SUPEROXIDE RADICAL AND UV IRRADIATION IN ULTRASOUND ASSISTED OXIDATIVE DESULFURIZATION (UAOD): A POTENTIAL ALTERNATIVE FOR GREENER FUELS

by

Ngo Yeung Chan

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LIST OF ABBREVIATIONS

2MBT	2-Methyl Benzothiophene
2MT	2-Methyl Thiophene
4,6DMDBT	4, 6-Dimethyl dibenzothiophene
ADS	Adsorptive Desulfurization
AED	Atomic Emission Detector
BDS	Biodesulfurization
BT(s)	Benzothiophene(s)
BTO	Benzothiophene Sulfone
CFCs	Chlorofluorocarbons
CMFR	Completely Mixed Flow Reactor
DBT(s)	Dibenzothiophene(s)
DBTO	Dibenzothiophene sulfone
DW	Deionized Water
EIA	Energy Information Administration
EPA	Environmental Protection Agency

FID	Flame Ionization Detector
FPD	Flame Photometric Detector
FUS	Focused Ultrasound Surgery
GC	Gas Chromatography
HCFCs	Hydrochlorofluorocarbons
HDS	Hydrodesulfurization
HECD	Electroconductivity Detector
IL(s)	Ionic Liquid(s)
IMO	International Maritime Organization
LSD	Low Sulfur Diesel
MCD	Microcoulometric Sulfur Detector
MEPC	Marine Environment Protection Committee
MS	Mass Spectroscopy Detector
NDXRF	Non-Dispersive X-Ray Fluorescence
ODS	Oxidative Desulfurization
OSC(s)	Organic Sulfur Compound(s)
PAHs	Polycyclic Aromatic Hydrocarbons

PCE	Perchloroethylene
PFPD	Pulse Flame Photometric Detector
PM	Particulate Matter
POM(s)	Polyoxometalate(s)
PTC(s)	Phase Transfer Catalyst(s)
QAS(s)	Quaternary Ammonium Salts
RTIL(s)	Room Temperature Ionic Liquid(s)
SCD	Sulfur Chemiluminescence Detector
SECAs	Sulfur Emission Control Areas
SO_x	sulfur oxides
S-Zorb SRT	S-Zorb Sulfur Removal Technology
T(s)	Thiophene(s)
TCE	Trichloroethylene
TFA	Trifluoroacetic Acid
TMC	Transition Metal Catalysts
TOAF	Tetraoctylammonium Fluoride
UAOD	Ultrasound Assisted Oxidative Desulfurization

ULSD	Ultralow Sulfur Diesel
UV	Ultraviolet
VOC(s)	Volatile Organic Compound(s)

ABSTRACT

This study is aimed at improving the current ultrasound assisted oxidative desulfurization (UAOD) process by utilizing superoxide radical as oxidant. Research was also conducted to investigate the feasibility of ultraviolet (UV) irradiation-assisted desulfurization. These modifications can enhance the process with the following achievements:

- Meet the upcoming sulfur standards on various fuels including diesel fuel oils and residual oils
- More efficient oxidant with significantly lower consumption in accordance with stoichiometry
- Energy saving by 90%
- Greater selectivity in petroleum composition

Currently, the UAOD process and subsequent modifications developed in University of Southern California by Professor Yen's research group have demonstrated high desulfurization efficiencies towards various fuels with the application of 30% wt.

hydrogen peroxide as oxidant. The UAOD process has demonstrated more than 50% desulfurization of refractory organic sulfur compounds with the use of Venturella type catalysts. Application of quaternary ammonium fluoride as phase transfer catalyst has significantly improved the desulfurization efficiency to 95%. Recent modifications incorporating ionic liquids have shown that the modified UAOD process can produce ultra-low sulfur, or near-zero sulfur diesels under mild conditions with 70°C and atmospheric pressure.

Nevertheless, the UAOD process is considered not to be particularly efficient with respect to oxidant and energy consumption. Batch studies have demonstrated that the UAOD process requires 100 fold more oxidant than the stoichiometic requirement to achieve high desulfurization yield. The expected high costs of purchasing, shipping and storage of the oxidant would reduce the practicability of the process. The excess use of oxidant is not economically desirable, and it also causes environmental and safety issues. Post treatments would be necessary to stabilize the unspent oxidant residual to prevent the waste stream from becoming reactive or even explosive.

High energy consumption is another drawback in the UAOD process. A typical 10 minutes ultrasonication applied in the UAOD process to achieve 95% desulfurization for 20g of diesel requires 450 kJ of energy, which is equivalent to approximately 50% of the energy that can be provided by the treated diesel. This great expenditure of energy is impractical for industries to adopt.

In this study, modifications of the UAOD process, including the application of superoxide and selection of catalysts, were applied to lower the oxidant dosage and to improve the applicability towards heavy-distillates such as residual oil. The results demonstrated that the new system required 80% less oxidant as compared to previous generations of UAOD process without the loss of desulfurization efficiency.

The new system demonstrated its suitability towards desulfurizing commercial mid-distillates including jet fuels, marine gas oil and sour diesel. This process also demonstrated a new method to desulfurize residual oil with high desulfurization yields. The new process development has been supported by Eco Energy Solutions Inc., Reno, Nevada and Intelligent Energy Inc., Long Beach, California.

A feasibility study on UV assisted desulfurization by replacing ultrasound with UV irradiation was also conducted. The study demonstrated that the UV assisted desulfurization process consumes 90% less energy than the comparable process using ultrasonication.

These process modifications demonstrated over 98% desulfurization efficiency on diesel oils and more than 75% on residual oils with significantly less oxidant and energy consumption. Also the feasibility to desulfurize commercial sour heavy oil was demonstrated. Based on the UAOD process and the commercialized modifications by Wan and Cheng, the feasible applications of superoxide and UV irradiation in the UAOD process could provide deep-desulfurization on various fuels with practical cost.

