. Additionally, hydrogen peroxide can be employed for varied purposes to consume its high choosiness. Through merely fine-tuning the order of the response, hydrogen peroxide can frequently be constructed to corrode one impurity over one more, or still take as positive the diverse corrosion artifacts from identical contaminants (Greenwood, 1997 and Hess, 1995).

Accessible in a variety of potencies and ratings is $H_2O_2$, discussed respectively. (a) 3% Pharmaceutical Grade: This type is locally available in the market. This item is employed as a gentle peroxiding cause and from medicinal viewpoint as an antibacterial product (Greenwood, 1997). (b) 35% Technical Grade: This type is a more strenuous produce as compared to the Reagent Grade; it is somewhat different in one aspect: addition of phosphorus to facilitate to counterbalance any chlorine from the water exercised to thin it (Greenwood, 1997). (c) 35% Food Grade: This type is applied in the fabrication of provisions similar to cheese, eggs, and whey-containing produces. It is also showered on the foil strips of aseptic packs which enclose fruit liquid and milk produces (Greenwood, 1997). (d) 90% Grade: This type is employed as an oxygen basis for soaring energy (Greenwood, 1997).

Regardless of its prospective significance as an oxidant, hydrogen peroxide holds several grave downsides. It is intrinsically acidic and, particularly in great absorptions, is flat to catalytic corrosion. Using thin aqueous explanations is able to diminish these hitches. Conversely, the overload water time and again generates a bi-periodical combination with the natural substrate and the oxidant existent in diverse levels (Remias, et al. 2003). Hence, in this part, four diverse H2O2 applications have been put to examination.

Figure 4.10 shows the desulfurization efficiencies of different hydrogen peroxide concentrations on high sulfur content Valley Oil in batch scale. The outcomes with 0% $H_2O_2$ as the managed conducted test show that there was no sulfur deduction which can be obtained. With 3 % $H_2O_2$, the sulfur deduction was about 97.3%. Faintly inclining the applications of hydrogen peroxide permitted the improvement of competence of sulfur lessening. The absorption at 10 % is possibly to add to the sulfur deduction to 98.8 %. Nevertheless, under the same process order that used 30 % and 50% $H_2O_2$, the sulfur deduction can reach approximately 99.9%.

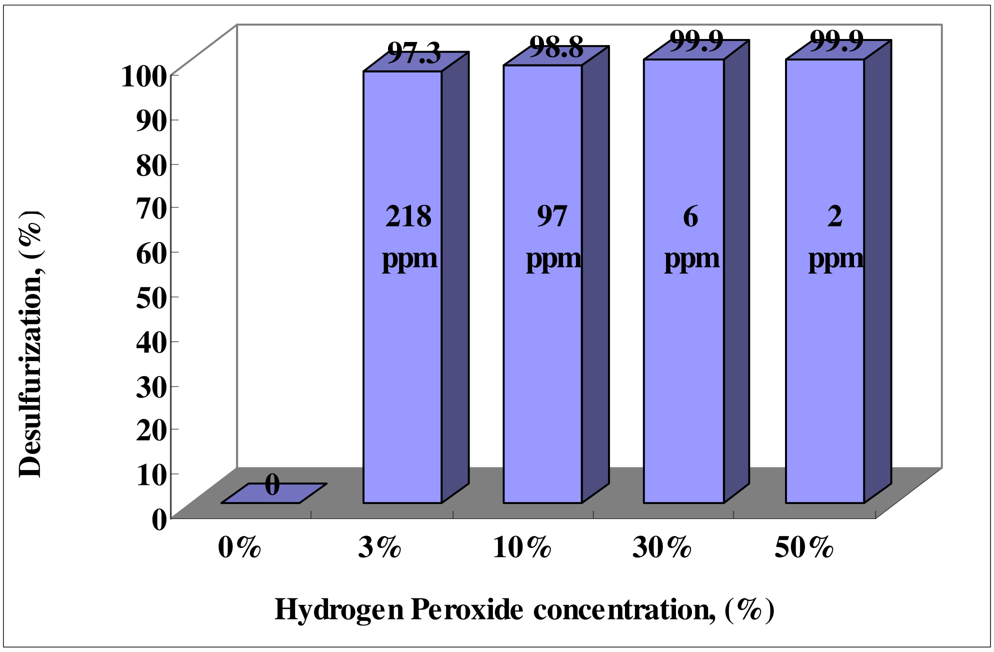


Figure 4.10 Desulfurization efficiency with $H_2O_2$ concentration

From stoichiometric computation, 3% $H_2O_2$ has sufficient oxidant to desulfurized Valley Oil; however, the outcome did not demonstrate towering sulfur decrease transfer. This is for the reason that it needs more time to act in response: despite the 3 hour reaction time, it is likely to require extended time to total the desulfurization procedure because of molecular. In line with the kinetic assumption, oxidant and sulfur molecules are move in constant and random motion. Due to low concentration of oxidant, the chance of rapidly moving particles constantly collide with each other that allow oxidize will become less. In this regards, 30% $H_2O_2$ will be the most suitable oxidant concentration for modified UAOD process.

### 4.6.8 Catalyst and RTIL Recovery

In the entire process, oxidation of organic sulfur compounds was carried out in the presence of ultrasound, excess $H_2O_2$, RTILs, acid catalyst, and PTA. Different studies have shown that the raw materials are found to be very expensive, and the capital cost will be too high and will exceed from the budget due to their one-time usage during the process. In this regard, one of the most expensive materials are the RTILs, which are used during the entire process. Some of the reasons of its high value and expense are that its commercialization has been done in recent years, and this green solvent is new in the market, which has accelerated its value in the market. Therefore, when the organic solvents are compared with the RTILs, the cost comes to be very high, which is not appreciable by most of the research or commercialize purposes. Therefore, it has been observed that the catalysts are responsible for the commercial viability of UAOD process that performs the utilization of these raw materials during their reactions.

In addition, RTIL recovery also plays a vital role in providing support to these raw materials during the entire process of oxidation of organic sulfur compounds, as mentioned earlier in our study. In this regard, the spent aqueous phase was utilized during the conduction of several experiments that were based on the recycle. RTILs, PTA, and $H_2O_2$ were contained in the above mentioned aqueous phase. The desulfurization process was run, in order to get the same results by Treated Valley Oil and check its capability, as compared to the other raw materials that are found to be new and fresh in the market. During the process, it was found out that more than 99% of desulfurization efficiency was achieved, even after the utilization of aqueous phase for three times. Thus, it indicated that the oxidation process of organic sulfur compounds to its corresponding sulfones can be allowed by the excess amount of acid catalyst PTA, and $H_2O_2$ in the spent aqueous phase. All these findings have been shown in the Table 4.5.

Table 4.5 Spent catalyst & RTIL reused in new desulfurization process with Treated Valley Oil

| | **Initial conc. (ppm)** | **Final Conc. (ppm)** | **Desulfurization (%)** | **Solvent Extraction (ppm)** | **Desulfurization (%)** |
|---|---|---|---|---|---|
| **[EMIM][EtSO$_4$] (New)** | 560 | 84 | 80.5 | <1 | 99.9 |
| **[EMIM][EtSO$_4$] (Spent 1st time)** | 560 | 141 | 74.8 | <1 | 99.9 |
| **[EMIM][EtSO$_4$] (Spent 2nd time)** | 560 | 182 | 67.5 | <1 | 99.9 |
| **[EMIM][EtSO$_4$] (Spent 3rd time)** | 560 | 265 | 52.7 | 9 | 98.4 |

Same experiment has been repeat with Valley Oil that shows in Table 4.6, again, the recycle catalyst and RTIL shows that high desulfurization can be achieved by three times recycling.

Table 4.6 Spent catalyst & RTIL reused in modified UAOD process with Valley Oil

| | **Initial conc. (ppm)** | **Final Conc. (ppm)** | **Desulfurization (%)** | **Solvent Extraction (ppm)** | **Desulfurization (%)** |
|---|---|---|---|---|---|
| **[EMIM][EtSO$_4$] (New)** | 8,100 | 1,372 | 83.1 | 6 | >99.9 |
| **[EMIM][EtSO$_4$] (Spent 1$^{st}$ time)** | 8,100 | 2,987 | 63.1 | 8 | >99.9 |
| **[EMIM][EtSO$_4$] (Spent 2$^{nd}$ time)** | 8,100 | 4,110 | 49.2 | 11 | >99.8 |
| **[EMIM][EtSO$_4$] (Spent 3$^{rd}$ time)** | 8,100 | 4,844 | 40.2 | 15 | >99.8 |

### 4.6.9 Polish Treated Valley Oil with Solid Catalyst

Figure 4.11 shows the chromatogram of Treated Valley Oil before and after polished. 93.2% of desulfurization achieved by using Ti-B solid catalyst. The sulfoxidation reaction with $H_2O_2$ can be used as method for removing OSCs from diesel fuel without hydrogen consumption and high pressure equipment utilization.

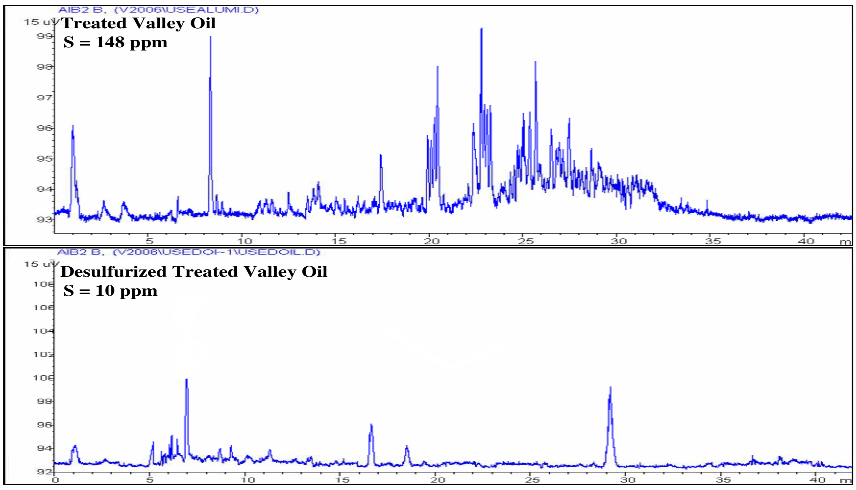


Figure 4.11 GC-SCD chromatogram of Treated Valley Oil before & after polish stage

### 4.7 Summary

In this study, modified UAOD process on commercial diesel fuels was developed to consist of three steps: Stirring, UAOD and solvent extraction. The desulfurization efficiency was also enhanced with the application of RTILs, PTA and acid catalyst. In order to keep the cost economical and the reaction efficient, the efficient protocol condition are summarize and shown on Table 4.7.

Table 4.7 Efficient protocol condition of desulfurization on diesel fuels

| | |
|---|---|
| Diesel sample | 5 gram |
| 30% $H_2O_2$ | 5 gram |
| 20% TFA | 1.5 gram |
| TAOF & $CH_3CN$ | 0.3 gram |
| [EMIM][$EtSO_4$] | 5 gram |
| Reaction temperature | 50°C |
| UAOD time | 10 min |
| Stir time | 170 or 350 min |

Three different sulfur content diesel fuels has been examined, such as: low sulfur diesel fuel: JP-5 (740 ppm) and Treated Valley Oil (560 ppm), median sulfur diesel fuel: Naval F-76 (4,220 ppm) and high sulfur diesel fuel: Valley Oil (8,100). Among these diesel fuels, average 99.9% desulfurization efficiency can be achieved under protocol condition. The sulfur content of the low and median sulfur diesel fuel reduced to 0 ppm, and high sulfur diesel fuel reduced to 6 ppm, respectively. The results of the desulfurization of diesels fuels by modified UAOD process are summarized in Table 4.8.

Table 4.8 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 |

In desulfurized Valley Oil, the refractory OSCs belong to the groups of tri-methyl DBTs and tetra-methyl DBTs, respectively. The results have been confirmed by sulfur analyzer and GC-SCD. According to previous studies (Wan, et al. 2005 and Mei, et al, 2000), four major refractory sulfur compounds left behind after UAOD process, such as $C_3$-BTs, $C_4$-BTs, $C_5$-BTs and $C_3$-DBTs. In modified UAOD process, none of these refractory sulfur compounds has been found qualitatively and quantitatively. Therefore, it can be concluded that no refractory OSCs left behind after modified desulfurization method. More than 99.9% efficiency of the desulfurization is achieved remarkably which, met the regulations that have been given by the EPA. Therefore, 100% desulfurization or “Zero” sulfur diesel fuel is not impossible to achieve.

In the modified UAOD procedure, the acid catalyst and RTILs performed a central part to hasten the response speed and improve the oxidation competence. Yet, the exhausted catalyst is possibly to bring into force the amplification of the principal price and the atmospheric contaminations. The total catalyst recuperation was fundamental to improve the marketable feasibility of customized modified UAOD procedures. The present study points out that the used aqueous (catalyst and RTIL) are likely to be recuperated completely after the oxidation response by affixing new share of diesel fuel. The outcomes display that reprocessed catalyst solution possessed just about the identical oxidation competence as with the original catalyst. This is a necessary knowledge to stop the intense cost of catalyst and RTIL to execute the optimization process of desulfurization procedure.

$H_2O_2$ held a significant part in oxidation, devoid of $H_2O_2$ to modified UAOD procedure: as such no sulfur reduction. Yet, employing small amount of $H_2O_2$ is likely to carry out the towering desulfurization competence; however, it needs more time to achieve 15 ppm desulfurization. Hence, in the present research, with 30% and 50% $H_2O_2$, 99.9% sulfur decrease for diesel fuel can be attained in procedural circumstances. This information is necessary to comprehend the back-bounce of a variety of hydrogen peroxide absorptions in oxidative circumstances, and to zoom onto the response consideration in modified UAOD process. Yet, 50% $H_2O_2$ have carried out difficulties with likely outbursts. Because of security measures, 30% $H_2O_2$ absorption has been chosen for the whole procedure for all types of diesel.

# CHAPTER 5

# PILOT STUDY

## 5.1 Introduction

The objective of developing modified UAOD process is to produce ultra low sulfur or “0” sulfur diesel fuel with high desulfurization efficiency under ambient temperature and pressure. Chapter 3 and 4, with modified UAOD process, provide high selective removal of organic sulfur compounds either model sulfur compounds or various kinds of diesel fuels by combination process of oxidation, solvent extraction, and/or solid adsorption.

From chapter 3 and 4, the process is carried under batch process. Until the needed end result was reached in the process, all the reactive ingredients were put together into the process in a controlled manner. It is to be noted for reactions tend to be sluggish (usually spanning over hours). Moreover, the conduct volume is low. On the other hand, it is possible to process the continually running scheme at a constant rate in the manner that the reactive components constantly enter the reaction pot so that the end produce leaves on a constant pace. The point worth-mentioning, with regard to the continually flowing system, is that it can be highly contributing to large production resulting a higher profit turn outs or financial gains as compared to the cyclic system of operation (Levenspiel, 1999).

For the success of an industry, it is generally known that it is necessary for a new chemical process to take into account chief key components both technology and finance-related. These must be clearly realized and feasible for use. As such there is the petroleum refining system which prioritizes the constantly flowing method so that high scale production with great fuel outlets can be met. Moreover, it is easier to manage and measure the constantly flowing reactive components than those of group. It is because in the continuously flowing system the hitches are not so many; the produce becomes organized; and, the yearly cost for capital is also less. (Schmidt, et al. 1998). Henceforth, it is necessary to execute a pilot study.

In the social sciences research, the term "Pilot study" is defined and executed in two different paradigms. One is the small-scale check-up study which is done to execute a large study of the same nature. (Polit, et al. 2001). However, according to previous study (Baker, et al. 1994), a pilot study may also be the one which tries out a specific research tool. One very salient feature of performing a pilot study is that it can in time tell the researcher about the possible failure that a study may meet, or the hurdles that might rise, or that where the suggested tools and methods may not be appropriate or may be out-of-the-fit. Before executing a major study, numerous pilot studies may be performed. They can be conducted either from naturalistic or qualitative paradigm. Thus, a pilot study can help the research to gather qualitative data and its analysis for a major study and its design and so forth (Tashakkori, et al. 1998).

Here, a thoroughly new system for desulfurization was established. Modified UAOD (continuous-flow) system and fluidized bed adsorption processes were developed. The efficiency of the system was measured on two diesel fuels. Eventually, a primary financial study for new desulfurization scheme was performed.

## 5.2 Materials and Experimental Procedure

### 5.2.1 Materials

Two diesel fuels were used as the feedstock in this study. (1) Diesel fuel with sulfur content of 8,100 ppm (Valley Oil) were received from Golden Eagle Oil Refinery, Inc. (2) Marine logistic fuel (F-76) with sulfur content of 4,220 ppm were received from U.S Army.

Tetraoctylammonium fluoride used as phase transfer agent (PTA) was synthesis from (Dermeik, et al. 1989). Acetic acid, tri-fluoro acetic acid (TFA) as catalyst, 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][$EtSO_4$] as ionic liquid and aluminum oxide (activated, acidic, Brokmann I, standard grade, ~150 mesh, 58A) as adsorption media were obtained from Aldrich Chemical. 30% hydrogen peroxide ($H_2O_2$) as oxidant and acetonitrile as extraction solvent were obtained from VWR Inc.

### 5.2.2 High Shear Mixer

In a group mixing environment of high cut off and huge flow is the high cut off blending generator which has single stage rotor or stator. It can generate a high blend of both automatic and cavitational shear. This is turn produces condition which is perfect for blending (Figure 5.1 manifests this).

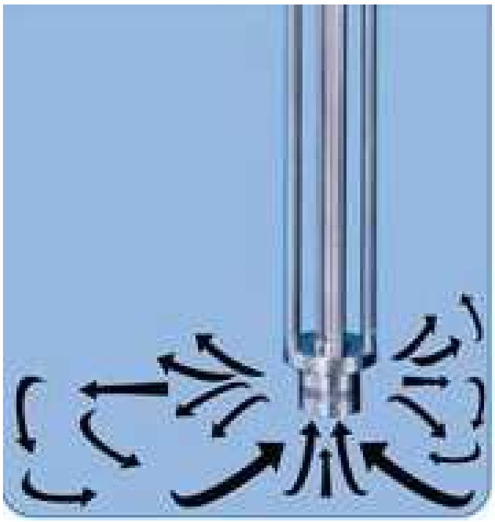


Figure 5.1 Flow pattern of high shear mixer (Charles Ross & Son Inc.)

For the present research for pilot study, a high shear mixer, HSM-100L, was rented from Charles Ross & Son Company. Figure 5.2 is the photograph of the model; and Figure 5.3 displays the rotating blade.

Figure 5.2 High shear mixer

Figure 5.3 Rotating blade

One of the salient characteristics of this mixer is its rotation speed from 1 to 10,000 rpm. However it can only provide 1,000 rpm with magnetic stir bar and batch study so falling short of the requirements of the pilot study, although the mixing conditions may be sound enough.

### 5.2.3 Batch Type Continuous Flow System and Its Operation

In Figure 5.4 is the diagram of the batch type continuous flow system. Commonly, two feed streams of reactive nature, i.e. (1) aqueous phase with $H_2O_2$, IL and catalyst (2) sulfur content diesel fuel were pumped into the reactor through one side of the reactor. As a result, the reactor emitted exit mixture in overflow state out of the port positioned on the other side of the reactor. With working volume of 1liter, the maximum capacity of the reactor is 1.8 liter. The fact that the high shear mixer is "dipped" directly into the reaction mixture (proficient here to generate mixing condition), the system, as such, can be classified as continuous stirred tank reactor (CSTR) system. The reactor has been custom made by USC glass blower shop, the reactor size is 15 cm diameter with 30 cm height with 0.3 mm thickness. Figure 5.5 shows the photo of the reactor that has been used for the entire pilot study.

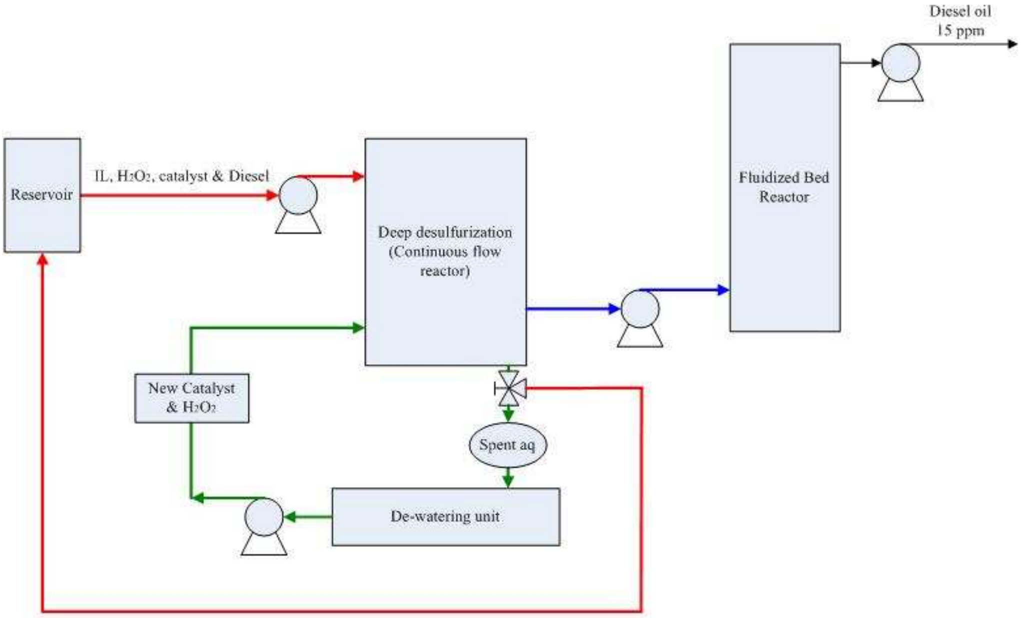


Figure 5.4 Block diagram of continuous flow system

Figure 5.5 Photo of glass reactor

Oxidation takes place while mixing in the reactor. At mean time, portion of the oil/aqueous mixture were recycled again to tank. Until 99.9% or organic sulfur compounds (OSCs) are oxidized, the very process is constantly taking place. Once oxidization is complete, aqueous phase passed through dewatering units so that water formed from reaction can be wiped off. More quantity of catalyst and oxidant was added to reactor. The oxidized diesel fuel was then pumped through fluidized bed reactor with alumina. Ultimately, the effluent will be the ultra low sulfur.

### 5.2.4 Fluidized Bed Reactor and Its Operation

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 (Photo follows with Figure 5.6). 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; Figure 5.7 shows the fluidized bed reactor set up for pilot study.

Figure 5.6 Alumina packing

Figure 5.7 Fluidized bed reactor setup

### 5.2.5 Experimental Methods

As discussed in the previous section, the batch type continuous flow system which excludes fluidized bed reactor was set up. Figure 5.8 shows the photo of this experiment with arrows pointing to the directions.

Reactants were stored in two solutions, that is, (i) diesel fuel and (ii) hydrogen peroxide (30 vol% solution). Acid catalyst and RTIL was pump into the reactor by two peristaltic pumps: Masterflex, Cole-Parmer, USA. The flow rates of each solution were adjusted with the chosen residence time and a constant oil/water ration of 10:1 in the reactor was maintained.

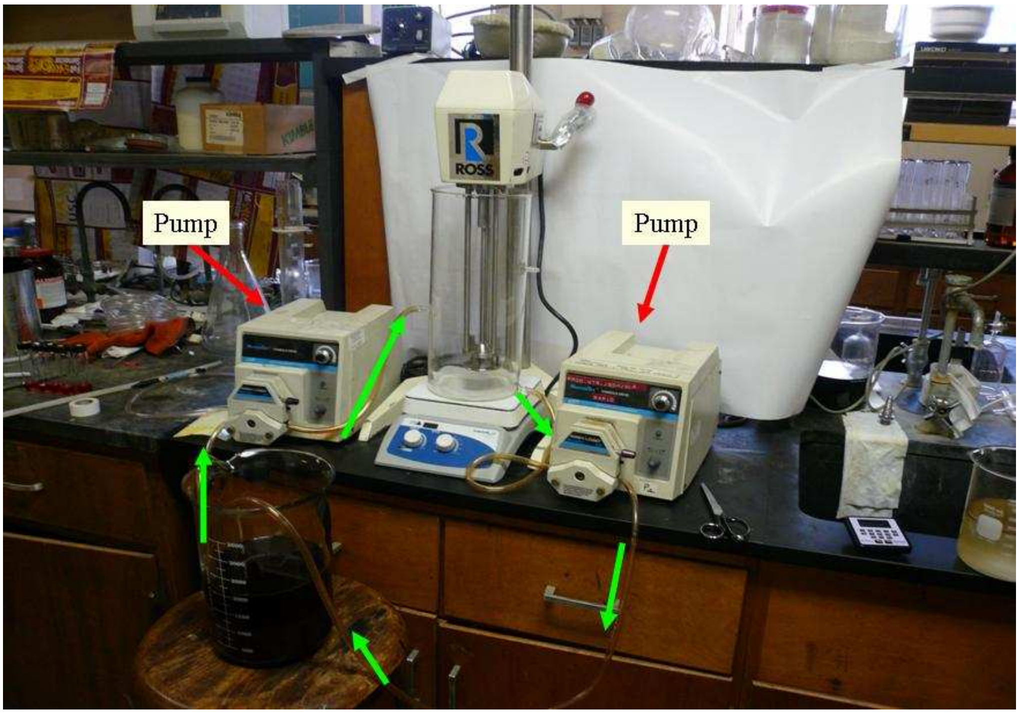


Figure 5.8 Experimental setup for batch type continuous flow system

The mixture in the reactor was stirred by high shear mixer. The samples of the effluent were at the time intervals of 10, 20, 30, 40, 60, 80, 140, and 200 minutes to collect 3 ml of samples at each interval. Several experiments were done: (1) different mixing strategy; (2) different amount of RTIL, (3) different amount usage and concentration of catalyst.

After oxidation of diesel fuel, it was extracted with acetonitrile for three times and each time the solvent-to-oil (S/O) ration was maintained at 1:1 by weight (1 gram diesel fuel per 1 gram acetonitrile). The mixture was then stirred vigorously for 5 minutes at the room temperature and which finally separated the phase by centrifuge. Moreover, the total sulfur content was analyzed by a Sulfur-in-Oil Analyzer (SLFA-20).

With adsorption, fresh alumina was poured into the glass vessels described previously. The oxidized diesel fuel was passed through fluidized bed reactor by centrifugal magnetic pump (polypropylene, Cole-Parmer, USA). The pump has a flow rate of 2.9 gallon per minute with enough power to pump the oil down from the bottom of the fluidized bed reactor up to the top. Effluent was collect into 30 ml glass vial for total sulfur analysis. Arrows in Figure 5.9 show the experimental set up for fluidized bed reactor.

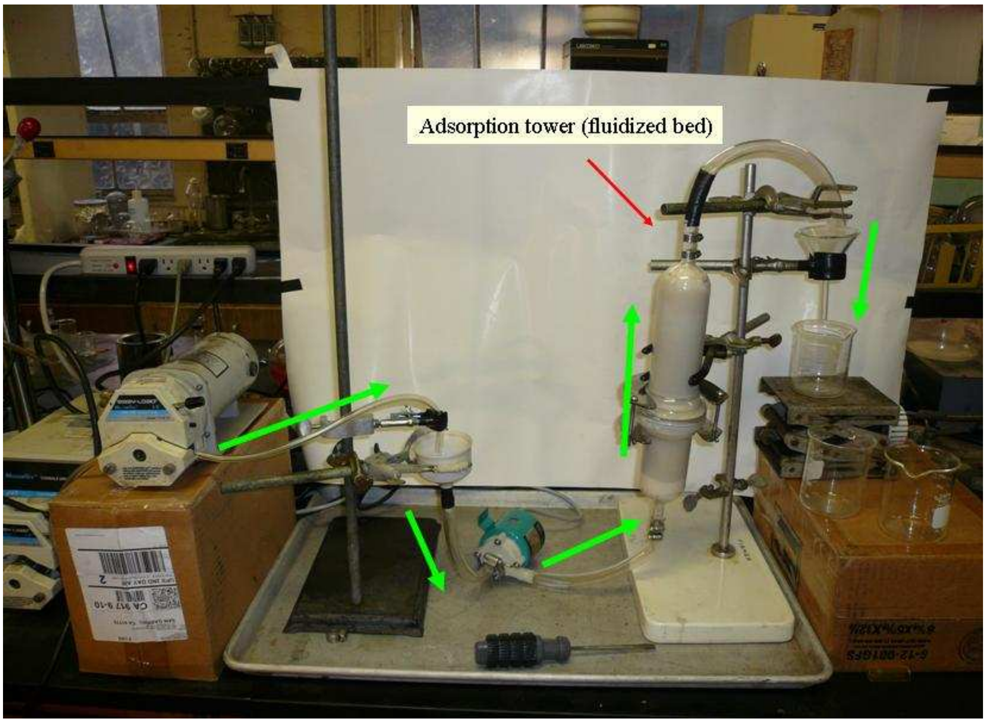


Figure 5.9 Experimental setup for fluidized bed reactor

To recycle the alumina, the saturated alumina was claimed with furnace and the starting oven temperature were 200$^{o}$C for 30 minutes to evaporate the aqueous solution. Then, it was increased 25°C for every 10 minutes, until the temperature reached 500°C which was held for 6 hours.

The acid catalyst and RTIL were key players in the process of increasing the rate of reaction and the enhancement of the efficiency of oxidation all taking place in the modified UAOD process. None the less, it is possible for the waste catalyst to accelerate the capital cost and cause threats of environment pollution; as such, it was essential to recover the catalyst and improve the viability of the process from the viewpoint of commerciality of the process. The study suggests that the acid catalyst and RTIL can be recuperated. It also manifests that the same oxidization efficiency as was originally found in catalyst. The know-how of all this process is essential in order to prevent costs or RTIL from inclining and for acid catalyst to conduct the desulfurization process to the optimal level.

## 5.3 Results and Discussion

### 5.3.1 Effect of Mixing Strategy

As has been discussed in Chapter 2, to improve the ODS process, the ultrasound component is found to be crucial. However, in actual life, it is possible for ultrasound to utilize a good deal of power. Moreover, such devices as amplifier, sono-reactor and function generator are prone to increase the capital cost. Henceforth, for the commercialization of the ODS process, it is essential that an alternative strategy be developed for chances to replace ultrasound.

In the present study, four different mixing strategies are compared, which are, magnetic stir bar, motor stir, ultrasound, and high-shear mixer. Table 5.1 displays the desulfurization efficiency of Valley Oil by four different types of mixing methods. Figure 5.10 displays the desulfurization efficiency of 4 different mixing methods.

Table 5.1 Sulfur concentration change by using different mixing method

| | **Magnetic Stir** | **Motor Stir** | **High Shear Mixer** | **Ultrasound** |
|---|---|---|---|---|
| | 900 RPM | 1,400 RPM | 10,000 RPM | |
| **Time** | Concentration | Concentration | Concentration | Concentration |
| 0 | 8,100 | 8,100 | 8,100 | 8,100 |
| 10 | 6,380 | 6,047 | 2,667 | 6,741 |
| 20 | 5,781 | 4,152 | 1,984 | 5,114 |
| 40 | 4,219 | 3,480 | 1,208 | 3,741 |
| 60 | 2,874 | 1,729 | 811 | 2,218 |
| 140 | 1,847 | 914 | 312 | 1,426 |
| 200 | 986 | 471 | 174 | 691 |

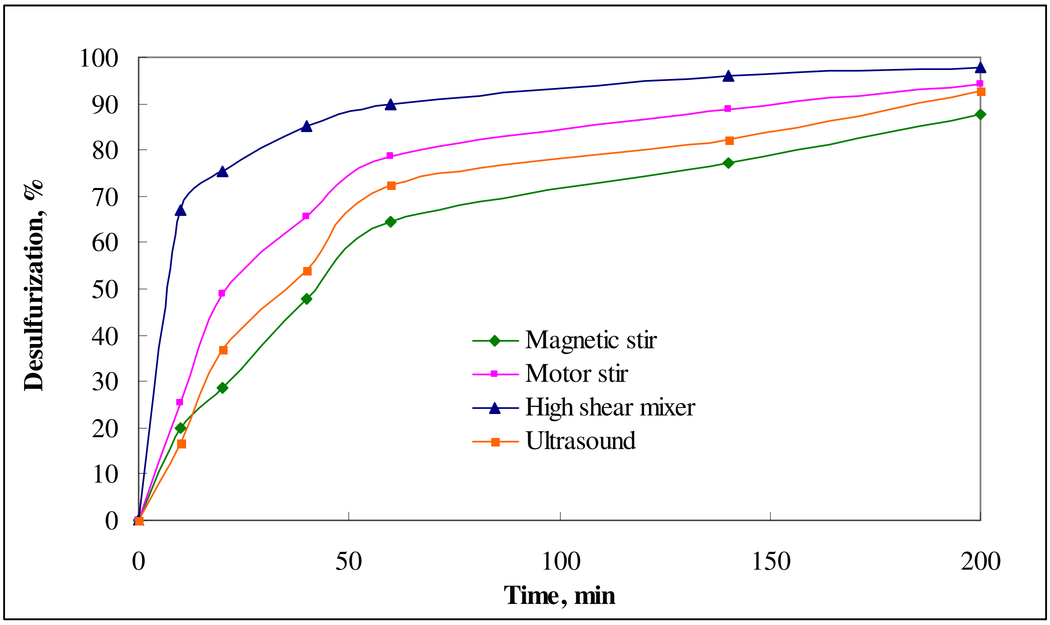


Figure 5.10 Plot of desulfurization vs reaction time with different mixing method

It is clearly shown that different RPM speed will produce higher efficiency for desulfurization. When compared to desulfurization, the following result were met. (1) As compared to the stir method, the ultrasound did not yield better desulfurization. Hence it is possible to replace the ultrasound with the mechanical stir. (2) From Chapter 4, at batch sale, concentration for sulfur diminishes to 187 ppm after it was stirred for 6 hours; it diminishes to 6 ppm when it was stirred 12 hours. However, with high-shear mixer, it requires half as much time to attain the low sulfur concentration. From the results, it can be concluded that it was essential to mix regimes to make sure that aqueous and diesel phase can be perfectly mixed to obtain desulfurization of high efficiency.

From the experimental observation it was obtained that with 10,000 RPM, after 10 minutes, due to high shear-mixing, all the mixtures reach up to 95°C. With this degree of temperature, it is possible for hydrogen peroxide and acid catalyst to decompose, evaporate, and lose their activity, because boiling points for hydrogen peroxide and tri-fluoroacetic acid were 106°C and 72°C correspondingly. To avoid the lose of row reactants, it was necessary to lower the reaction temperature. As such, instead of 95°C, as new reaction condition 50°C as the reaction temperature and 5,000 rpm as the mixing speed were chosen. Table 5.2 displays the desulfurization efficiency of two different reaction conditions.

Table 5.2 Effect of temperature on modified UAOD process

| **Time** | **10,000 rpm, 95°C** Concentration | **5,000 rpm, 50°C** Concentration |
|---|---|---|
| 0 | 8,100 | 8,100 |
| 10 | 2,667 | 914 |
| 20 | 1,984 | 779 |
| 40 | 1,208 | 564 |
| 60 | 811 | 314 |
| 140 | 312 | 84 |
| 200 | 174 | 15 |

From Table 5.2, the following observations are met. (1) With 50°C being the reaction temperature, sulfur reduction is better than with that of 95°C, (2) Moving along the same line of observation, it is found that after the span of 200 minutes, there is no loss in the weight of aqueous phase with lower operating temperature. (3) In this operation condition, high sulfur content Valley Oil can reduce to 15 ppm after liquid extraction was done three times although it meets the new sulfur regulations. Therefore, by using high shear mixer, 5,000 rpm will be used as mixing speed with 50°C as the reaction temperature, which is same reaction temperature as batch study.

### 5.3.2 Desulfurization Efficiency with Catalyst Usage

#### 5.3.2.1 Amount of Catalyst Usage

Based on successful experiments on batch scale, it is observed that with the efficient protocol condition of modified UAOD process on diesel fuels, the amount of catalyst usage is 0.3 gram per gram of diesel. Therefore, with 1,000 gram of Valley Oil, the amount of catalyst required for the procedures were 300 gram of catalyst. Due to the feasibility of economical concerns, much catalyst may not be necessarily needed to run the entire process; henceforth, in this section, different amounts of catalyst usage and catalyst concentration have been put to the procedural testing.

The diverse quantities of utilization of acidic catalyst have been employed to batch type continuous flow system for Valley Oil is shown in Table 5.3 and Figure 5.11. In this study, the sulfur lessening touched 7 ppm in the span of 140 minutes with 300g of method. Still, with 35g of channel, the sulfur lessening went up to 6 ppm in the time span of 200 minutes. This manifests that about 1/10 of catalyst can climb up to the equal desulfurization competence when we compare it to the batch level. The only shortcoming come across in this case is that it is in need of an additional 60 minutes to accomplish the lowest amount requisite of sulfur instruction.