CHAPTER 1: INTRODUCTION

1.1 General Overview

Petroleum was discovered several thousands years ago and has been extensively used starting from the Industrial Revolution. Nowadays, petroleum and its derivative products provide approximately 37% of the world's energy consumption (Energy Information Administration, 2009) and 90% of the vehicular fuel. While sulfur is one of the major contaminants in petroleum, it generates air pollution that leads to severe environmental and health consequences. The U.S. Environmental Protection Agency (EPA) and other similar groups across the world have started proposing regulations to lower sulfur content in various fuels since 1990s, and as a result stringent sulfur content regulations are established for diesel and residual oil in the upcoming future.

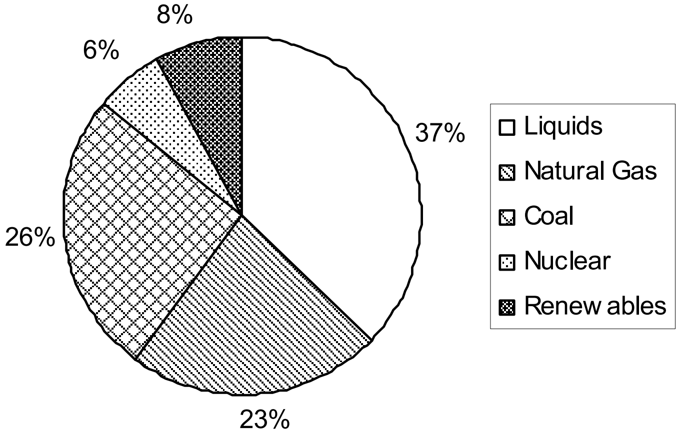


Figure 1.1 World Marketed Energy Use by Fuel Type (EIA, 2009)

1.2 Diesel Fuel

1.2.1 Diesel Fuel and Organic Sulfur Compounds (OSCs)

Diesel, also known as petrodiesel, is a petroleum product through fractional distillation of catalytic cracking of crude oil. It is a mixture of hydrocarbons with typical carbon chain length of 8 to 21, having a boiling point ranged from 200°C to 325°C (Collins, 2007). Depending on its original sources and the refinery conditions, properties such as sulfur content of a diesel fuel vary. Diesel fuel consists of approximately 70% of aliphatic hydrocarbons including paraffins and naphthalenes, with approximately 30% of aromatic hydrogen carbons (Steynberg et al, 2004).

Comparing with gasoline engine, diesel engine is generally operated under oxygen-rich conditions, which leads to a more complete combustion thus releasing less carbon monoxide and hydrocarbons. Besides, diesel engine has a lower fuel per mile consumption, thus releasing less carbon dioxide. However, more soot, or particulate matter (PM) including $PM_{2.5}$ and PM_{10}, are emitted in burning diesel fuel. These particulate matters are identified as contributing to variety of health problems such as asthma, emphysema and bronchitis, while sulfur compounds in diesel is one of the major factors causing the emission of these particulate matters. Recent studies report that emission of diesel particulate matter increases significantly with sulfur content in the diesel fuel burnt (Saiyasitpanich, 2005). In 1998, the California Air Resources Board declared diesel PM as a toxic air contaminant and a potential cancer risk; and in 2000, the U.S. EPA identified diesel PM as a likely human carcinogen.

Emission of sulfur oxides (SO_x) is another problem on using high sulfur diesel. SO_x can dissolve in water vapour in the atmosphere resulting in acid rain, which is known to be harmful to plants, aquatic animals, and infrastructure.

Sulfur compounds, or more specifically organic sulfur compounds (OSCs), are considered as the most important non-hydrocarbon constituents in petroleum. There are three major types of OSCs: thiols (R-SH), sulfides (R-S-R’) and thiophenes. In mid-range distillates such as diesel, the OSCs are primarily cyclic sulfide derivates, benzothiophene derivates and dibenzothiophene derivates (Speight, 1999). The chemical structures of the major OSCs in petroleum are listed in Table 1.1.