Table 5.3 Summery of desulfurization by using different amount of acid catalyst

| **Reaction Time (min)** | **5g catalyst** | **25g catalyst** | **35g catalyst** | **300g catalyst** |
|---|---|---|---|---|
| | **ppm** | **ppm** | **ppm** | **ppm** |
| 0 | 8,100 | 8,100 | 8,100 | 8,100 |
| 10 | 3,145 | 1,344 | 914 | 841 |
| 20 | 2,889 | 1,141 | 779 | 588 |
| 30 | 2,457 | 1,020 | 642 | 476 |
| 40 | 2,180 | 890 | 564 | 311 |
| 60 | 1,874 | 612 | 314 | 206 |
| 80 | 1,544 | 489 | 227 | 76 |
| 140 | 1,317 | 279 | 84 | 7 (99.9%) |
| 200 | 984 (87.9%) | 129 (98.4%) | 15 (99.8%) | |

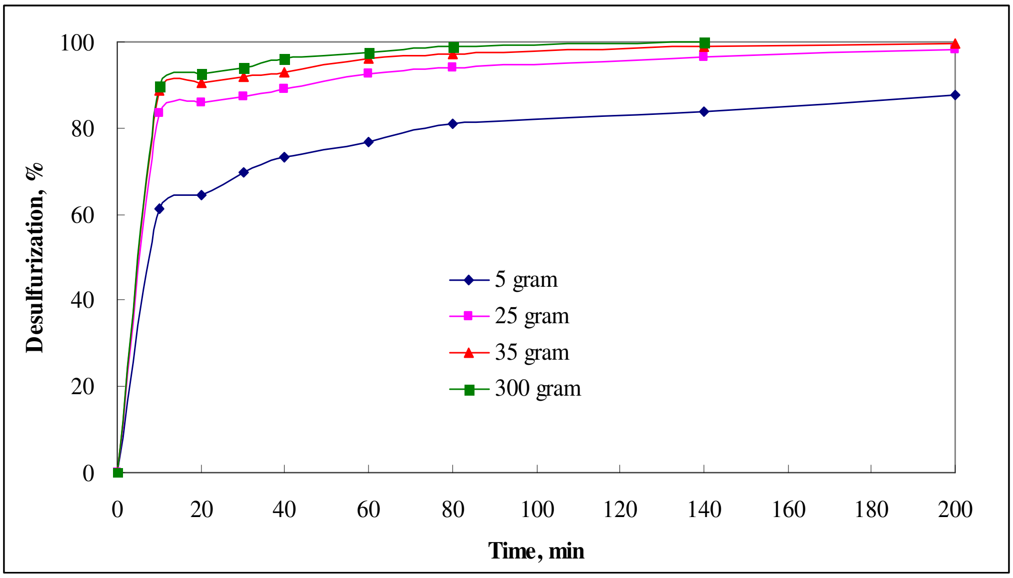


Figure 5.11 Plot of desulfurization vs reaction time with different catalyst usage

Although the amount of catalyst usage increases, that is, from 5 gram to 35 gram, the desulfurization efficiency also increases to a significant degree. These phenomena prove in this modified UAOD process that acid catalysts play a very important role for the process of oxidation. Besides this, the present procedure indicates that using more catalyst can fulfill the requirements of practical applications; it also comes to the observation that it can permit much faster operation time.

With kinetic study of catalyst usage, (registering the fact that oxidant is in excess amount) the reaction data were tailor-made to fit to a first order rate equation. A plot of ln (Co/Ci) versus reaction time is illustrated with the help of Figure 5.12. The upshot exhibits a sequential association that endorses the imitation first arrangement reaction kinetics. With 35 gram catalyst utilization, it the greatest tempo steady of K= 0.0211 min$^{-1}$.

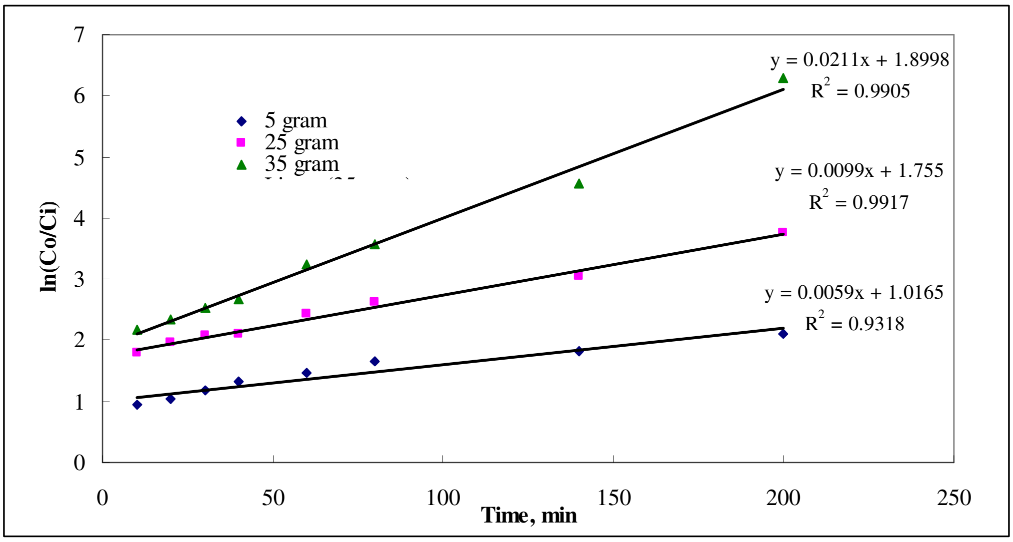


Figure 5.12 Plot of ln ($C_i/C_o$) vs time for Valley Oil desulfurization with catalyst usage under pseudo first order condition

### 5.3.2.2 Concentration of Catalyst

Another parameter that may affect the desulfurization efficiency was acid catalyst concentration. Illustrations in Table 5.4 and Figure 5.13 display the data of desulfurization efficiency of different acid catalyst concentrations with 10%, 20% and 40%, in a respective order. From the batch study, by using 20% TFA, it is found that the concentration can reduce sulfur concentration to 15 ppm. However, in the pilot study, the outcome manifests that sulfur reduction can only reach to 189 ppm after 200 minute of reaction time. This is owing to the observation that on the nonstop running procedure, employing inferior TFA absorption, it requires comparatively higher time to touch the correspondent rate (high sulfur lessening). However, with 40% TFA, 15 ppm sulfur concentration can be obtained. The point worth the notice here is that the results clearly make it known that higher TFA concentration can fulfill the requirements of a pilot study at a given time.

Table 5.4 Summery of desulfurization by using different catalyst concentration

| Reaction Time (min) | 10% TFA | 20% TFA | 40% TFA |
|---|---|---|---|
| | ppm | ppm | ppm |
| 0 | 8,100 | 8,100 | 8,100 |
| 10 | 1,754 | 1,159 | 914 |
| 20 | 1,547 | 909 | 779 |
| 30 | 1,424 | 842 | 642 |
| 40 | 1,315 | 745 | 564 |
| 60 | 1,222 | 621 | 314 |
| 80 | 1,054 | 555 | 227 |
| 140 | 901 | 444 | 84 |
| 200 | 787 (90.3%) | 279 (96.6%) | 15 (99.8%) |

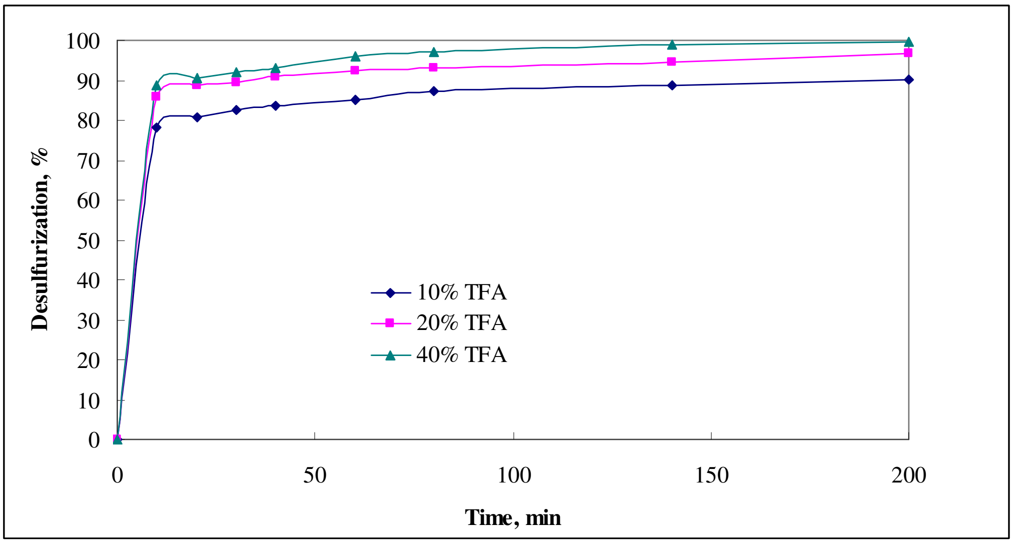


Figure 5.13 Plot of desulfurization vs reaction time with different catalyst concentration

As for the kinetic examination of channel absorption, (registering the fact that oxidant is in extra quantity), the response data were modified to get in to an earliest arrangement pace of equation. A scheme of ln ($C_i/C_o$) in opposition to reaction span is given in Figure 5.14. The end result manifests a sequential link that give consent to the first order reaction kinetics. With 40% TFA absorption, it leaves out the greatest pace steadiness of K= 0.0211 min$^{-1}$. Consequently, to desulfurize 1,000 gram of Valley Oil, it entails 35 gram of 40% TFA means to append to the incessant running scheme that allows to go of 99.8% (15 ppm) of desulfurization.

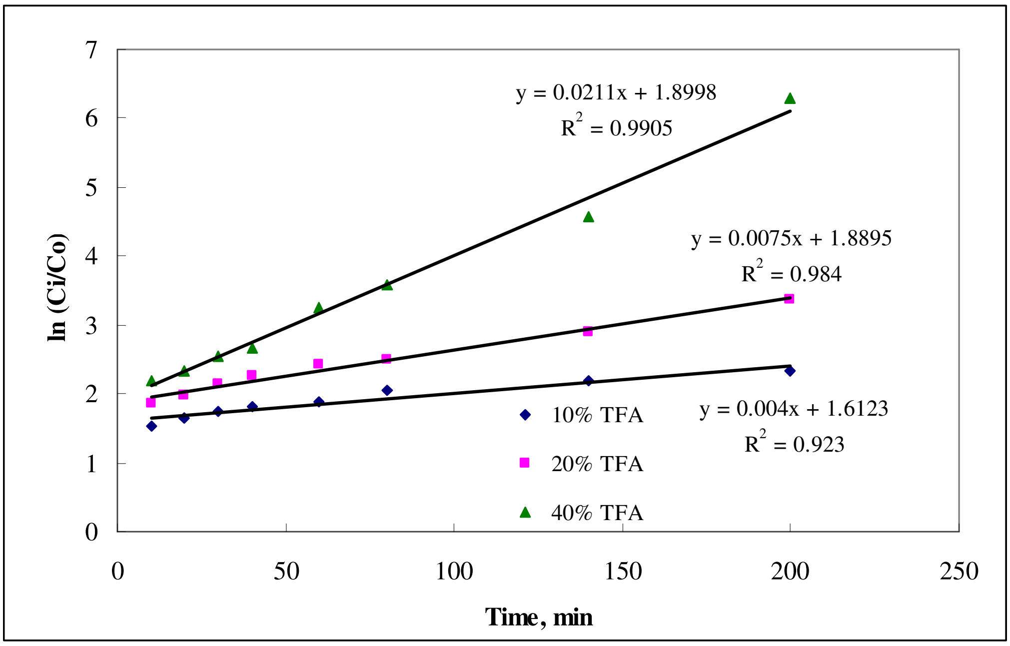


Figure 5.14 Plot of ln ($C_i/C_o$) vs time for Valley Oil desulfurization with catalyst conentration under pseudo first order condition

### 5.3.3 Desulfurization Efficiency with RTIL Usage

As already been discussed in the earlier chapters, it has been observed that the role of catalyst, as well as, a surfactant can be played by the ionic liquid, subject to the model compounds and the batch scale. Moreover, another concern has been felt by the experts, which tends on the economical side. In this regard, it was evaluated that the cost of the ionic liquid is very high, and thus, high capital cost will not be affordable during the pilot study, whereas, batch scale could be employed with large volume of the ionic liquid. Therefore, a continuous desulfurization system has been employed for the experimenting ionic liquid several times in different volumes. In addition, Valley Oil and the feedstock were also used during these experimental series. In this regard, Figure 5.15 and Table 5.5 have been used for the representation of these results. During the research on model compounds and batch scale, it has been found that a significant role of catalyst or surfactant is played by the ionic liquid, which has also been studied in the previous chapters.

Table 5.5 Summery of desulfurization with IL usage

| **Time (min)** | **10g IL** | **25g IL** | **50g IL** |
|---|---|---|---|
| | **Removal percentage (%)** | **Removal percentage (%)** | **Removal percentage (%)** |
| 0 | 8,100 | 8,100 | 8,100 |
| 10 | 956 | 934 | 914 |
| 20 | 821 | 814 | 779 |
| 30 | 701 | 684 | 642 |
| 40 | 603 | 571 | 564 |
| 60 | 387 | 340 | 314 |
| 80 | 284 | 274 | 227 |
| 140 | 96 | 101 | 84 |
| 200 | 18 | 16 | 15 |

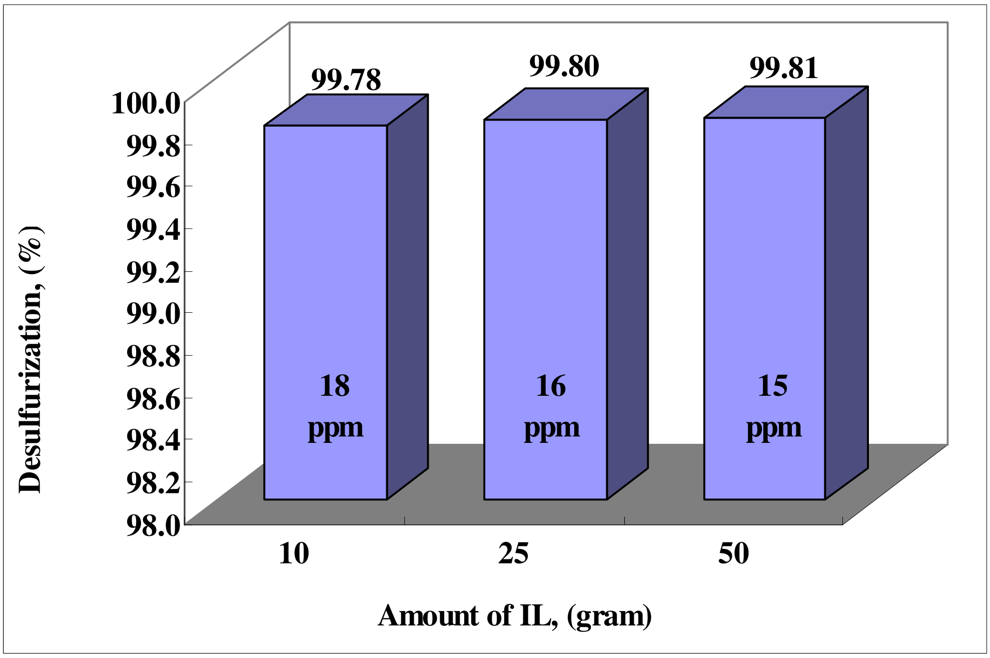


Figure 5.15 Plot of desulfurization vs IL usage

Almost identical outcomes have been shown by the utilization of ionic liquid in three different volumes during the calculation of desulfurization efficiency. During these experimental series, it was evaluated that 200 minutes of reaction time was enough for the removal of more than 99.8% of sulfur. It was indicated by the results that desulfurization requires only small amount of ionic liquid, and thus, it was noted that practical application required only a small amount of ionic liquid, and cheap operating conditions can be permitted by it. In addition, 1:1 was the ratio of ionic liquid and organic portion during the batch study, and a significant change was observed in the ratio, as 1:100 was the ratio during the pilot study. Thus, it was evaluated that desulfurization efficiency cannot be affected by a small amount of ionic liquid, which has been noted by the above mentioned information.

Since excess amount of hydrogen peroxide was present, referral of a first-order rate equation was regarded for the reaction. In this regard, Figure 5.16 has shown a plot of reaction time versus In ($C_i/C_o$). It was displayed by the results that the pseudo-first-order reaction kinetics was confirmed by a liner relationship. Moreover, the utilization of 50g ionic liquid has shown that smaller higher rate of reaction can be achieved, as compared with the utilization of 10g ionic liquid.

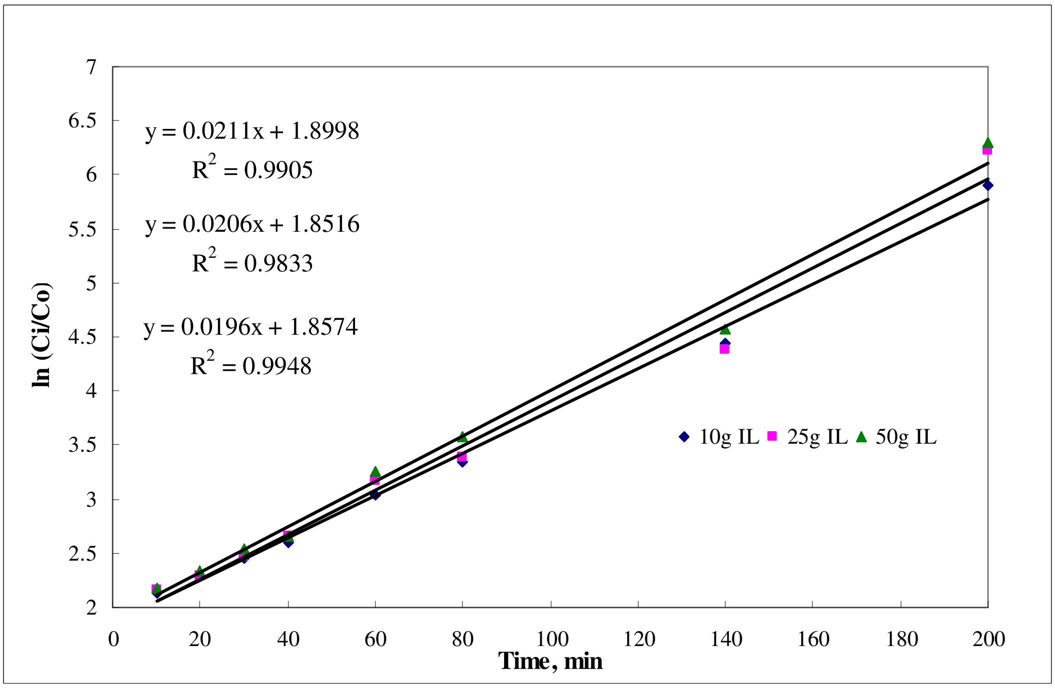


Figure 5.16 Plot of ln ($C_i/C_o$) vs time for Valley Oil desulfurization with IL usage

### 5.3.4 Design Parameter of Continuous Flow Reactor (CSTR)

By using a continuous agitated-tank reactor in order to obtain a particular output, the Continuous Stirred-Tank Reactor (CSTR) model is used to measure the key unit operation variables. It has been observed that all kinds of fluids, slurries, as well as, gases can be utilized in the mathematical model. Moreover, some advantages have been analyzed by the experts while studying the operations of a stirred-tank reactor over batch reactor (Levenspiel, et al. 1999). Moreover, span of 24 hours a day has been operating capacity of the reactor that can be continued for weeks. One of the examples of a cheap and easily constructed reactor is the CSTR. In this regard, simple catalyst charging, as well as, replacement has been allowed by the CSTR. Its well-mixed nature allows uncomplicated control of the reaction and the provision or elimination of gases over the temperature and pH (Harriott, 2003).