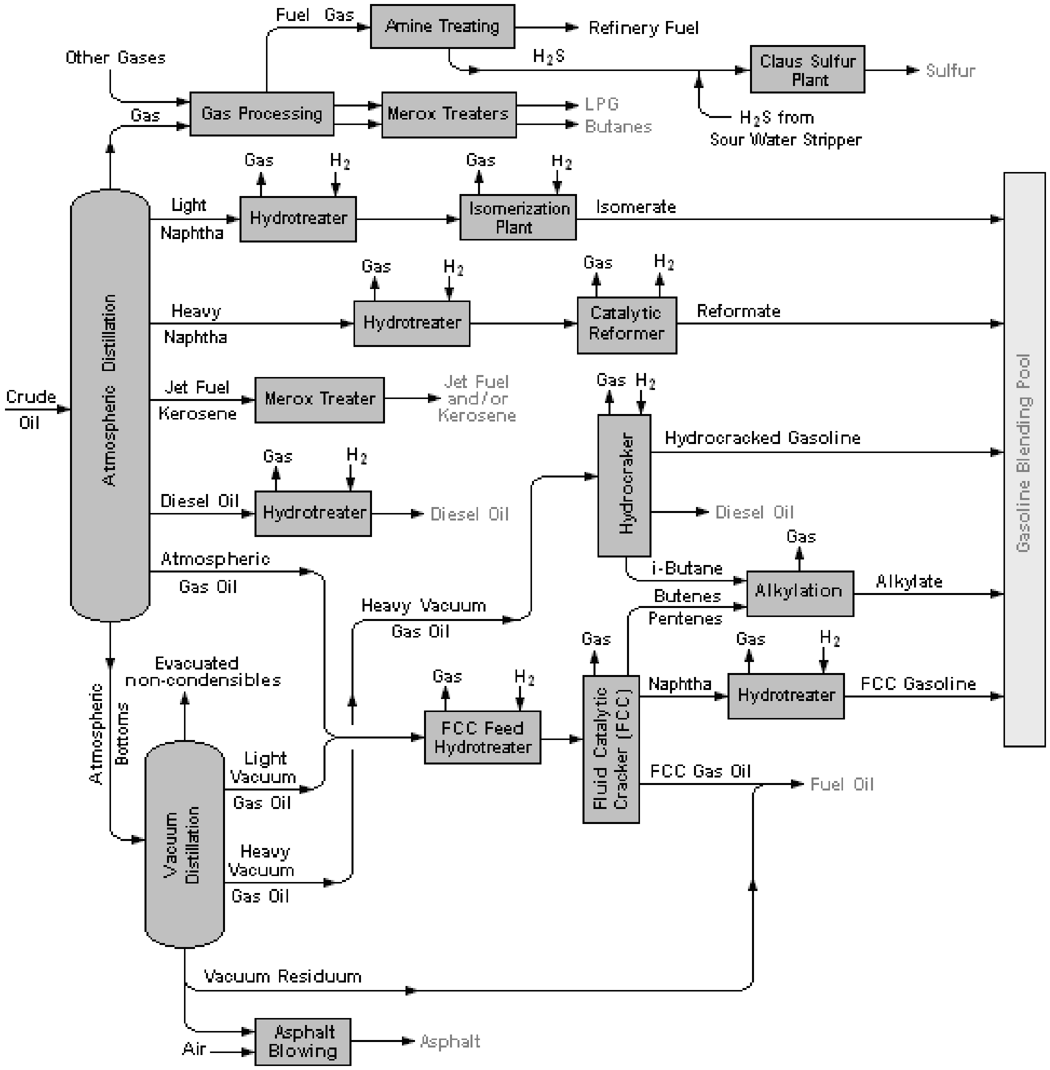
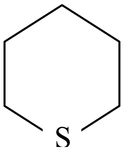
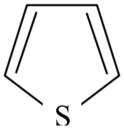
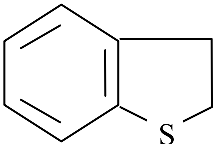
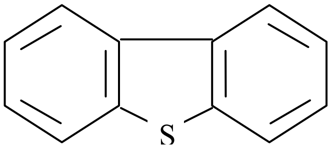
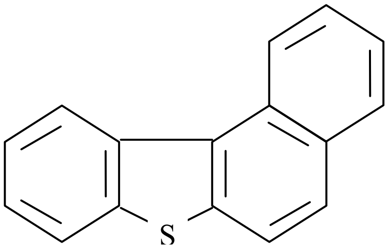
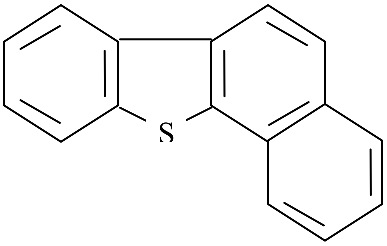


Figure 1.2 Schematic diagram of oil refinery (Beychok, 2005)

Table 1.1 Major types of OSCs in petroleum

Thiols	RSH
Sulfides	RSR’
Cyclic Sulfides (thiacyclanes)	
Thiophene	
Benzothiophene	
Dibenzothiophene	
Naphthobenzothiophene	 

1.2.2 Diesel Fuel and Sulfur Regulations

In order to lower the particulate and sulfur oxides emissions, the U.S. EPA has established regulations to limit sulfur content in diesel fuels. Established in November 1990 as promulgated by the EPA Clean Air Act Title II, all commercial motor vehicle diesel fuels (highway diesel fuel) are required to be Low Sulfur Diesel (LSD) with maximum sulfur content of 500 ppm_w as of October 1st, 1993. In January 2001, the EPA established the Highway Diesel Rule (the 2007 Highway Rule) with tightened limit on sulfur content.

Starting from June 1st, 2006, refiners in U.S. are required by the U.S. EPA to produce ultralow sulfur diesel (ULSD) with maximum sulfur content of 15ppm_w for highway vehicle uses. By December 1st, 2010, all highway diesel fuel in U.S. must be ULSD (Energy Information Administration, 2001). In California, the use of ULSD for all highway diesel fuel is required by the California Air Resource Board since September 2006 (California Air Resource Board, 2003).

Non-road diesel refers to land-based non-road, locomotive and marine engines diesel use. Before June 2004, sulfur content in non-road diesel fuels was not regulated by the EPA; except for an industrial specification of 0.5% (5000 ppm_w) sulfur. In June 2004, the EPA released the new standards for non-road diesel fuels. For land-based non-road diesel fuel, the sulfur reductions will be accomplished in two steps: (i) from uncontrolled levels to a 500 ppm_w cap starting in June, 2007; and (ii) to 15ppm_w in June, 2010. Similarly, sulfur content limit for locomotive and marine diesel fuels have been changed from uncontrolled levels to a 500 ppm_w cap starting in June, 2007; and will be further reduced to a 15 ppm_w in June, 2012 (U.S. EPA, 2004).

Table 1.2 Sulfur content standards for diesel (U.S. EPA, 2004)

Diesel Type	**Maximum Sulfur Content (ppm_w)**	**Implementation Date**
Highway	500	October 1993
Highway	15	June 2006
Land-base non-road	500	June 2007
Land-base non-road	15	June 2010
Locomotive & Marine	500	June 2007
Locomotive & Marine	15	June 2012

1.3 Residual Oil

1.3.1 Residual Oil and OSCs

Residual fuel oil, also known as heavy fuel oil or bunker oil, is manufactured from the residuum obtained from petroleum non-destructive distillation. Residual oil is a highly viscous material with carbon chain length ranged from 12 to 70. Depending on the distillation conditions and the nature of the crude oil, residual oil could be a liquid or a solid in room conditions. Generally, a “liquid” residual oil is produced from atmospheric distillation, while a “solid” or “almost solid” residual oil is produced from reduced pressure distillation. Residual oil may be blended with medium distillate such as heating oil or diesel to reduce its viscosity to acceptable level.

Similar to crude oil, residual oil is a composition of asphaltenes, resins, aromatic hydrocarbons and saturated hydrocarbons, while asphaltenes and resins are the predominant components of residual oil. Asphaltenes are generally combination of aromatic-naphthenic systems with substitution of different alkyl groups. They are heteroatomic organic compounds which may contain atoms such as oxygen, nitrogen, sulfur or metals in addition to carbon and hydrogen (Yen et al, 1994). It is considered as the most complicated known organic components in petroleum, due to high molecular weight, chemical structure diversity, tendency to associate and other properties (Simanzhenkov et al, 2003).

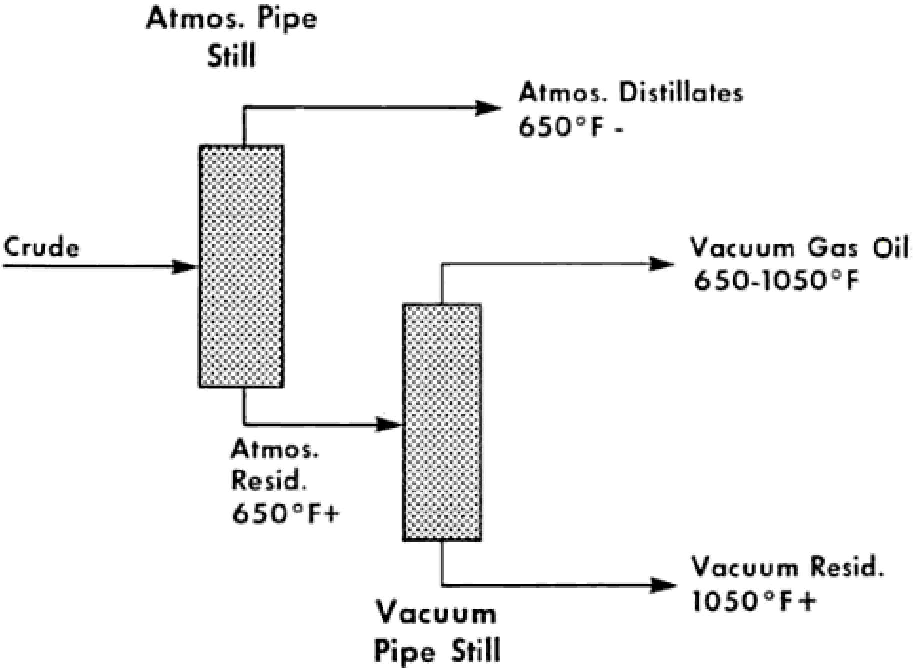


Figure 1.3 Schematic diagram of residual oil production (Sunggyu Lee et al, 2007)

The word “asphaltene” was first used by J.B. Boussingault in 1837, to describe the components of bitumen which are alcohol insoluble, turpentine soluble solid. In 1945 J. Marcusson classified asphaltenes as the insoluble fraction in light gasoline and petroleum ether. More recently, asphaltenes are widely accepted as fraction derived from carbonaceous sources such as petroleum and coal. They are soluble in benzene but insoluble in low boiling point paraffin solvent such as n-pentane.

In contrast, resins are the soluble fraction in n-pentane (Priyanto et al, 2001). Therefore, asphaltenes and resins can be separated with appropriate solvents. Similar concept to separate components in petroleum is illustrated in Figure 1.4. A simple classification of residual oil's components with respect to solubility in different solvents is illustrated in Table 1.3.

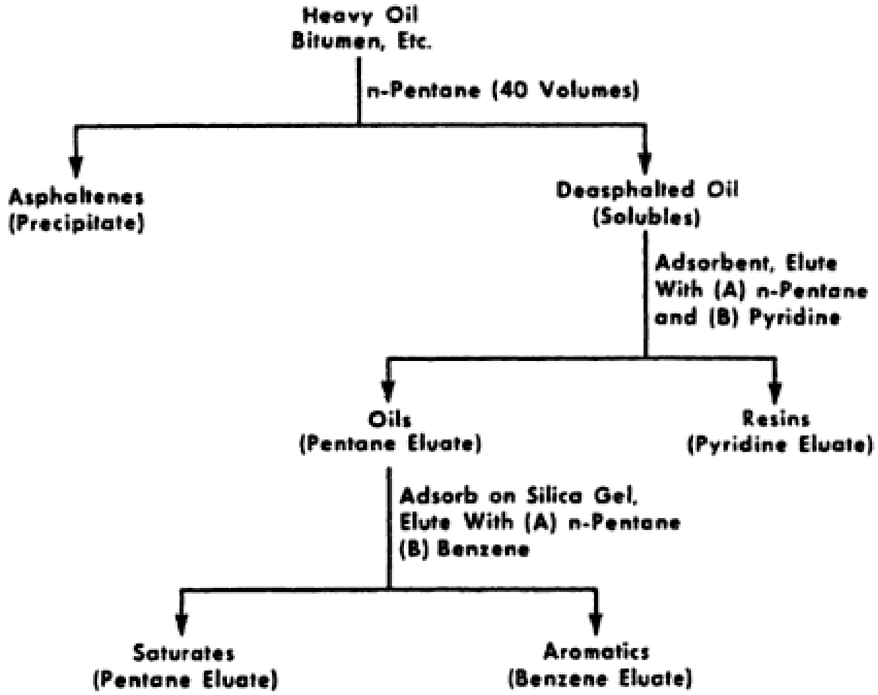


Figure 1.4 Separation of petroleum into four major fractions (Speight, 1999)