In Figure 5.17 is displayed diagram of CSTR with a sequence. In an inlet port at a constant rate the reactants were continuously propelled. Good mixing was prioritized so the reactor was vigorously stirred. As a result, the reactant solution that was driven in shoved out an equal volume of the solution

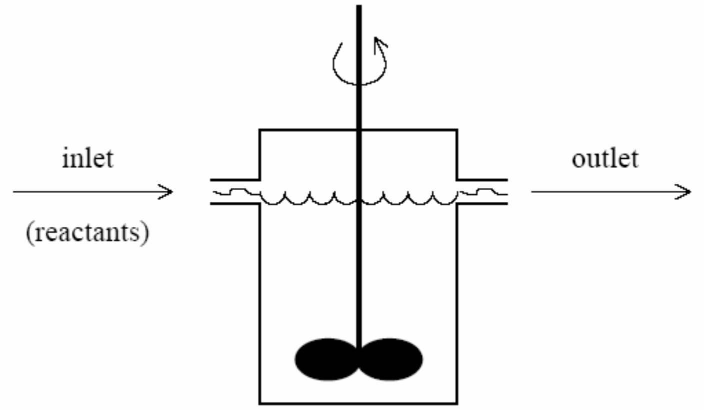


Figure 5.17 CSTR (Harriott, 2003)

The overall volumetric flow rate of feed streams with CSTR (which was observed under normal order of operation) equals to the flow rate of effluent torrent, *Q*. In the vessel, to maintain adequate oxidant, the ration of oil/water was set at 1:1 (v/v). Same rates of the flow of volumes have been observed during the study of aqueous $H_2Os$, as well as, the organic stream. Moreover, rate of 0.5Q has been considered as one of the requirements in this respect. Specifically, $C_{AO}$ has been considered the total sulfur concentration that has been observed in the feed stream by the experts (Levenspiel, 1999 & Harriott, 2003).

As the reactor is flawlessly mixed, in consequence, the volume *V* the concentration of OSCs is uniformed and is equivalent to the exit concentration, $C_A$. It results in the observation that the reaction rate is also coherent through the reactor and is a function of $C_A$, $r(C_A)$. Henceforth, the material balance equation can be written as:

$$V\frac{dC_A}{dt} = QC_{AO} - QC_A + Vr(C_A) \tag{5.1}$$

The accumulation rate of OSCs in the reactor, *V*dCA/dt* stand for the accumulation rate of sulfur in the reactor. Similarly, $QC_{AO}$ and $Q_{CA}$ represent the mass flow rate of OSCs which are respectively going into and flowing out of the reactor. The difference found between these items is the new mass flow rate into the reactor. *Vr(CA)* is the disappearing rate of sulfur which takes place owing to the oxidation reaction in the system (Levenspiel, 1999 and Harriott, 2003).

Due to the observation that the design in generally based keeping in view the steady state of an operation, for which the rate of accumulation becomes zero, the Equation 5.1 becomes:

$$V\frac{dC_A}{dt} = QC_{AO} - QC_A + Vr(C_A) \tag{5.2}$$

As has already been discussed in the Chapter, here, in a batch process, the pseudo-first-order kinetics for oxidation of OSCs has been instituted. Henceforth, $r(C_A) = -kC_A$, substituting into Equation 5.2 becomes:

$$QC_{AO} - QC_A + V(-KC_A) = 0 \tag{5.3}$$

Equation 5.3 (as shown) may be reorganized in order to obtain the fractional conversion, fs:

$$f_s = \frac{C_{AO} - C_A}{C_{AO}} = \frac{VK}{Q + VK} \tag{5.4}$$

The mean residence time and space time come to be at par with each other for CSTR, and $t = V/Q$. Equation 5.4 becomes

$$f_s = \frac{Kt}{1 + Kt} \tag{5.5}$$

From Equation 5.5, with known value of rate constant, $K$, and a chosen space time, $t$, it is proficient to predict the oxidation conversion of OSCs, $fs$ and calculate the performance of the continuous modified UAOD system.

Flow reactors utilize different performance measures, and space-time and space velocity are some of the measures in this respect. It has been noted that these measures have been related with a natural performance quantity. In Equation 5.6 and 5.7, define these terms.

Space-time: Space-time is the time required to process one reactor volume of feed deliberated at particularly worked out conditions (Levenspiel, 1999).

$$\tau = \frac{1}{s} \tag{5.6}$$

Space-velocity is the number of reactor volumes of feed at particularly worked out conditions which can be operated in unit time (Levenspiel, 1999).

$$s = \frac{1}{\tau} \tag{5.7}$$

The temperature, pressure, and state at which it is selected to measure the volume of material (being fed to the reactor) may now be arbitrarily chosen. Without doubt, then, the value for space-velocity or space-time relies on the conditions chosen. If these are of the stream flowing into the reactor, the reaction between s and τ and the other pertinent variables is shown in Equation 5.8:

$$\tau = \frac{1}{s} = \frac{C_{AO}V}{F_{AO}} = \frac{V}{v_o} = \frac{reactor\ volume}{volumetric\ \ feed\ rate} \tag{5.8}$$

$$\tau = \frac{V}{v_o} = \frac{1{,}000}{95.2} = 10.5 \text{ min}$$

Henceforth, a space-time of 10.5 min denotes that each 10.5 minutes one reactor volume (1,000 ml) of feed on specified conditions is being handled by the reactor.

It was requested by the oil company to have daily production of 20,000 gallon per day with ultra-low sulfur diesel (15 ppm) from Valley Oil with initial sulfur concentration 8,100 ppm. As such, in order to lower the total sulfur content of Valley to less than 15 ppm, for each single organic operation, sulfur compounds need to attain more than 99.9% oxidized; and sulfur can be removed by solvent extraction or alumina adsorption.

In Chapter 4, the GC-SCD the analysis of Valley Oil by modified UAOD process manifests that 4,6-DMDBT is one of the richest sulfur species in original Valley Oil and has approximately 88 ppm sulfur absorption. Consequently, 4,6-DMDBT was crafted for reactor design. The oxidation of 4,6-DMDBT in Valley Oil under modified UAOD conditions follows pseudo-first-order kinetic with rate constant of 0.0231 $\text{min}^{-1}$ at $50^{o}$C.

In order to obtain over 99.9% oxidation of 4,6-DMDBT in Valley Oil, the size of batch type continuous flow reactor can be acquired from Equation 5.4 and, subsequently, Equation 5.9 can be used to uncover the suitable reactor size.

$$V = \frac{C_{AO} - C_A}{C_A} * \frac{Q}{K} \tag{5.9}$$

Where:

$Q$ = 20,000 gallon/day = 476 barrel/day = 0.05 $m^3$/min

$C_{AO}$ = 8,100 ppm, $C_A$ = 15 ppm

$K$ (4,6-DMDBT)= 0.0231 $\text{min}^{-1}$

Therefore, the volume of the batch type continuous flow reactor is

$$V = \frac{88-15}{15} * \frac{0.05}{0.0231} = 10.5\ m^3$$

The treatment rate of Valley Oil for batch type continuous flow system, in the previous section, is 0.303 kg/hour (known as 2.4 gallon per day), reached 99.8% sulfur removal in 1 hours. However, this outcome is still inadequate for the practical application. In the present study, the treatment capacity of Valley Oil has been scaled up ten times with 3.03 kg; similarly, the working volume of the reactor has been increased to 2 liters instead of 1 liter. This is to be noted that the feed rate of has increased to 160 ml/min instead of 95.2 ml /min. Table 5.6 manifests the operation conditions of both studies.

Table 5.6 Operation conditions for CSTR

| Parameters | Small Scale CSTR | Large Scale CSTR |
|---|---|---|
| Valley Oil | 1 kg | 10 kg |
| Sulfur concentration | 8,100 ppm | 8,100 ppm |
| Hydrogen Peroxide (30%) | 100 g | 1000 g |
| RTIL | 25 g | 250 g |
| Acid Catalyst (40% TFA) | 35 g | 350 g |
| Temperature | $50^oC$ +/- $5^oC$ | $50^oC$ +/- $5^oC$ |
| Working volume of reactor | 1 L | 2 L |
| Feed rate | 95.2 ml/min | 152 ml/min |
| Space time | 10.5 min | 13.2 min |

In Table 5.7 are displayed the result for desulfurization efficiency for large scale treatment. Moreover, 88% of desulfurization efficiency has been indicated by the results. In addition, ten minutes has been noted as the period of attainment of the above mentioned efficiency.

This observation also indicates that increase in the treatment volume does not highly affect desulfurization efficiency. During the span of 200 min, 99.7% was the final sulfur reduction rate during the treatment of 3.03 kg/hour. However, 15 ppm was not reached in these conditions. Thus, it was analyzed that 99.9% with 13 ppm was a possible result for the extension of another 30 minutes.

Table 5.7 Summery of desulfurization for both small and large scale CSTR application

| **Time (min)** | **Small scale** | **Desulfurization (%)** | **Large scale** | **Desulfurization (%)** |
|---|---|---|---|---|
| | **Conc. (ppm)** | | **Conc. (ppm)** | |
| 0 | 8,100 | 0 | 8,100 | 0 |
| 10 | 914 | 88.7 | 987 | 87.8 |
| 20 | 779 | 90.4 | 801 | 90.1 |
| 30 | 642 | 92.1 | 684 | 91.6 |
| 40 | 564 | 93.0 | 624 | 92.3 |
| 60 | 314 | 96.1 | 366 | 95.5 |
| 80 | 227 | 97.2 | 265 | 96.6 |
| 140 | 84 | 98.9 | 101 | 98.8 |
| 200 | 15 | 99.8 | 22 | 99.7 |
| 230 | | | 13 | 99.9 |

From literature (Te, et al. 2001; Otsuki, et al. 2000; Collins, et al. 1997), with excess of $H_2O_2$, the oxidation of organic sulfur compounds follow pseudo first order kinetics via carboxylic acid/$H_2O_2$ and polyoxornetalate/$H_2O_2$ systems. As $H_2O_2$ was at hand in excess under modified UAOD process, it is needed for the reaction data to be adjusted to a first-order rate equation. A plot of ln ($C_i$ /$C_o$) versus reaction time is shown in Figure 5.18. From the plot, it shows a linear relationship which substantiates the pseudo-first-order reaction kinetics.

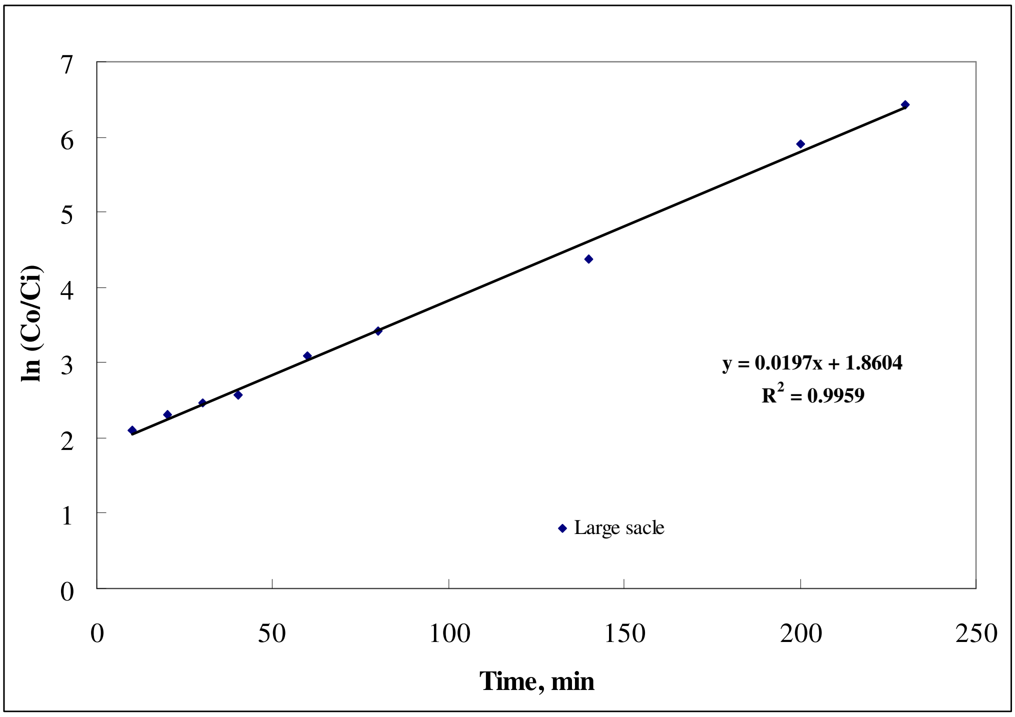


Figure 5.18 Plot of ln ($C_i/C_o$) vs time for Large scale CSTR

The apparent rate constant for oxidation of Valley Oil was determined to be 0.0197 $min^{-1}$. Compare to the oxidation reaction rate of T (0.0196 $min^{-1}$), 2MT (0.0199 $min^{-1}$), 2ET (0.021 $min^{-1}$), BT (0.0276 $min^{-1}$), 2MBT (0.0218 $min^{-1}$), DBT (0.0228 $min^{-1}$) and 4,6-DMDBT (0.0231 $min^{-1}$), it is relatively lower than these OSCs in batch scale.

Because of the fact that the diesel petroleum impel composite schemes there is present viable oxidation among natural sulfur complexes and other unsoaked ingredients, like olefinic complexes. Moreover, the incessant desulfurization component cannot get up to as idealized function conditions as that of in batch scale. This outcome is a highly significant stride in the procedure and can be related to compute the execution of modified UAOD method on diesel fuels as well as to develop the competence of nonstop desulfurization component.

Keeping in view the reason and execution of the qualitative and quantitative models of investigation, manifold reactors can be put to exercise to bond in either series or parallel arrangement. In the current investigation, the elevated sulfur diminution of Valley Oil (99.8%) was effectively manifested by a distinct batch type constant run reactor at conduct rate of 3.03 kg / hour. Therefore, for the amount and execution reason, two or more reactors can be associated in equivalent manner to attain elevated desulfurization competence (99.8%) with superior conduct rate which also gets up to the preliminary requisite of marketable scale.

### 5.3.5 Consumption of Oxidant in Modified UAOD Process

#### 5.3.5.1 Hydrogen Peroxide Concentration Analysis (Standard Method)

It has been noted by most of the experts that different types of analyses can be done for the calculation of concentration of hydrogen peroxide in the aqueous phase. In this regard, some of the analyses are colorimetric, gasometric, volumetric analysis, and quantitative analysis. In this respect, cheaper cost and faster speed has resulted in the selection of volumetric analysis.

In this regard, the concentration of hydrogen peroxide can be quantitative determine by titration methods. In this respect, titration methods are iodimetric, cerium, and permanganate titration methods. In particular, the accuracy and reliability has been achieved by the permanganate titration method. One of the features of this method is that both dilute and concentration solutions can be applied with this method. In this regard, the mechanism of permanganate titration has been shown by the following equation:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

It has been observed that accuracy can be affected by the oxidation of a chloride ion into chlorine, which is presented in the solution. In such cases, the reaction between chloride and permanganate can be slowed down by the addition of manggnous salt.

During the procedure of analysis, a clean weighing bottle is used to transfer around 0.7 gram of hydrogen peroxide, which provides exact calculation of the sample. Subsequently, a 500 ml volumetric flask is used for the transfer of sample, and 500 ml of diluted sample is prepared in this flask. Afterward, a 250 ml Erlenmeyer flask is used for the pipette of 25 ml diluted sample, which was prepared in the volumetric flask. Later, concentrated sulfuric acid in the volume of 1 ml is added, and then, 0.1N $KMnO_4$ is used for the titration during the procedure.

### 5.3.5.2 Results and Discussion

It has been shown by the Chapter 3 and 4 that sulfone formation is facilitated by the modified UAOD process, which also included consumption of hydrogen peroxide. During the modified UAOD process, heat and acid catalyst were also the influencing factors. Moreover, the reduction of hydrogen peroxide may results in a number of possible reactions that may occur in the aqueous solution. In this regard, a number of reactions have been noted, such as hydrogen peroxide has been decomposed with the molecular oxygen, as well as, water thermally. Subsequently, outcome of water is achieved after the conversion of hydrogen peroxide after the oxidation of OSCs. Afterward, acid catalyst decomposed hydrogen peroxide catalytically, and a microenvironment may be decomposed by hydrogen peroxide, with subject to a high-speed rotor.

The following calculation shows the stoichiometric requirement and actual dosage usage for the experiment. Stoichiometric mole ratio between sulfur and oxidant is 1:2. That means one mole of sulfur requires two mole of oxidant to be oxidized. In the experimental condition, 1000 gram of Valley Oil is treated with 100 gram of 30% grade hydrogen peroxide.

Amount of sulfur in Valley Oil:

$$mole(sulfur) = \frac{8{,}100}{1{,}000} \times \frac{1}{32} = 0.253 \frac{mole\ of\ sulfur}{kg\ diesel}$$

With stoichiometric mole ratio, the oxidant needs to be at least 0.506 mole/kg diesel. Therefore, amount of oxidant that actually used:

$$mole(oxidant) = 100 \times 30\% \times \frac{1}{32} = 0.882 \frac{mole\ of\ oxidant}{kg\ diesel}$$

The theoretical stoichiometric ratio was compared with the real stoichiometric mole ratio, and slightly high ratio of the later one was found, as 1:3.53

was the ration of sulfur and oxidant. In other words, the requirement of desulfurization process was fulfilled by the presence of enough oxidants. In this regard, the stoichiometric consumption of hydrogen peroxide has been shown by the Figure 5.19. Moreover, the concentration of residual hydrogen peroxide has been related with the consumption. Thus, good selectivity has been shown by the sulfur oxidants during the process.