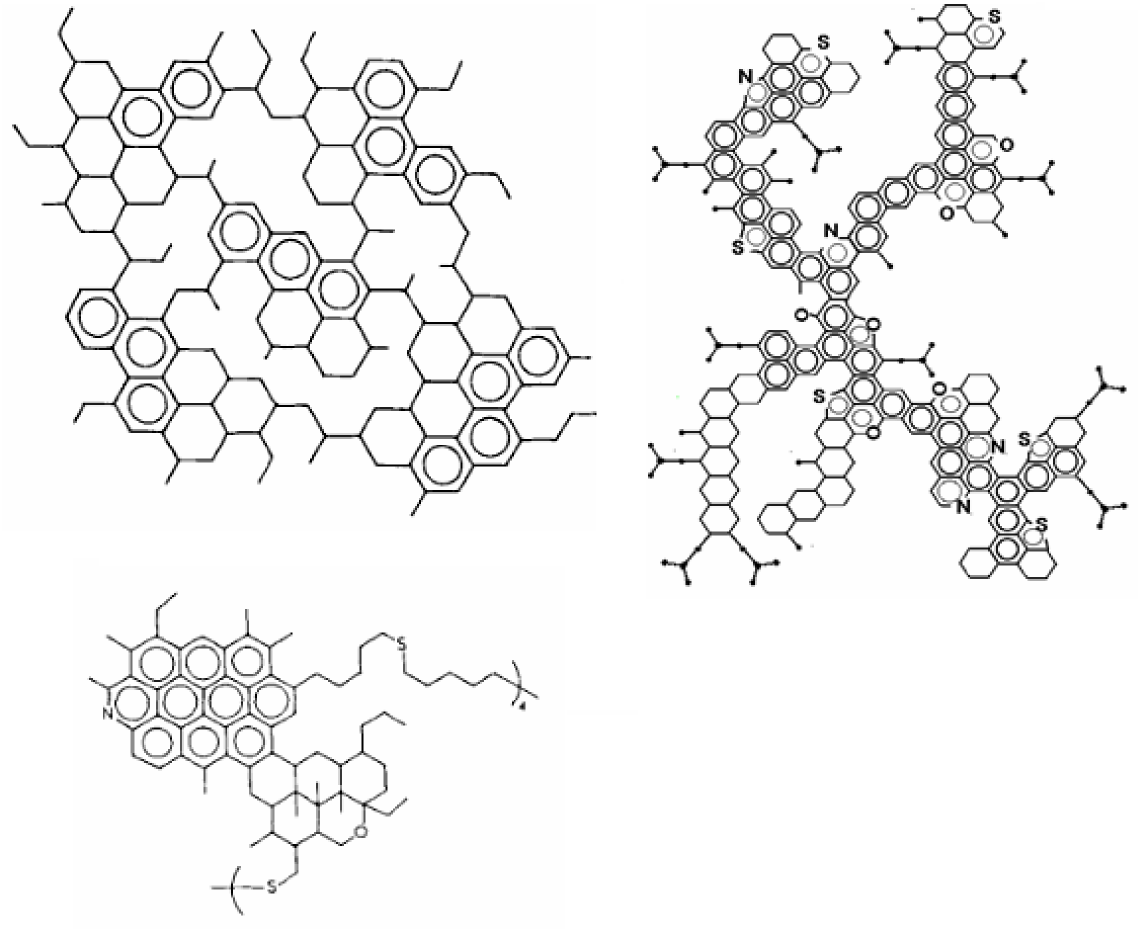


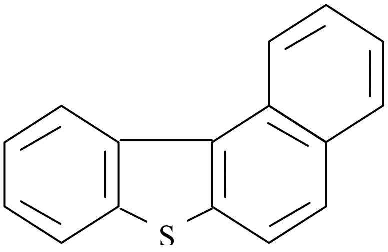
Figure 1.5 Examples of asphaltene formulae (Yen et al, 1994)

Table 1.3 Classification of residual oil's components (Yen et al, 1994)

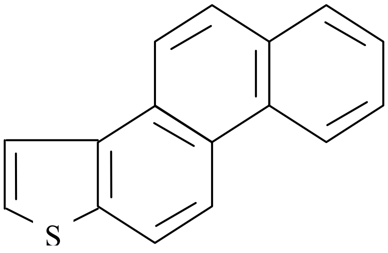
Fraction	**Solubility**	**Remarks**
Gas oils	Propane soluble	Saturated and aromatic hydrocarbons
Resins	Propane insoluble Pentane soluble	Combined distillates and resins are also known as maltene or petrolene
Asphaltenes	Pentane insoluble Benzene soluble	

In general, residual oil contains approximately 79% to 88% w/w carbon, 7% to 13% w/w hydrogen, trace to over 6% w/w sulfur, 2% to 8% w/w oxygen, less than 3% w/w nitrogen and trace metals such as vanadium, copper, titanium, zinc, calcium, iron which can be found in crude oil. Due to the nature of non-destructive distillation process used to produce residual oil, majority of sulfur compounds which are generally considered as higher molecular weight fractions and metals in the form of salts or organometallic constituents are concentrated in the residual oil (Sunggyu Lee et al, 2007).

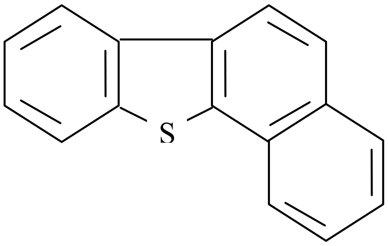
Among all non-hydrocarbon constitutes, sulfur compounds are considered as the most important due to the corrosiveness which can severely damage piping and processing units. The major sulfur species in residual oil are alkyl benzothiophene derivates, dibenzothiophene derivatives, benzonaphtho-thiophene derivatives and phenanthro-thiophene derivatives (Speight, 1999). Some of the common OSCs found in residual oil are listed in Figure 1.6.