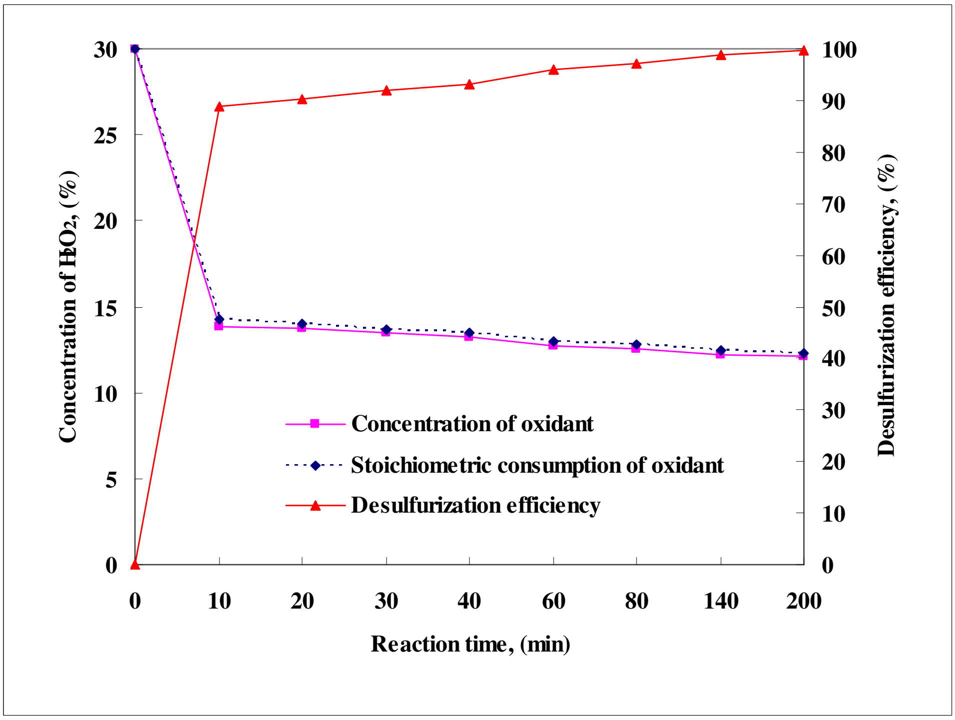


Figure 5.19 $H_2O_2$ comparisons between stoichiometric and actual consumption

The desulfurization efficiency has been shown by the following Figure 5.20, and a aqueous phase has been considered for the spending of this efficiency. In this regard, it was found that catalyst, IL, as well as, hydrogen peroxide was included in this phase. Subsequently, the presence and utilization of oxidants has been indicated by the 69% of the desulfurization efficiency in the spent oxidant.

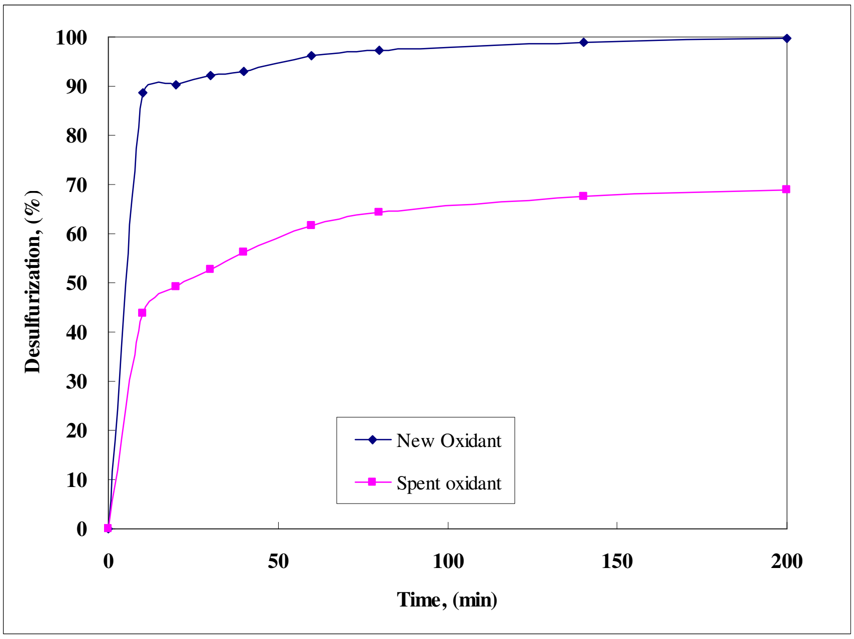


Figure 5.20 Desulfurization of Valley Oil with new and spent $H_2O_2$

Desulfurization that has occurred second time has been shown by the Figure 5.21, which has also noted the consumption of hydrogen peroxide. In addition, it has been shown by the results that the reduction of hydrogen peroxide has resulted in the ending of desulfurization process. Specifically, 14,080 ppm came out to be the required amount of sulfur that was required for the process with hydrogen peroxide in the volume of 100g. However, from the experimental data, total amount of sulfur that can be treated is 13,674 ppm .In this regard, an error of 2.9% was observed during the comparison of actual and experimental data.

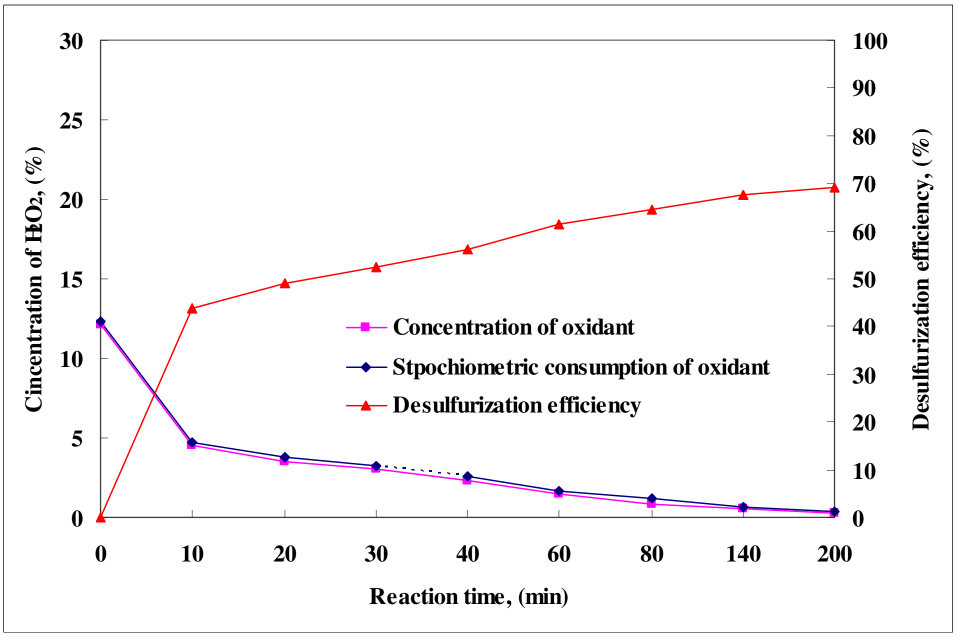


Figure 5.21 Spent $H_2O_2$ comparisons between stoichiometric and actual consumption

### 5.3.6 Effect of Modified UAOD Process on Distillation Properties of Diesel Fuel

Nowadays, petroleum industry has become one of the most sectors of the industrial world. In particular, a number of processes are utilized and implemented for the best-possible outcomes; however, one of the most widely used processes for the separation of elements is the distillation. It has been noted by most of the experts that a number of procedures have to be implemented before the market distribution. Secondly, control should be maintained during the refining process, and physical limitations should be estimated and evaluated during the whole process. In this regard, it has been evaluated by most of the experts that all the above mentioned procedures and tasks require the boiling point distribution, as well as, its proper knowledge, which is very important for all these procedures. In fact, it has been an observation that engineering calculations can be made adequately by the utilization of a distillation curve's general shape (Speight, 1999).

For diesel fuels, as well as, for almost every chemical reactions and processes, the boiling points at the initial period, as well as, at the final period, and their determination is very important for the successful carrying out of the processes. In addition, $T_{10}$, $T_{50}$, and $T_{90}$ also have to be determined for the diesel fuels, which can be found in the distillation curve. By the carrying out of the above mentioned determinations, fuel specifications can be met, and the cetane index, which is a very important factor, can be calculated easily (Song, et al. 2000).

Conventionally, distillation curve for the crude oil and related products was used for the determination by the utilization of procedures of physical distillation. In particular, the American Society of Testing and Materials (ASTM), was responsible for the provision of necessary specifications related to it. In the past, more than 0.5 L sample was required during the carrying out of above mentioned procedures, and completion used to take around two, and sometimes, even more days. Moreover, relatively poor accuracy was the outcome of these processes, which was manual, and used to consume a lot of time (Roussis, et al. 2000).

Nowadays, a new process has been innovated in the petroleum industry, which has fastened the previous processes, and has provided accurate outcomes. In this regard, true distillation profile is simulated precisely by an automatic and faster process by GC-SIMDIS, which has been referred as the development of gas chromatographic simulated distillation. Unlike previous procedures, boiling points of hydrocarbons have been given due consideration with their relationship with the retention times on non-polar GC columns. Thus, the above mentioned linear relationship is used and determined for this innovative method.

The original and desulfurized Valley Oil has been considered for the showing of GC-SIMIDIS weight percent data, as been done in the Table 5.8. Subsequently, Figure 5.22 has been utilized for the representation of distillation profiles of the above mentioned distillation profiles according to the results. In particular, different stage of diesel fuel, such as, original, oxidized, and desulfurized kinds have been considered in the above mentioned distillation profiles.

Conclusively, the diesel fuels have been benefited by modified UAOD process, and has provided better results without the provision of any side or negative effects on the characteristics of the diesel fuels. Thus, the process does not change any chemical or physical characteristics of the diesel fuels, which is one of the most important features of this process.

Table 5.8 Raw data of GC-SIMDIS wt% for original and desulfurized Valley Oil

| **Yield, wt%** | **Boiling Point, $^oF$** | **Boiling Point, $^oF$** |
|---|---|---|
| | **Original Valley Oil** | **Desulfurized Valley Oil** |
| IBP(0.5%) | 144 | 149 |
| 5 | 197 | 202 |
| 10 | 208 | 216 |
| 15 | 215 | 220 |
| 20 | 221 | 229 |
| 25 | 227 | 232 |
| 30 | 232 | 240 |
| 35 | 237 | 248 |
| 40 | 243 | 252 |
| 45 | 249 | 257 |
| 50 | 255 | 264 |
| 55 | 262 | 268 |
| 60 | 272 | 275 |
| 65 | 280 | 285 |
| 70 | 290 | 293 |
| 75 | 303 | 305 |
| 80 | 319 | 320 |
| 85 | 340 | 337 |
| 90 | 377 | 371 |
| 95 | 460 | 450 |
| End Pt (99.5) | 479 | 484 |

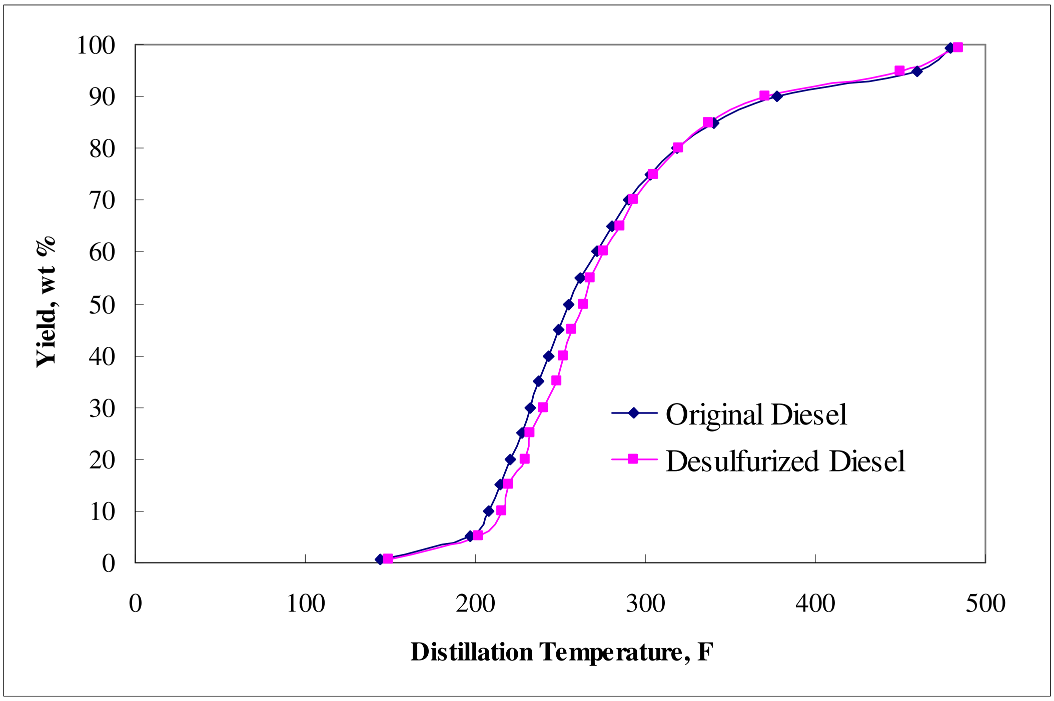


Figure 5.22 GC-SIMDIS profile of original and desulfurized Valley Oil in modified UAOD process

### 5.3.7 Adsorption Model: Fluidized Bed

In Figure 5.23, is shown the idealized breakthrough curve, the role of effluent concentration of solute has been played by the *C*, and effluent per unit cross-sectional area has been determined by the total volume, *V*. It has been observed that $C_B$ and $C_E$ are the breakpoint and exhaustion point respectively, which shares a sharp rise in the curve. Moreover, the main segment of the adsorption process has been represented by these points (Yen, et al. 1999).

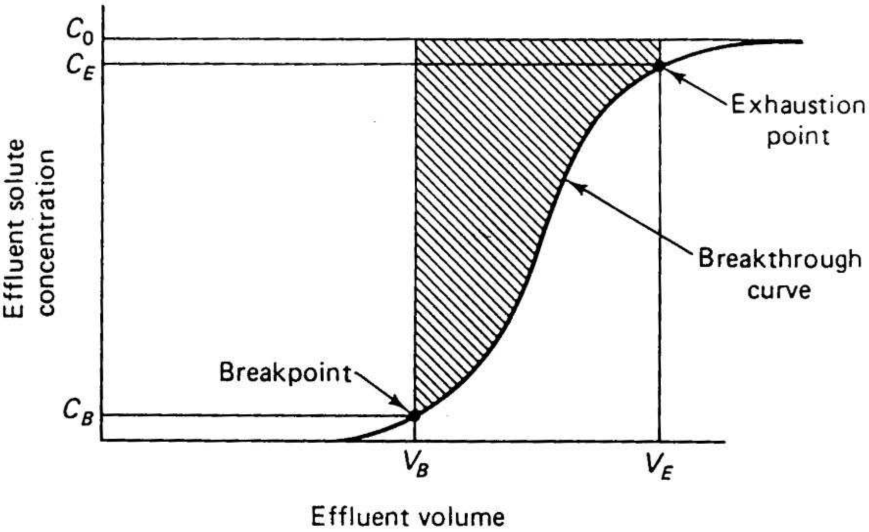


Figure 5.23 Idealized breakthrough curve for fixed-bed adsorber (Yen, et al. 1999)

The rationale of the analysis is to predict the total quantity of the effluent (sulfur) at the cut-off point and to envisage the shape of the breakthrough curve between $C_B$ and $C_E$. With the help of the scheme shown in Figure 5.24 (Yen, et al. 1999), some of the parameters can be defined upon which the formulations are based. Firstly, a constant height has been determined by $Z_a$, which represents the height, as well as, length of the primary adsorption zone, which has been supported by an adsorption from points of $C_E$ to $C_B$.

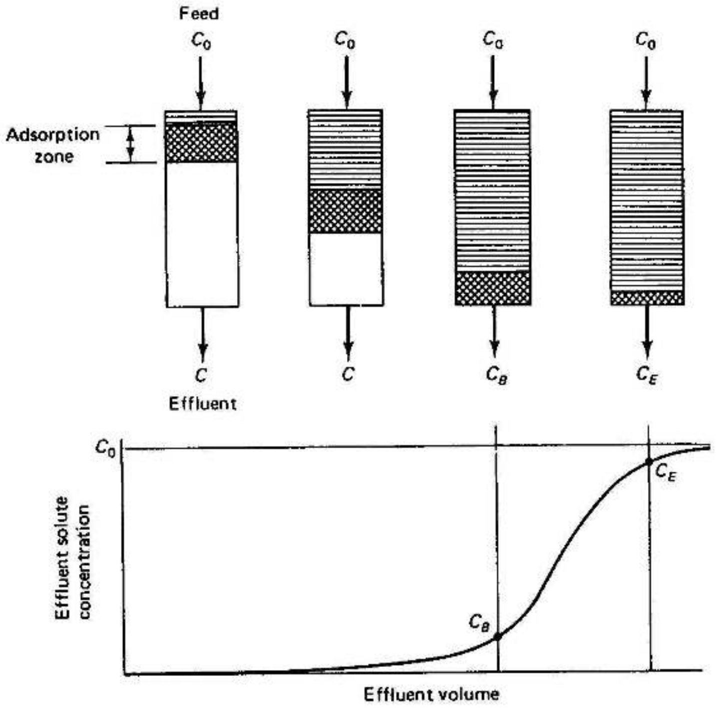


Figure 5.24 Movement of adsorption zone for fluidized bed (Yen, et al. 1999)

Equation 5.10 shows the total time, $t_E$, for the primary adsorption zone which is to be established and moved down and out of the column:

$$t_E = \frac{V_E}{Q_t} \tag{5.10}$$

Equation 5.11 shows the time required for the shifting of the entire zone in the column is $t_A$. Here $V_E$ is the volume at exhaustion and $Q_t$ is the flow rate to the absorber.

$$t_A = \frac{V_E - V_B}{Q_t} \tag{5.11}$$

Equation 5.12 below is written the total amount of adsorbate (solute) $S_s$ which accrues at the point of whole dissemination (the entire column of adsorbent is in equilibrium with $C_o$ in the influent):

$$S_s = V_B * Initital\ concentration\ of\ diesel\ fuel \tag{5.12}$$

The quantity of adsorbate (oxidized sulfur) is represented by the grey area on the breakthrough curve. It is adsorbed by the adarobent (alumina) between the breakpoint and the exhaustion. This total of adsorbate can be calculated by incorporating the quantity of ($C_o$-$C$) over $V$ between the limits of $V_E$ and $V_B$. This integration can be done on Microsoft Excel application of Windows and is shown in Equation 5.13 below:

$$S_{SE} = Total\ shaded\ area \tag{5.13}$$

#### 5.3.7.1 Adsorption Study on F-76

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. The comparative concentration of the effluents from the acidic alumina is shown below in Table 5.9, and Figure 5.25 shows the breakthrough curve of acidic alumina for F-76 diesel fuel.

Table 5.9 Effluent sulfur concentration through FBR with F-76

| Sample No. | Effluent Vol. (ml) | Effluent Conc. (ppm) |
|---|---|---|
| 0 | 0 | 0 |
| 1 | 30 | 3 |
| 2 | 60 | 4 |
| 3 | 90 | 4 |
| 4 | 120 | 5 |
| 5 | 150 | 2 |
| 6 | 180 | 2 |
| 7 | 210 | 1 |
| 8 | 240 | 1 |
| 9 | 270 | 9 |
| 10 | 300 | 7 |
| 11 | 330 | 6 |
| 12 | 360 | 4 |
| 13 | 390 | 5 |
| 14 | 420 | 8 |
| 15 | 450 | 9 |
| 16 | 480 | 12 |
| 17 | 510 | 10 |
| 18 | 540 | 8 |
| 19 | 570 | 7 |
| 20 | 600 | 6 |
| 21 | 630 | 18 |
| 22 | 660 | 8 |
| 23 | 690 | 9 |
| 24 | 720 | 12 |
| 25 | 750 | 8 |
| 26 | 780 | 7 |
| 27 | 810 | 5 |
| 28 | 840 | 13 |

Table 5.9: Continued

| Sample No. | Effluent Vol. (ml) | Effluent Conc. (ppm) |
|---|---|---|
| 29 | 870 | 15 |
| 30 | 900 | 17 |
| 31 | 930 | 9 |
| 32 | 960 | 22 |
| 33 | 990 | 16 |
| 34 | 1020 | 12 |
| 35 | 1050 | 15 |
| 36 | 1080 | 15 |
| 37 | 1110 | 9 |
| 38 | 1140 | 198 |
| 39 | 1170 | 1225 |
| 40 | 1200 | 1704 |
| 41 | 1230 | 2417 |
| 42 | 1260 | 2800 |
| 43 | 1290 | 3137 |
| 44 | 1320 | 3404 |
| 45 | 1350 | 3551 |
| 46 | 1380 | 3716 |
| 47 | 1410 | 3810 |
| 48 | 1440 | 3944 |
| 49 | 1470 | 4018 |
| 50 | 1500 | 4121 |
| 51 | 1530 | 4133 |
| 52 | 1560 | 4176 |
| 53 | 1590 | 4199 |
| 54 | 1620 | 4201 |
| 55 | 1650 | 4210 |
| 56 | 1680 | 4228 |

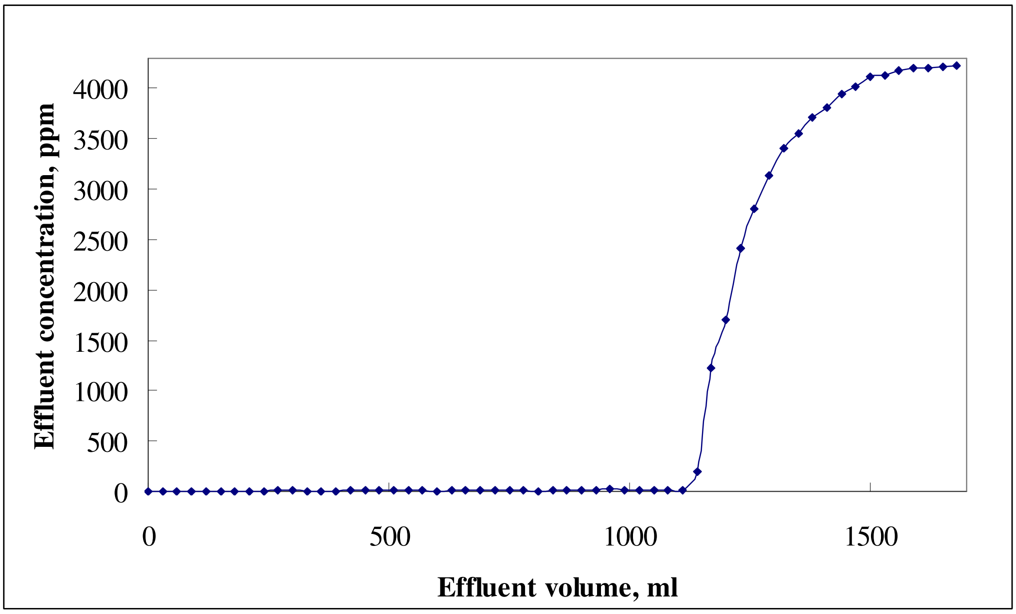


Figure 5.25 Breakthrough curve of acidic alumina for F-76

As shown below, with the help of Equation 5.10, $t_E$ can be put to a sound calculation of the quantities as:

$$Q_t = \frac{volume}{time} = \frac{30ml}{4.5\min} = 6.67ml/\min$$

$$t_E = \frac{V_E}{Q_t} = \frac{1{,}620\ ml}{6.67} = 242.8\min$$

As shown below, with the help of Equation 5.11, $t_A$ can be put to a sound calculation of the quantities as:

$$t_A = \frac{V_E - V_B}{Q_t} = \frac{1{,}620 - 1{,}140}{6.67} = 72\min$$

As shown below, with the help of Equation 5.12, $S_s$ can be put to a sound calculation of the quantities as:

$$S_s = V_B * diesel\ conc. = \frac{1.14 * 0.8 * 1000 * 4{,}200}{1{,}000} = 3{,}830\ mg$$

As shown below, with the help of Equation 5.13, $S_{SE}$ can be put to a sound calculation of the quantities as:

$$S_{SE} = 1{,}561\ mg$$

From the data in Table 5.9, the area behind the curve in Figure 5.25 is calculated (1,680 ml):

1,620 ml F-76 diesel x 0.8 g/ml = 1,296 g F-76

1,296 g F-76 / 480 g alumina = 2.7 g F-76 / g alumina

Original sulfur concentration in F-76 diesel is 4,220 ppm. Therefore in 2.7 g of F-76, total amount of sulfur can be adsorb per gram alumina is:

2.7 g x (4,220 /$10^6$) x (1,000 mg/g) = **11.34** mg sulfur / g alumina

As shown in the calculation above, 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, Etemadi et al. used packed column instead of fluidized bed reactor. However, according to his thesis and published literature on MGO diesel, his adsorption ability is 12.59 mg sulfur per gram of alumina (Etemadi, et al. 2007). The percentage is 6.1%. 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 fluidized 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.

The photo in Figure 5.26 shows the increment of sulfur concentration by change in color of solution, from left to right. As the alumina reaches its saturation point in the process, the oxidize sulfur cannot be adsorbed, therefore, the color of the diesel fuel being processed tends to have a brownish shade.

Figure 5.26 Color change of effluent due to saturation of adsorbent

### 5.3.7.2 Adsorption Study on Valley Oil

After adding passing Valley Oil through the fluidized bed, effluent samples were collected, the sample concentration was measured by SLFA-20 sulfur analyzer. The comparative concentration of the effluents from the acidic alumina is shown below in Table 5.10, and Figure 5.26 shows the breakthrough curve of acidic alumina for Valley Oil.

Table 5.10 Effluent sulfur concentration through FBR with Valley Oil

| **Sample No.** | **Effluent Vol. (ml)** | **Effluent Conc. (ppm)** |
|---|---|---|
| 0 | 0 | 0 |
| 1 | 30 | 4 |
| 2 | 60 | 5 |
| 3 | 90 | 1 |
| 4 | 120 | 3 |
| 5 | 150 | 3 |
| 6 | 180 | 7 |
| 7 | 210 | 5 |
| 8 | 240 | 9 |
| 9 | 270 | 12 |
| 10 | 300 | 15 |
| 11 | 330 | 10 |
| 12 | 360 | 9 |
| 13 | 390 | 10 |
| 14 | 420 | 11 |
| 15 | 450 | 13 |
| 16 | 480 | 8 |

Table 5.10: Continued

| Sample No. | Effluent Vol. (ml) | Effluent Conc. (ppm) |
|---|---|---|
| 17 | 510 | 7 |
| 18 | 540 | 11 |
| 19 | 570 | 12 |
| 20 | 600 | 13 |
| 21 | 630 | 425 |
| 22 | 660 | 1879 |
| 23 | 690 | 2548 |
| 24 | 720 | 3604 |
| 25 | 750 | 4667 |
| 26 | 780 | 5111 |
| 27 | 810 | 5741 |
| 28 | 840 | 6112 |
| 29 | 870 | 6666 |
| 30 | 900 | 7225 |
| 31 | 930 | 7778 |
| 32 | 960 | 7989 |
| 33 | 990 | 8019 |
| 34 | 1020 | 8088 |
| 35 | 1050 | 8119 |

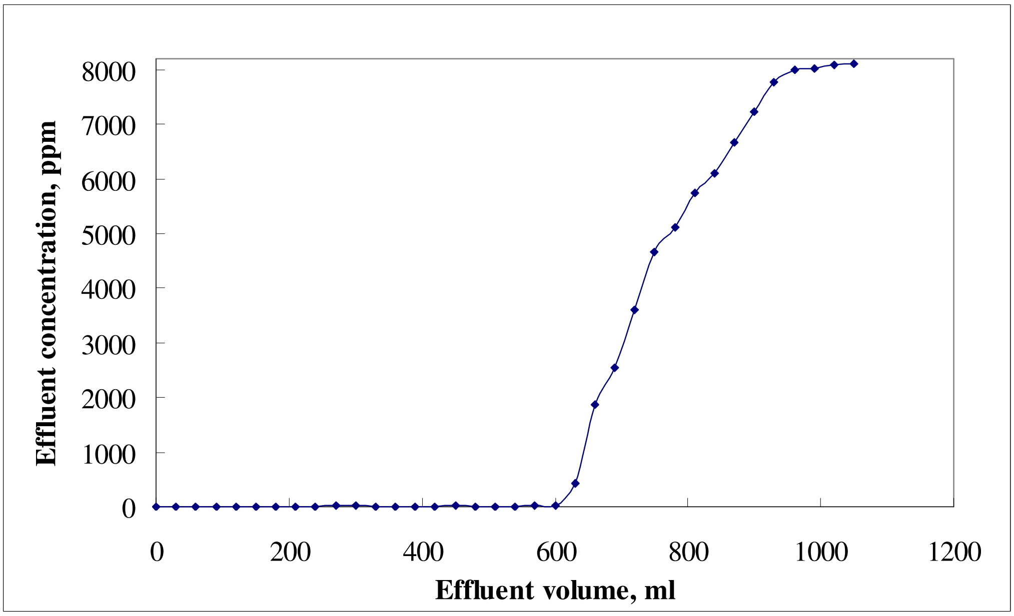


Figure 5.27 Breakthrough curve of acidic alumina for Valley Oil

As shown below, with the help of Equation 5.10, $t_E$ can be put to a sound calculation of the quantities as:

$$Q_t = \frac{volume}{time} = \frac{30ml}{4.5\,\text{min}} = 6.67ml/\text{min}$$

$$t_E = \frac{V_E}{Q_t} = \frac{1{,}022\ ml}{6.67} = 153.2\,\text{min}$$

As shown below, with the help of Equation 5.11, $t_A$ can be put to a sound calculation of the quantities as:

$$t_A = \frac{V_E - V_B}{Q_t} = \frac{1{,}022 - 630}{6.67} = 59\,\text{min}$$

As shown below, with the help of Equation 5.12, $S_s$ can be put to a sound calculation of the quantities as:

$$S_s = V_B * diesel\ conc. = \frac{0.63 * 0.8 * 1000 * 8{,}100}{1{,}000} = 4{,}082\ mg$$

As shown below, with the help of Equation 5.13 (on the Excel application program of Windows), $S_{SE}$ can be put to a sound calculation of the quantities as:

$$S_{SE} = 1{,}980\ mg$$

From the data in Table 5.10, the area behind the curve in Figure 5.26 is calculated (1,022 ml):

1,022 ml Valley Oil x 0.8 g/ml = 817.8 g Valley Oil

817.8 g Valley Oil / 480 g alumina = 1.7 g Valley Oil / g alumina

Original sulfur concentration in Valley Oil diesel is 8,100 ppm. Therefore in 1.7 g of Valley Oil, total amount of sulfur can be adsorb per gram alumina is:

1.7 g x (8,100 /$10^6$) x (1,000 mg/g) = **<u>13.8</u>** mg sulfur / g alumina

As has been discussed and shown from the calculation above, 1 gram of alumina can adsorb 13.8 mg of organic sulfur compound. This is to be noted once again that this is very close to the previous results by results by Etemadi, et al. 2007. According to results by Etemadi, et al. 2007, experiment the result is 12.59 mg sulfur per gram of alumina and the error percentage is 8.7%. Here it is to be registered that it is obvious at that higher sulfur content diesel, the adsorption becomes saturated in a shorter span of time.

In addition, alumina recycle has been used for the conduction of other experiments. It has been noted that the recycling ability of the alumina has not been considered by the comparison that has been done in this study. In the result, a reasonable range of capacity has been acquired from it. It has been studied and analyzed by various experts that 91% of the capacity can be kept by the alumina in the conditions of 550ºC during the process of its regeneration.

The above statement has been confirmed by 2 time recycles. Table 5.11 illustrates the relative concentration of the effluents from the acidic alumina with 2 recycles. In Figure 5.27 is illustrated the breakthrough curve with recycles. Moving along the same line of our analysis, it is found that the result shows that after 2 times of recycling, the adsorption ability remains constant as compared to the fresh alumina. Henceforth, the alumina structure does not become decomposed or is not lost after calcine stage. In this regard, ability of reduction of huge amount of adsorbent cost by the process has been shown by it. However, a large-scale study has been considered for the above mentioned capability of the process. In addition, one of the advantages of this process is that recycling can be done many times of the alumina, if proper care is given to it.

Table 5.11 Effluent sulfur concentration with recycle acidic alumina

| **Sample No.** | **Effluent Vol. (ml)** | | **Effluent Conc. (ppm)** | |
|---|---|---|---|---|
| | | Fresh | Recycle 1 | Recycle 2 |
| 0 | 0 | 0 | 0 | 2 |
| 1 | 30 | 4 | 0 | 2 |
| 2 | 60 | 5 | 1 | 1 |
| 3 | 90 | 1 | 4 | 0 |
| 4 | 120 | 3 | 7 | 2 |
| 5 | 150 | 3 | 9 | 3 |
| 6 | 180 | 7 | 5 | 7 |
| 7 | 210 | 5 | 4 | 5 |
| 8 | 240 | 9 | 8 | 11 |
| 9 | 270 | 12 | 8 | 12 |
| 10 | 300 | 15 | 7 | 15 |
| 11 | 330 | 10 | 6 | 9 |
| 12 | 360 | 9 | 5 | 7 |
| 13 | 390 | 10 | 12 | 5 |
| 14 | 420 | 11 | 7 | 4 |
| 15 | 450 | 13 | 2 | 8 |
| 16 | 480 | 8 | 9 | 9 |
| 17 | 510 | 7 | 8 | 18 |
| 18 | 540 | 11 | 22 | 12 |
| 19 | 570 | 12 | 14 | 8 |
| 20 | 600 | 13 | 22 | 17 |
| 21 | 630 | 425 | 501 | 478 |
| 22 | 660 | 1879 | 1944 | 1789 |
| 23 | 690 | 2548 | 2640 | 2341 |

Table 5.11: Continued

| **Sample No.** | **Effluent Vol. (ml)** | | **Effluent Conc. (ppm)** | |
|---|---|---|---|---|
| | | Fresh | Recycle 1 | Recycle 2 |
| 24 | 720 | 3604 | 3714 | 3588 |
| 25 | 750 | 4667 | 4799 | 4479 |
| 26 | 780 | 5111 | 5325 | 5219 |
| 27 | 810 | 5741 | 5688 | 5510 |
| 28 | 840 | 6112 | 6344 | 6071 |
| 29 | 870 | 6666 | 6798 | 6547 |
| 30 | 900 | 7225 | 7410 | 7100 |
| 31 | 930 | 7778 | 7912 | 7691 |
| 32 | 960 | 7989 | 8014 | 7880 |
| 33 | 990 | 8019 | 8088 | 7994 |
| 34 | 1020 | 8088 | 8079 | 8048 |
| 35 | 1050 | 8119 | 8158 | 8088 |

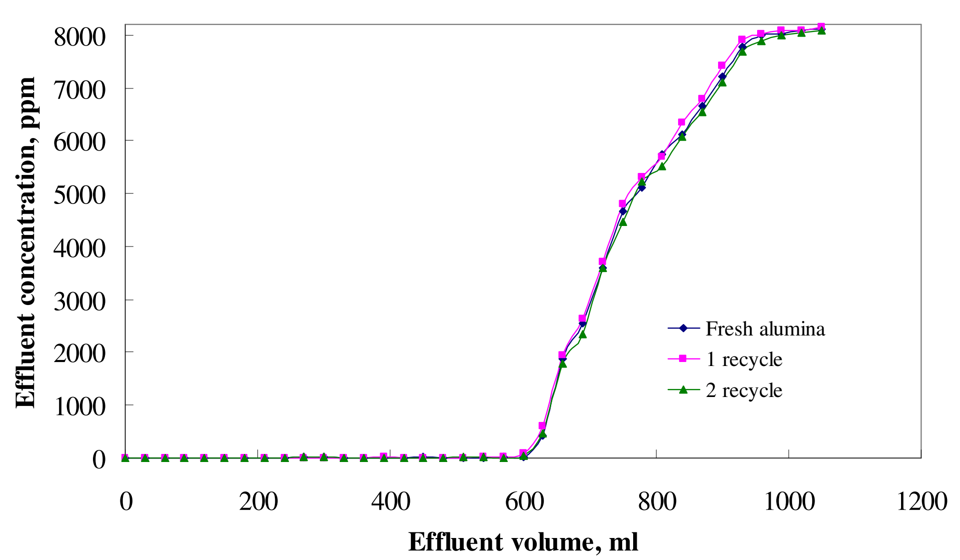


Figure 5.28 Breakthrough curve with recycle acidic alumina

### 5.3.8 Economic Analysis

Based on the experimental results acquired from the batch type continuous flow system on Valley Oil, an analysis for economic feasibility is conducted to obtain information for the purpose of cost and maintenance estimate for industrial continuous flow system.

This constantly operated and monitored desulfurization system has been successfully demonstrated at the treatment rate of 0.06 bpd. From the concerned study also indicates that the used acid catalyst, that is, RTIL and alumina, can be recycled for at least 3 times. However, owing to the reaction, the reactivity of catalyst will debase gradually at some stage in the reaction procedure. Literally, the market value for the in use material takes into account primarily the expenditure of electricity and employment of chemicals e.g. hydrogen peroxide and acid catalyst.