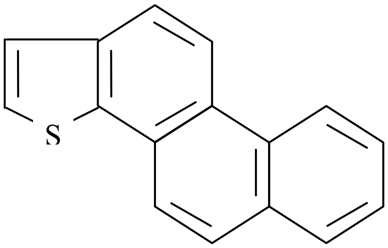
Benzo[*b*]naphtho[1,2-*d*]thiophene



Phenanthro[2,1-*b*]thiophene



Benzo[*b*]naphtho[2,1-*d*]thiophene



Phenanthro[1,2-*b*]thiophene

Figure 1.6 Examples of OSCs in residual oils

1.3.2 Residual Oil and Sulfur Regulations

Residual oil is mainly used in marine vessels and power plants for power generation; and in some commercial or industrial buildings for heating and other processing purposes. Because residual oil is rarely used in dense areas but remote sites, specifications on residual oil are generally set based on technical instead of environmental issues. Among all, kinematic viscosity and sulfur content are the most critical specifications for residual oil. Kinematic viscosity at 100°C for residual fuel oil should be in the range of 10 to 55 centistoke (mm^2/s). For residual fuel oil with higher viscosity, it is usually blended with lighter distillates such as diesel to achieve a lower viscosity for handling and processing.

Table 1.4 Standard properties of residual oil

Properties	**Range**
Density (at 15°C)	0.975-1.01 (g/cm^3)
Kinematic Visocity (100°C)	10-55 (cSt)
Flash Point	>60°C
Pour Point	0-45°C
Water Content	< 1%

In the past, maximum sulfur content in residual oil was limited at the range of 3.5% to 5% in order to protect the engines or boilers. Using higher sulfur content fuel could cause severe corrosion on engine, due to the formation of sulfur dioxide and sulfur trioxide during combustion. With excess air, appropriate temperature and pressure, sulfur dioxide and sulfur trioxide would be converted to sulfurous acid and sulfuric acid causing damages. This is also known as "cold end corrosion" because the conversions of sulfur oxides to the corresponding acids happen in relatively low temperature locations (lower than 150°C) of engines.

In the United State, there is no sulfur cap on heavy oil or residual oil for land-based uses such as fossil fuelled electricity generation plant. Instead, sulfur dioxide emission is regulated by EPA's Acid Rain Program. In some states such as Tennessee, SO_2 emission from specific fuel is also regulated in certain locations. According to Tennessee Air Quality Act, any fuel burning installation in Shelby County using No. 5 and No. 6 fuel oils, which are considered as residual oils, has a emission limit of 2.7 lbs $SO_2/10^6$ BTU. A sulfur cap of 0.3% on all liquid and gaseous fuels has also been adopted recently to limit SO_2 emission from all stationary gas turbines in the State of Tennessee (Environment and Conservation, 2009).

While another major use of residual oil is on marine vessels, regulations established by the Marine Environment Protection Committee (MEPC) of the International Maritime Organization (IMO) are generally applicable to residual oil. The Protocol of 1997 (MARPOL* Annex VI - Regulations for the Prevention of Air Pollution from Ships) is the first international agreement that limits the sulfur content in all fuel oil including residual oil to 4.5% by mass. Sulfur content of fuel oil used in Sulfur Emission Control Areas (SECAs) has to be lower than 1.5% by mass. The SECAs regulation is applied only to Baltic Sea (enforced in 2005); North Sea and English Channel (enforced in 2007). The protocol is active since May 19th, 2005 (MEPC, 1997).

MARPOL Annex 13, also known as the Revised MARPOL Annex VI, was adopted in October 10th, 2008. A new set of global sulfur caps for all fuel oil will be applied gradually so as to further reduce SO_x emission from ships. This new regulations will be accomplished in two steps: (i) instead of 4.5%, a 1.5% cap will be effective starting from January 1st, 2012; and (ii) a progressive reduction on sulfur level to 0.5%, which will be effective from January 1st, 2020. Similarly, the new regulations for SECAs will first be reduced from the current 1.5% to 1% sulfur cap strating from July 1st, 2010; then be further reduced to a 0.1% sulfur cap starting from January 1st, 2015 (MEPC, 2008).

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* MARPOL 73/78 is the major international convention for preventing pollution of the marine environment by ships from operational or accidental causes

Table 1.5 Sulfur content standards for all marine-use fuel oils

Area of Effect	Maximum Sulfur Content (%)	Implementation Date
Global	4.5	May 2005
Global	3.5	January 2012
Global	0.5	January 2020
SECAs	1.5	May 2005
SECAs	1	July 2010
SECAs	0.1	January 2015

1.4 Current Desulfurization Technologies

Before the introduction of tightened sulfur standards, blending with low sulfur containing fuels was a common practice to lower the sulfur content in high sulfur containing fuels for technical purposes. Nowadays, various technologies on desulfurization have been developed. It is, however, an important issue to identify if the technologies developed are able to produce ultra-low sulfur diesel and other low sulfur fuels so as to meet the sulfur standards set locally and globally; and if these technologies are cost effective.

Up to now, hydrodesulfurization is the main stream in the desulfurization technology adopted commercially. Due to the tightening of sulfur regulation, traditional hydrodesulfurization faces its limitation to produce ultralow sulfur fuel. Development of new technologies becomes a necessity in the refinery industry. As a result, alternative desulfurization processes including adsorptive desulfurization, biodesulfurization and oxidative desulfurization are widely discussed as possible technologies to produce ultralow sulfur diesel.

1.4.1 Hydrodesulfurization (HDS)

Hydrodesulfurization, or hydrotreating, is a conventional refinery process for desulfurization. This is one of the most common desulfurization technologies which have been applied on naphtha desulfurization since 1950s. Hydrodesulfurization is a catalytic hydrogenolysis which would result in breaking the C-S chemical bond and forming C-H and H_2S.