Keeping as the foundation the retail price (provided by Sigma-Aldrich), the chemical price for each chemical item goes through a fluctuation of price proportionate to the bulk purchase. This simply means that the chemical cost used on the commercial level, is much cheaper as compared to the chemical used for lab purposes, which are certainly purchased in low amount and obviously with higher price fluctuation. It was found that the bulk (and cheaper) price relativity is based on 5,000 gallon of daily purchase of Valley Oil production except for RTIL, because Sigma-Aldrich did not have commercialized price for RTIL. On the contrary, for lab usage the retail price cost is \$300/kg. On the commercial scale, the price is usually three times less than the lab retail price. Therefore, the cost of RTIL on commercial level can be safely assumed to be \$100/kg. Table 5.12 provided by Sigma-Aldrich displays the cost of chemical items.

Henceforth, it is assumed that RTIL and acid catalysts can be used for 20 times recycling, and alumina can be used for 100 times recycling. It is shown from section 5.3.5 that the hydrogen peroxide can be utilized 95% (only oxidized OSCs). The operating cost of hydrogen peroxide used in the form of 35% aqueous solution is 7 cent/gallon of desulfurization Valley Oil. Furthermore, the acid catalyst is estimated to be 9 cent/gallon; the alumina is 12 cent/gallon and RTIL is 23 cent/gallon of desulfurization Valley Oil. The total chemical cost, thus, to desulfurize Valley Oil is 52 cent. In Table 5.12 the illustration of the summery of economical analysis is given.

Table 5.12 Economic analysis of modified UAOD process

| ***Chemical Row Material Calculation*** | | |
|---|---|---|
| **Row Material Cost** | | |
| **Item** | **US$** | |
| Cost of $H_2O_2$ (35%), $/kg | 0.51 | |
| Cost of Acid Catalyst 1 (99.7%) , $/kg | 15.50 | |
| Cost of Acid Catalyst 2 (99%), $/kg | 24.54 | |
| Cost of Alumina Oxide, $/kg | 13.15 | |
| Cost of Ionic Liquid, $/kg | 100 | |
| **Calculation of Row Material Cost** | | |
| **Item** | **Amount (gram)** | **US$** |
| $H_2O_2$ | 86 | 0.04 |
| Acid Catalyst 1 (20X recycle) | 42 | 0.03 |
| Acid Catalyst 2 (20X recycle) | 28 | 0.03 |
| Alumina Oxide (100X recycle) | 620 | 0.08 |
| Ionic Liquid (20X recycle) | 30 | 0.15 |
| | | |
| **Total Cost, $/1000 gram of Valley Oil** | | 0.34 |
| | | |
| **Total Cost, $/gallon** | | 0.52 |

This kind of consignment incessant running scheme is for the time being in its early years. The current work is focused onto the exploration and growth of its prospective so that others can tailor-make and convert this expertise for practical large-scale operations. For instance, low-priced RTIL can be substituted with existing RTIL with lesser monetary charge. To a great extent, hefty level maneuvers can decrease the expenditure of hydrogen peroxide, RTIL, and acid channel with notion of reprocessing and reutilization of the catalyst.

## 5.4 Summary

A pilot study has been carried out in this chapter. In this regard, a perspective of a continuous flow stirred tank reactor (CSTR) has been related for the observation of a batch type continuous flow system. In this chapter, optimized reaction conditions, as well as, reactor configurations have been considered for the indications of the experimental results. In the above mentioned system, both F-76, as well as, Valley Oil can attain ultra low sulfur diesel, which has been referred as ULSD in the chapter. Although, desulfurization efficiency has been the same, as it was in the batch operation, ninety-nine percent.

Several changes have been observed during the process, in order to optimize the reaction condition of CSTR. In this regard, utilization of catalyst, IL, as well as, mixing method has been included for the achievement of above mentioned changes. In addition, ultrasound, magnetic stir, and several other mixing strategies were compared in this respect. Specifically, 5,000 rpm with the 50°C of reaction temperature was observed during the process with high shear mixer. Under this condition, aqueous phase was maintained, and ULSD fuel was achieved. In addition, better desulfurization was provided by it as compared with the ultrasound. The oxidation would be enhanced by the ultrasound, as it has been explained in the previous works. (Mei, et al. 2003 and Wan, et al. 2005). However, necessity of ultrasound has not been observed in the modified UAOD process. In the result, saving of high cost related to the instrument and equipment of electricity and ultrasound can be done, and several other advantages can be achieved through it.

In batch study, to achieve 99.9% desulfurization, it required 20% TFA as the catalyst concentration. However, in pilot study, 20% TFA is not sufficient to desulfurize high sulfur content diesel fuel (Valley Oil), therefore, 40% TFA has been used for new catalyst concentration. Although, 1/10 of catalyst usage has been used in pilot study compare to batch study, and still achieve high desulfurization efficiency. Therefore, cost of acid catalyst can be saved.

It has been observed that weight ratio of IL does not affect the desulfurization efficiency, as it has been with the ratio of 1:1 in batch study, as well as, 1:100 with the ionic liquid in pilot study. In other words, system only required small amount of ionic liquid. Thus, transfer of oxidant from aqueous phase can be done with high affinity of ionic liquid into the organic phase, as observed during the process.

The interaction of organic sulfur compound from diesel fuels with the oxidant has been uniquely illustrated by the hydrogen peroxide consumption technique. In this regard, the changes of OSCs have been traced by the employment of this technique during the study. It has been indicated during the study that sulfur compounds can only react the oxidant, and hydrocarbon compound will be saved from diesel fuel. Moreover, high efficiency, as well as, high selectivity has been demonstrated by the modified UAOD process. In addition, the applicability of modified UAOD on diesel fuels has been confirmed by the GC-SIMDIS analysis.

Specifically, high sulfur reduction of Valley Oil with 99.9% of desulfurization efficiency has been successfully demonstrated by the study that has considered the large-scale operations of the continuous modified UAOD process. However, treatment rate of 3.03 kg/hr has been considered during the study.

Moreover, very short time was utilized during the study by the desulfurization efficiency that reacted at 90%. In the result, it was indicated that oxidation reaction could be accelerated powerfully by the above mentioned continuous flow system. Additionally, the pseudo first order kinetics was followed by the process, as the $H_2O_2$ was present excessively during the study.

It has been observed that removal of oxidized sulfur is usually done by the fluidized bed reactor. In addition, 11.8 mg S/g alumina and 13.8 mg S/g alumina has shown similar adsorption capacity during the study of diesel fuels, such as F-76 and Valley Oil. Although, similar results were shown by the fluidized bed reactor regarding the adsorption capacity, as compared to the packed column study. However, higher adsorption capacity was one of the advantages that have been provided by the fluidized bed reactor. In addition, adsorption ability of this reactor cannot be weakened by its recycling. Thus, lower cost would be borne for the replacement of new adsorbent.

Production of ULSD fuel can be done effectively by the provision of a commercially viable solution by the modified UAOD process, if proper process design and chemicals are utilized during the process, as indicated by the preliminary economic analysis.

# CHAPTER 6

# CONCEPETUAL MODEL OF MODIFIED UAOD PROCESS

## 6.1 Introduction

In modified UAOD process, results indicate that OSCs can be oxidized and catalysis by acid catalyst and IL in a bi-phase system. The reaction include ion pair catalysis, phase transfer catalysis and oxygen transfer between organic phase and aqueous phase. The desulfurization can be improved by multi ion pair catalysis with quandary ammonium salt and IL, unlike normal phase transfer catalysis with only one ion pair. Multi ion pair catalysis can enhances the desulfurization significantly. This study has developed the mechanism of modified UAOD process based on the previous batch and pilot studies.

## 6.2 Mechanism of Modified UAOD Process

Modified UAOD process is designed to combine the following complementary techniques: IL, oxidant, acid catalyst, phase transfer agent and mixing. The reaction was carried under liquid-liquid mixing with two immiscible phases (organic and aqueous phase). Organic phase is substrate contain organic sulfur compound, and aqueous phase include oxidant, IL and acid catalyst. A conceptual model of mechanism for modified UAOD process has been developed, shown as Figure 6.1 which consists of seven steps.

Step (1): In the presence of excess of $H_2O_2$, the acid catalyst: acetic acid and tri-fluoro acetic acid, are peroxidized and disaggregated to form anionic per-acetic ion [$CH_3COOO^-$] and per-trifluoro acetic ion [$CF_3COOO^-$].

Step (2): With the presence of quaternary ammonium salts [$Q^+F^-$], it has larger lipophilic cations and smaller hydrophilic anion can function as PTA to transfer per-acetic and per-trifluoro acetic anion into organic phase. In other words, active nucleophile anion ([$Y^-$]: $CH_3COOO^-$ and $CF_3COOO^-$) is transferred from aqueous phase into organic phase that allow reaction occur. Figure 6.2 shows the phase transfer catalysis also named Starks' extraction mechanism. Nucleophile anion [$Y^-$] is extract with quaternary ammonium cation [$Q^+$] and forming ion-pair [$Q^+Y^-$] that enable transferred from the aqueous phase into the organic phase. Therefore, the reaction becomes an organic phase limited reaction. Most of ion pairs are thermodynamically distinct species coexisting in equilibrium with the free ions. From literature (Keller, 1979, 1986, 1992), for a given quaternary cation, anions with decreasing order extractability at following order: picrate > $MnO_4^-$ > $ClO_4^-$ > $SCN^-$ > $I^-$ > $ClO_3^-$ > $NO_3^-$ > $Br^-$ > ($CN^-$, $BrO_3^-$, benzoate) > ($NO_2^-$, $Cl^-$) > $HSO_4^-$ > ($HCO_3^-$, acetate) > ($F^-$, $OH^-$) > $SO_4^{2-}$ > $CO_3^{2-}$ > $PO_4^{3-}$. Tetraoctyl ammonium fluoride (TAOF) has lower lipophilicity that results better ability for hydration and dissociation. Henceforth, it permits the faster extractability rate of ion pair and transfer into the organic phases.

Step (3): Assume ion pairs in the aqueous phase transfer into organic phase were faster than the nucleophilic substitution reaction, with excess amount of the nucleophilic anion in the aqueous phase by a fixed concentration of catalyst. The concentration of nucleophile [$Y^-$] in the organic phase is in steady state and the rate of consumption of organic sulfur compound is follow by pseudo-first order, moreover, in organic phase, the nucleophilic reaction will be homogeneous. Therefore, the rate constant will be proportional to the catalyst concentration.

Step (4): In organic phase, organic sulfur compounds are oxidized to its corresponding sulfone by the ion pair [$Q^+Y^-$], ion pair also enhance the efficiency and transfer process. After oxidation, the reduced ion pair returns back to aqueous phase. With quaternary ammonium salts, hydrogen peroxide and catalyst are in excessive amount, there is no change in the concentration of [$Q^+CH_3COOO^-$] and [$Q^+CF_3COOO^-$] that allow reactive the ion pair catalytic cycle. Therefore, it results steady state approximation for [$Q^+CH_3COO^-$] and [$Q^+CF_3COO^-$].

Step (5): Another ion pair was form in the presence of ionic liquid (IL). The IL with phase transfer cation [$RMIM^+$] named as alkyl methylimidazolium and phase transfer anion [$RSO_4^{2-}$] named as alkyl sulfate ion. In the presence of excess of $H_2O_2$, alkyl sulfate anion are peroxidized and disaggregated to form alkyl persulfate anion [$RSO_6^-$]*, then lipophilic cations and hydrophilic anion can function as PTA to transfer alkyl persulfate anion into organic phase.

Step (6): In organic phase, organic sulfur compounds are oxidized to its corresponding sulfone by the ion pair [$RMIM^+$][[$RSO_6^-$]*. After oxidation, the reduced ion pair [$RMIM^+$][[$RSO_4^-$] returns back to aqueous phase. With IL and hydrogen peroxide are in excessive amount, there is no change in the concentration of [$RMIM^+$][[$RSO_4^-$] and can be reactive the ion pair catalytic cycle. Therefore, it results steady state approximation for [$RMIM^+$][$RSO_4^-$].

Step (7): Normally, to enhance the efficiency of phase transfer catalysis, stirring of the mixture provides mass and heat transfer. In modified UAOD process, various mixing methods including magnetic stir, ultrasound or high shear mixer were used to enhance the phase transfer catalysis. With well mixing in two phase system, the stirring can break droplet into small particles that create conditions favorable for mass transfer between organic sulfur compound and oxidant. Without mixing, two phases will separate that results reduced interfacial area. This is why well mixing can directly affect the rate of phase transfer catalysis reactions. Although, the possibility of obtaining optimal size of particles depends on both of stirrer type and properties of organic and aqueous phase. In modified UAOD process, with 5,000 rpm stir speed, highest desulfurization efficiency can be achieving compare to other mixing methods.

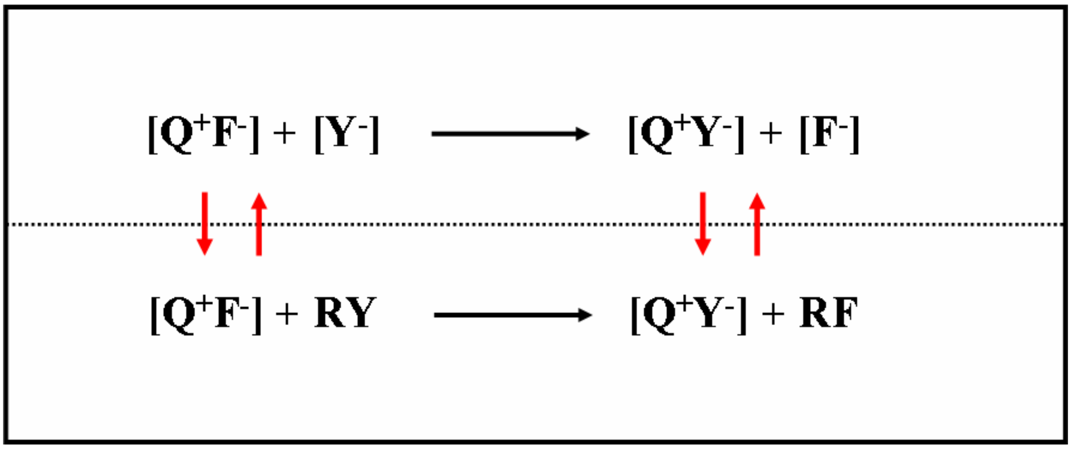


Figure 6.1 Ion pair catalysis

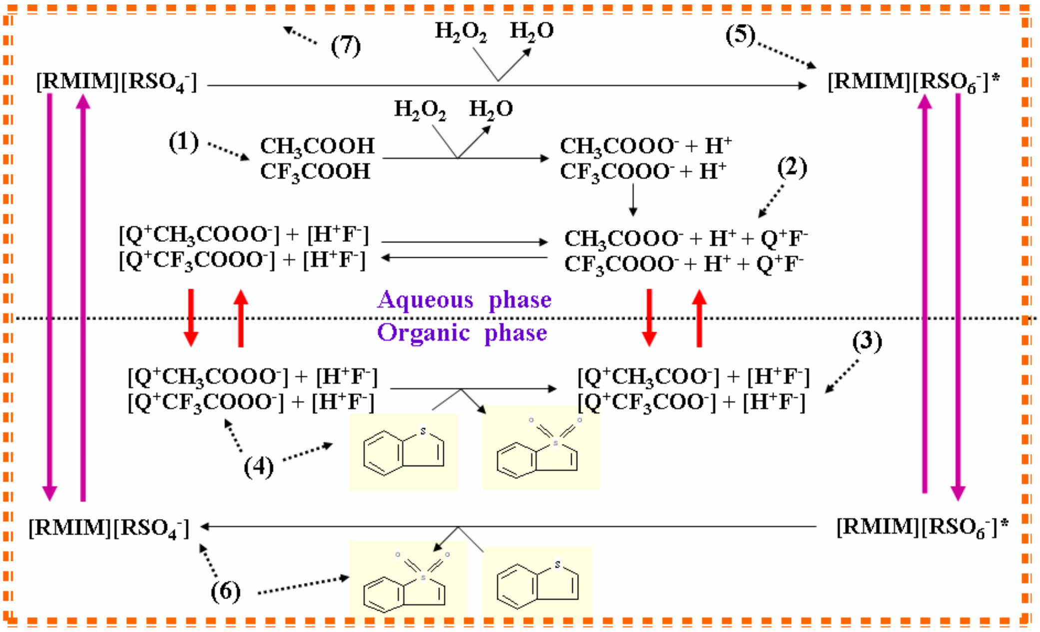


Figure 6.2 Conceptual model of Modified UAOD process (catalytic oxidation)

## 6.3 Summary

In this chapter, a conceptual model of modified UAOD process has been developed which consists of 7 steps: (1) Acid catalyst is peroxidized with oxidant and forming per-acetic anion and per-tri fluoro acetic anion. (2) Formation of ion pair between quaternary ammonium salts and peroxidized acid catalyst. (3) Ion pair transfer from aqueous phase into organic phase. (4) Organic sulfur compounds are oxidized into its corresponding sulfone. (5) IL is peroxidized with oxidant and forming alkyl per-sulfate anion. (6) Alkyl per-sulfate anion transfer from aqueous phase into organic phase that allow organic sulfur compound to be oxidized. (7) Well mixing enhances the mass transfer of oxidation reaction.

# CHAPTER 7

# SUMMARY AND RECOMMENDATION

## 7.1 Introduction

The production of ultra low sulfur diesel fuel has been considered for the development of a modified UAOD process that is utilized for the desulfurization purpose. In this regard, above mentioned process and its production has been one of the main objectives of this paper. It has been observed that more than 99% of oxidation of model compounds like thiophene's (T's), benzothiophene's (BT's) and dibenzothiophenes (DBT's) can be achieved by the employment of a bench-scale batch system. In addition, quaternary ammonium salts, ionic liquids (IL), as well as, acid catalyst has been contained in this system. Moreover, it was analyzed that ultrasound and stir mixing were also utilized for supporting the system. In this system, it has been observed that low temperature and similar low pressure can provide effective results in this system. Additionally, it was demonstrated that 99.9% of removal efficiency could be achieved by the employment of modified UAOD process in the diesel fuels having sulfur content.

Two parts have been included in a complete desulfurization system, which have been referred as continuous modified UAOD process and fluidized bed reactor (FBR). In this regard, the pilot study has considered the above mentioned parts. Specifically, high shear mixer, a treatment tank, pipeline, as well as, a pumping system has been contained in a continuous modified UAOD process. During the study, it was indicated by the investigation that a number of sulfur content diesel fuels provided high oxidation rate with the support of above mentioned parts. Removal of oxidized organic sulfur compound was done by the utilization of FBR. Finally, conduction of a preliminary economic analysis of pilot scale was done during the study.

A modified UAOD process was considered for the obtaining of experimental results. In this regard, following is the conclusion of important points that were indicated by the experiments:

(1) Modified UAOD process was designed to combine the following complementary techniques: acid catalyst, phase transfer catalysis, mixing, IL and oxidant. The oxidation of model sulfur compounds was carried out in presence of ultrasound and stir mixing with excess of $H_2O_2$ as oxidant, and acid catalyst (acetic acid and tri-fluoro acetic acid) was utilized as a catalyst. IL and quaternary ammonium salts (QAS) as phase transfer agents during the oxidation process.

(2) Phase transfer agent (PTA) including QAS and IL, both PTA can reduce the surface tension between two phases, which oxidant transfer from aqueous phase into organic phase that allow oxidation, therefore, enhance the oxidation efficiency. QAS in modified UAOD process is desirable to be used at low dosage to permit high reaction rate and to prevent side effects such as foaming.

(3) A combination of stirred method and sonication will give improved results. From DBT as the model sulfur compound, 89.3% of desulfurization efficiency has been achieved by the combination process of sonication and stirred method during the reaction.. In this regard, it was observed that it took 6 hours for the

treatment with the stirred method. On the other hand, the combination of sonication with the stirred method resulted in the treatment time of 3 hours.

(4) Desulfurization efficiency can be enhancing with acid catalyst, such as, acetic acid and tri-fluoro acetic acid (TFA). Studies have been carried out on the various capabilities and characteristics of TFA. In this regard, it has been observed that better catalytic reactivity can be given by the TFA. Acetic acid is found to be providing lower reactivity, as compared to the former one during the different reactions. However, 100% grade TFA may cause extreme effect such as explosion during the reaction; Therefore, it has been suggested to change the usage of catalyst with safe reaction conditions can be given by the combination of acetic acid and TFA. Therefore, 20% TFA has been used for model sulfur compound study.

(5) $[PF_6]$ anion based IL is not environmental friendly during the process, because a decomposition product of 1-butyl-3-methylimidazolium hydrate is created that has been identified crystallographically by the literature. Although, it has been observed that the $[BMIM][PF_6]$ ionic liquid extracts white fumes during the sonication. Observations have also been gathered during the experiments regarding the toxic and corrosive properties of these white fumes that contains hydrogen fluoride (HF).

(6) Non-toxic pharmaceutically suitable anions such as $Cl^-$, $Br^-$, $SO_4^{2-}$, $PO_4^{3-}$, $NO_3^-$ can be used to replace $[PF_6]$ anion based IL. In this regard, $[BMIM][OcSO_4]$ $[EMIM][EtSO_4]$, $[EDMIM][EtSO_4]$, $[TBMNH_4][MeSO_4]$ and $[TBMP][MeSO_4]$ are some of the ILs. It has been indicated by the results that the $[EMIM][EtSO_4]$

IL has provided one of the effective desulfurization efficiencies, as compared with the other ILs for DBT model sulfur compound, with 99% desulfurization efficiency.

(7) By using “Sulfur” free diesel as the solvent for model sulfur compound study, under modified UAOD process. In this regards, it has been observed that a remarkable result of average 99% sulfur reduction for all sulfur model compounds. However, sulfur was reduced at average 40% during the experiment, as exceptional and contrary results were shown by benzothiophenes (BT’s), as the role of solvent was played toluene.

(8) In the diesel fuels, representatives of different classes of sulfur compounds created a series of model molecules that was utilized during the kinetic study of modified UAOD process. In this regard, vulnerable results related to the reaction rates of oxidation were shown by reactive, as well as, resistant compounds in terms of hydrodesulfurization. In this regard, a linear relationship between oxidation rate and reaction time was displayed by it from the plot of ln (Ci/Co) vs. time. In the result, the pseudo-first-order reaction kinetics was confirmed by the creation of this relationship. The oxidation reactivity of these sulfur compounds was found in a decreasing order of BT > 4,6-DMDBT > DBT > 2MBT > 2ET > 2MT > T.

(9) Under the modified UAOD process, three hours of duration was taken for exceeding 99.9% of removal efficiency of sulfur on low, median, as well as, high sulfur diesel fuels. It has been indicated by the results that various kinds of diesel fuels contained $C_3$-BTs, $C_4$-BTs, $C_5$-BTs and $C_3$-DBTs that are some of

the major sulfur compounds. In addition, no by-products were left during the removal, which was quite different from the previous results. Under previous UAOD conditions, the characteristics of most refractory compounds were given to the above mentioned four sulfur compounds.

(10) Oxidation of organic sulfur compounds was carried out in the presence of ultrasound, $H_2O_2$, RTILs, acid catalyst, and PTA. Different studies have shown that the raw materials are found to be very expensive, and the capital cost will be too high and will exceed from the budget due to their one-time usage during the process. In this regard, the spent aqueous phase was utilized during the conduction of several experiments that were based on the recycling of IL, PTA, and $H_2O_2$. During the process, it was found out that more than 99% of desulfurization efficiency was achieved, even after the utilization of aqueous phase for more than three times. Thus, it has been indicated by the results that the oxidation process of organic sulfur compounds to its corresponding sulfones can be allowed by the excess amount of acid catalyst, PTA, and $H_2O_2$ in the spent aqueous phase.

(11) A significant role has been played by the hydrogen peroxide ($H_2O_2$), as the towering desulfurization competence would be carried out by 3% $H_2O_2$. However, achievement of 15 ppm desulfurization can be attained after spending of more time. In addition, protocol conditions can result in the 99.9% of sulfur reduction with the utilization of 30% $H_2O_2$, as well as, 50% $H_2O_2$. In this regard, the reactivity of various hydrogen peroxide concentrations under oxidative conditions can be understood effectively by the above mentioned information.

In addition, the reaction parameter can be optimized under oxidative conditions with the help of the same information. However, possible explosions can be confronted with the utilization of 50% $H_2O_2$. In the result, the entire process has considered and preferred the utilization of 30% $H_2O_2$ concentration for the safety concerns.

(12) A conceptual model of modified UAOD process has been developed which consists of 7 steps: (1) Acid catalyst is peroxidized with oxidant and forming per-acetic anion and per-tri fluoro acetic anion. (2) Formation of ion pair between quaternary ammonium salts and peroxidized acid catalyst. (3) Ion pair transfer from aqueous phase into organic phase. (4) Organic sulfur compounds are oxidized into its corresponding sulfone. (5) IL is peroxidized with oxidant and forming alkyl per-sulfate anion. (6) Alkyl per-sulfate anion transfer from aqueous phase into organic phase that allow organic sulfur compound to be oxidized. (7) Well mixing enhances the mass transfer of oxidation reaction.

(13) The evaluation of efficiency and selectivity of modified UAOD process on diesel fuels has been done by the successful employment of GC-Simulated Distillation (GC-SIMDIS) and hydrogen peroxide consumption methods. In addition, it has been indicated by the results that distillation profiles and other characteristics of diesel fuels cannot have any deleterious effects by the modified UAOD process. The quality assurance of diesel fuel can be done.

(14) Successful evaluation of a batch type continuous flow system has been done for the addressing of concerns related to the large-scale commercial production. It has been observed that a treatment tank, high shear mixer, pumping system and

pipeline system have been contained in the continuous system. Room temperature, as well as, normal pressure was considered for the conduction of the study. It has been indicated by the results that 99.9% (13 ppm) of sulfur reduction can be achieved by the continuous system under the above mentioned conditions. Moreover, similar results (6 ppm) were indicated by both batch, as well as, continuous study.

(15) Mixing play a very important parameter in modified UAOD process. Ultrasound, magnetic stir, and several other mixing strategies were compared in this respect. Specifically, 5,000 rpm with the 50°C of reaction temperature was observed during the process with high shear mixer. Under this condition, aqueous phase was maintained, and ULSD fuel was achieved.

(16) It has been observed that weight ratio of IL does not affect the desulfurization efficiency, as it has been with the ratio of 1:1 in batch study, as well as, 1:100 with the IL in pilot study. In other words, system only required small amount of IL. Thus, transfer of oxidant from aqueous phase can be done with high affinity of IL into the organic phase.

(17) In pilot study, 20% TFA is not sufficient to desulfurize high sulfur content diesel fuel (Valley Oil), therefore, 40% TFA has been used for new catalyst concentration. Although, 1/10 of catalyst usage has been used in pilot study compare to batch study, and still achieve high desulfurization efficiency.

(18) Removal of oxidized sulfur is usually done by the fluidized bed reactor. In addition, 11.8 mg S/g alumina and 13.8 mg S/g alumina has shown similar adsorption capacity during the study of diesel fuels, such as F-76 and Valley Oil.

Although, similar results were shown by the fluidized bed reactor regarding the adsorption capacity, as compared to the packed column study. However, higher adsorption capacity was one of the advantages that have been provided by the fluidized bed reactor. In addition, adsorption ability of this reactor cannot be weakened by its recycling.

(19) Figure 7.1 has been used for the illustration of a schematic flow diagram of continuous modified UAOD process on diesel fuels with 0.6 bpd production rate that as been development. Specifically, two stage operations have been consisted in the system. Firstly, IL, $H_2O_2$, and acid catalyst are utilized in the modified UAOD process with catalytic oxidation of sulfur. Secondly, adsorption of oxidized sulfur compound from diesel fuels was allowed by the alumina that was packed in the Fluidized bed reactor (FBR). It was indicated by the results that consideration of multistage treatment tanks in series should be done for the achievement of higher daily production rate.

(20) After the treatment tank, employment of separator is done for the purpose of phase separation, FBR achieves the diesel phase after its transformation, and feed stream is introduced with spent aqueous phase for its reutilization. For adsorption, alumina adsorbs the oxidized sulfur compounds, and the diesel fuels are separated from these compounds after their removal. During this process, chemical or thermal conversion of sulfone by-products is done, which results in the formation of sulfonate, and sometimes, hydrocarbons that are contained in a sulfone converter.

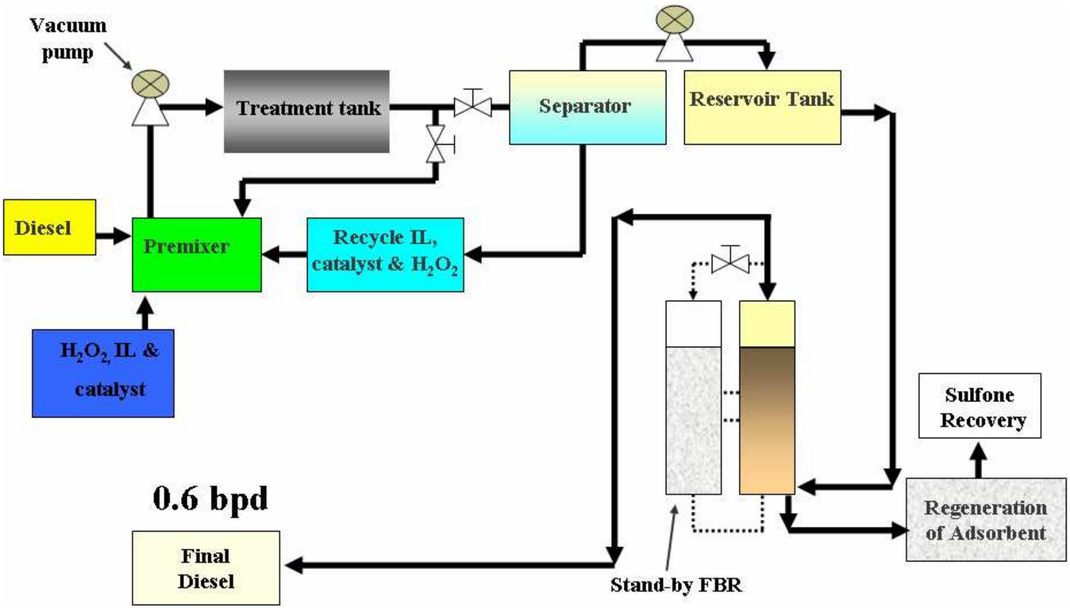


Figure 7.1 Block diagram of continuous modified UAOD process

(21) 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. Moreover, high production rate on daily basis can be achieved by the installation of these equipments. For instance, achievement of 0.6 bpd was done during the pilot study. Moreover, the modified UAOD process units can replace the existing technology (HDS) as per the requirements without any utilization of hydrogen. Additionally, ULSD fuels can be produced economically in this respect.

## 7.2 Recommendation

It is proposed that upcoming work should stress on the growth of an elegant incessant modified UAOD process scheme to present insight on its technological and financial viability for possible manufacturing functions. A number of significant matters are discussed in the lines that follow:

(1) Expanding the continuous CSTR reactor:

In Chapter 5, it is at length that the application of a batch type continuous scheme is very competent to construct ultra low sulfur diesel petroleum. At present, mechanisms to construct massive quantity CSTR are already established; there are numerous commercial appliances on CSTR reactors. Furthermore, a multifarious procedure which comprises two or more CSTR can be applied in sequence or in parallel, can be put to consideration.

(2) Solid phase adsorption:

Alumina is competent to adsorb natural sulfur complexes that can be taken as an alternate for liquid/liquid extraction after modified UAOD process. Alumina is employed as a adsorbent in natural warmth and atmospheric force. In Chapter 5, fluidized bed reactor has matching competence of sulfone elimination as liquid/liquid removal and packed column. The upturn of alumina from sulfone adsorbent had been shown in lofty speeds (94%) resurgence by a polar complex (N,N-Dimethyl Formamide) (Etemadi, et al. 2007) or calcination.

Multifarious columns for the adsorption tower are required for the sulfur diesel. Figure 7.2 is a graphic illustration of twofold adsorption towers. In this case, a solvent will be employed to extort the sulfone retained in the solid medium of the crammed tower. Monitoring for the paramount adsorbent will be developed at this phase with the appropriate adsorption isotherm examination and column breakthrough investigation. It is predictable that an ultra low sulfur-containing diesel can be attained after the residual sulfur is sifted away.

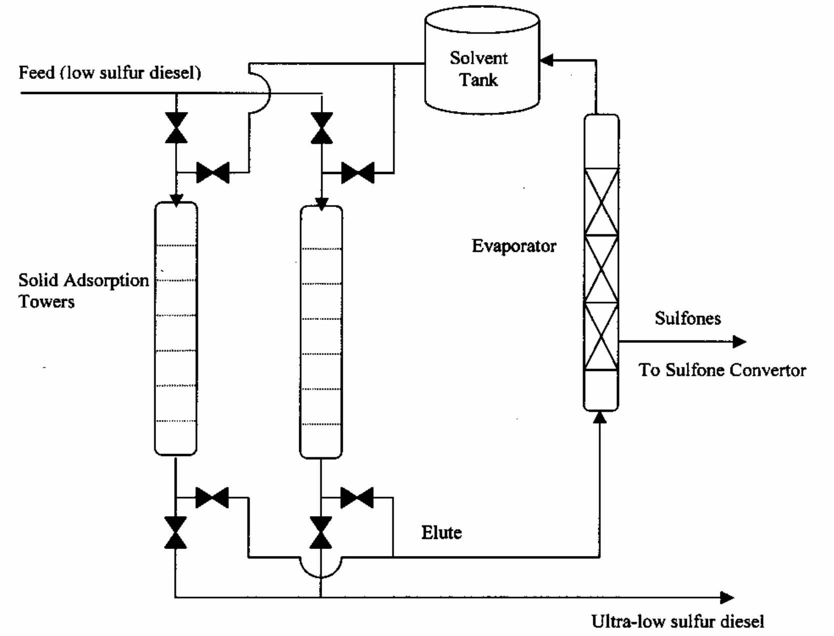


Figure 7.2 Schematic flow drawing of the solid adsorption tower after continuous UAOD procedure (Yen, 2003)

(3) Recovery of sulfone:

It turns out to be an out of the ordinary hitch in the face of putting for commercial use of modified UAOD process. Figure 1.6 manifests the "4S pathway" of DBT in BDS where 2-hydroxybiphenyl is the ultimate produce. It is displayed that modified UAOD products are only an intermediary of BDS. To facilitate to ooze complete benefit of sulfone, it requires changing them into either matching sulfonates or even hydrocarbons. As we are familiar, sulfonates can be applied as surfactants with industrial worth and hydrocarbons can be pushed back to fuel flows. Two techniques to attain this objective are as follows. One is thermal conduct. As we discern, the heats needed for the putrefaction of the majority of sulfones are in abundance of 500oC that ultimately takes us to considerable and unwanted thermal fractures of hydrocarbons (Black, et at. 1978). The other technique is alkali conduct.

For DBTO as an instance, under less energetic circumstances, the intermediary biphenyl-2-sulfonic acid can be separated. Further response will create 2-hydroxybiphenyl as the ultimate produce (Hartough and Meisel, 1954).

4) Sulfur density:

Quantum mechanics offers a formula for scheming the likelihood of ruling an electron at a meticulous end in space, and this amount is termed as the "electron density". Henceforth, a chart that illustrates how the likelihood thickness differs from end to end in a molecule is a form of the molecule's electronic arrangement (Shusterman, et al. 1997). In addition, Otsuki, et al., 2000 have accounted that the Computer Aided Chemistry (CAChe) work scheme offered by CAChe Scientific Inc. can possibly be employed to compute the electron thickness of the sulfur atom in the sulfur complexes by applying the Sony Tektronixs CAChe system (CAChe, 1995) and the Molecular Orbital Package (MOPAC, Version 6.00). Consequently, investigating the association between sulfur thickness of a choice of BT and DBT relations and their oxidation reaction rates can suggest a hypothesis to point to and give details of the most refectory complexes under modified UAOD circumstances.

(5) In situ $H_2O_2$ supply:

Hydrogen peroxide is an ecologically welcoming oxidizing driving force that puts behind only water and oxygen after reaction. Nonetheless, it is hazardous to stock up lofty absorption $H_2O_2$ on place. In-situ hydrogen peroxide production is required for commercialized modified UAOD process (Alfred, et al. 1959 & Hua, et al. 1997).

(6) Alternative Oxidant

There are some substitute oxidants that can change with $H_2O_2$; this includes air, ozone, and superoxide.

Certainly, the most economical oxidant supply on the earth comes from air and ozone. The working cost for ODS can be much more economical by making use of the air. Moreover, the air has no storage difficulty and is limitless when it comes to its availability. From ACS 2007 Chicago, Song, et al., illustrates that air can be made a good use of as oxidant for ODS procedure. He propels the air into a pressurized reactor with low sulfur diesel (500 ppm) and ultimate diesel absorption can be as low as 30 ppm. Owing to the technological trouble, this method can only be experienced in the lab and can only process slow sulfur substance diesel. For that reason, it yet calls for extensive investigation in order to be commercialized.

Air and dampness susceptible is potassium superoxide, a yellow paramagnetic solid. Its recipe is $KO_2$ and since potassium is +1, the superoxide bears a charge of -1. Potassium superoxide carries a good deal of extraordinary corporeal and compound features. The application of potassium superoxide as an oxygen source in chemical oxygen producers, for example those fabricated in the space shuttle and on submarines. Henceforth, it can be applied as the oxidant in modified UAOD procedures.

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