Traditional HDS reaction takes place in a fixed-bed reactor under high temperature and high pressure, typically in the range of 290°C to 455°C and 150psi to 3000psi, respectively. The oil feedstock and hydrogen gas are pumped to the reactor at high temperature and pressure with the presence of metal catalyst, for instance, cobalt-molybdenum supported by alumina ($CoMo/Al_2O_3$) or nickel-molybdenum supported by alumina ($NiMo/Al_2O_3$), producing desulfurized hydrocarbons and hydrogen sulfide. The HDS chemical equations for mercaptans and sulfides are listed as below:

$$RSH + H_2 \xrightarrow{CoMo/Al_sO_3} RH + H_2S \qquad \text{(Eq. 1.1)}$$

$$RSR' + H_2 \xrightarrow{CoMo/Al_sO_3} RH + R'H + H_2S \qquad \text{(Eq. 2.1)}$$

The mixture of hydrocarbons, hydrogen gas and hydrogen sulfide from the reactor would then pass through gas separator so as to separate the fuel from hydrogen and hydrogen sulfide. The mixture of hydrogen and hydrogen sulfide from the gas separator would be treated by amine gas so as to purify hydrogen gas for reusing in the reactor. Hydrogen sulfide can be oxidized to sulfur dioxide by air, which can be further converted to elemental sulfur through the Claus process or sulfuric acid through the contact process. Chemical equations for these two processes are listed in Table 1.6.

Table 1.6 Chemical reactions for the Claus process and the contact process

Process	**Chemical Equations**
Claus Process:	
Overall reaction:	$2H_2S + O_2 \rightarrow 2S + 2H_2O$
Hydrogen sulfide oxidation:	$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$
Catalytic conversion:	$2H_2S + SO_2 \xrightarrow{TiO_2} 3S + 2H_2O$
Contact Process:	
Sulfur dioxide oxidation:	$2SO_2 + O_2 \rightarrow 2SO_3$
Oleum formation:	$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$
Sulfuric acid formation:	$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

Fuel obtained from the gas separator would be further treated in stripper distillation unit with reflux so as to remove sour gas including hydrogen, hydrogen sulfide, methane, ethane, propane and other volatile organic compounds. Similarly, this gas mixture would be treated by amine gas to recover hydrogen sulfide. The remaining fraction can be used for other purposes such as refinery fuel gas.

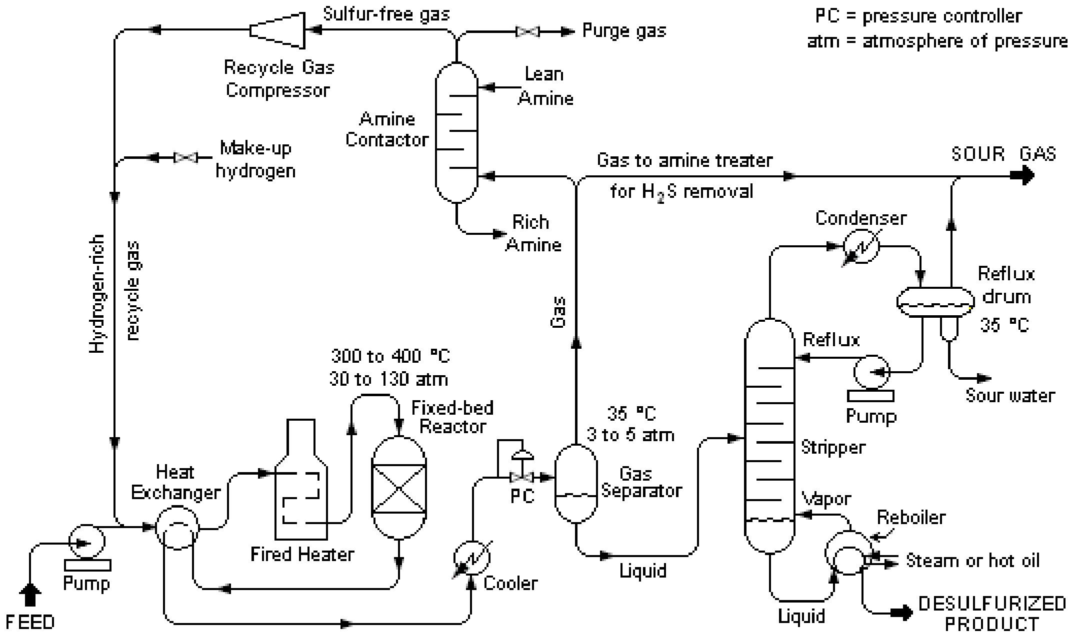


Figure 1.7 Schematic diagram of HDS unit

Although HDS has been used to produce low sulfur fuel for decades, the upcoming tightened regulations will be a new challenge on this process. HDS has been proven to desulfurize mercaptans, sulfides and thiophene. However, the more condensed derivatives including benzothiophenes (BTs) and dibenzothiophenes (DBTs) are more difficult to treat by HDS. The reactivity of the one- to three-ring OSCs decreases accordingly: Thiophenes > Benzothiophenes > Dibenzothiophenes (Girgis et al., 1991).

It is found that low sulfur diesel fuel produced from HDS contains approximately 500 ppm_w sulfur, mostly alkyl derivatives of DBTs which are considered as refractory compounds and cannot be easily desulfurized by HDS (Ma et al., 1994). 4-alkyl DBTs, 6-alkyl DBTs and 4, 6-alkyl DBTs have very low reactivity which can be explained by combinations of electronic density, bond order, and spatial, geometric and steric hindrance around the sulfur atom (Hans Schulz et al., 1999). 4, 6-dimethyl-dibenzothiophenes are well known for its high stability against HDS. Thus, traditional HDS is not applicable to produce ULSD required by the new sulfur regulations.

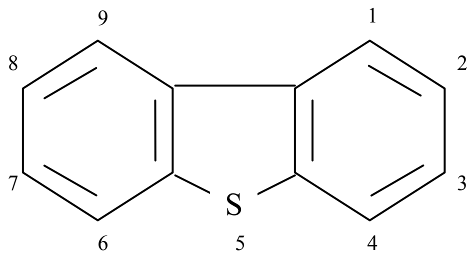


Figure 1.8 IUPAC numbering for DBT

Modifications on HDS, including increment of hydrogen, catalyst dosage, and also operating pressure, have been investigated. In general, hydrogen usage is the major operational cost for HDS. In order to lower the sulfur content from 500ppm$_w$ to 15ppm$_w$, an addition of 25% to 45% of hydrogen gas is required (Energy Information Administration, 2001). This implies that the operational cost will be doubled. On the other hand, doubling catalyst dosage can only lower the sulfur content by 100 ppm$_w$ (Whitehurst et al., 1998). Thus, a dramatic increase in catalyst dosage is required to produce ULSD.

Suggested by the National Petroleum Council, operating pressure has to be increased from 1100psi to 1200psi in order to produce diesel with less than 30 ppm$_w$ sulfur. This requires a specific thick-walled reactor to withstand such a high pressure, and thus increasing the capital and operational costs. Beside the huge increase in cost, safety issue is also a big concern for HDS which requires high operating temperature and pressure with the use of hydrogen gas. Reactor wall failure and even explosion can be resulted if uncontrollable “hot-spots” phenomenon (Speight, 1994), or any other operation errors happen.

1.4.2 Adsorptive Desulfurization (ADS)

Adsorption of OSCs in fuel is another possible desulfurization technology developed recently. In adsorptive desulfurization process, OSCs are adsorbed into a specified solid adsorbent so as to produce none- or low-sulfur fuel. Depending on the interaction between OSCs and the adsorbent, adsorptive desulfurization can be classified into direct adsorption desulfurization and reactive adsorption desulfurization. In direct adsorption desulfurization, OSCs are physically adsorbed on the adsorbent surface. Spent adsorbent can be regenerated by washing with a desorbent, usually a solvent, and the sulfur compounds can be concentrated simply by distillation.

PSU-SARS developed at Pennsylvania State University is an example of direct adsorption desulfurization. This process is basically a composition of direct adsorption desulfurization and hydrodesulfurization. Fuel feedstock is first treated with selective adsorption of sulfur compounds by specific transition metal compounds such as nickel phosphides. The spent adsorbent is regenerated by solvent washing and the sulfur rich fraction is further concentrated by evaporation so as to recycle the solvent. The concentrated sulfur fraction is then treated by hydrodesulfurization unit (Ma, 2001). Figure 1.9 shows the schematic diagram of PSU-SARS followed by HDS.

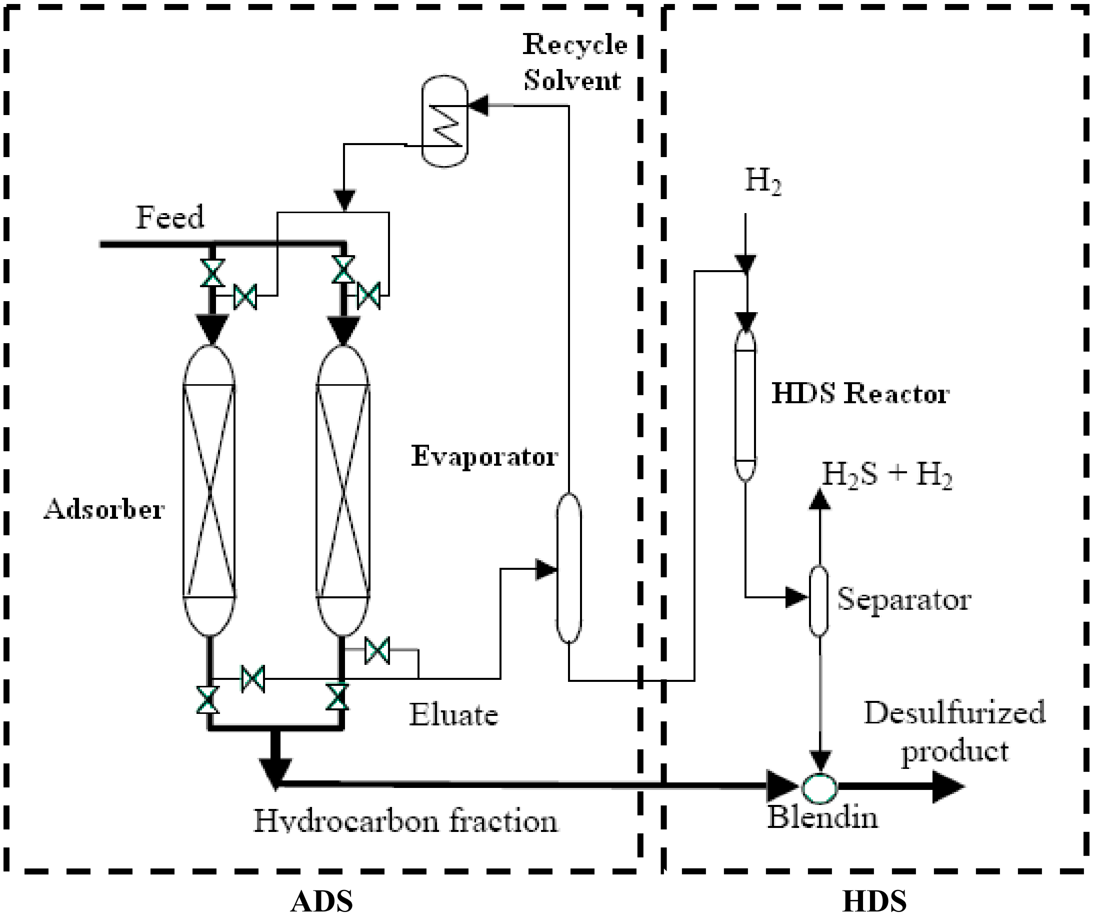


Figure 1.9 Schematic diagram of PSU-SARS followed by HDS (Ma, 2001)

Reactive adsorption desulfurization, on the other hand, is based on chemical interaction between OSCs and the adsorbents. In this process, sulfur portion of an OSC molecule is fixed on the adsorbent, and the sulfur-free hydrocarbon portion is released to the fuel. Regeneration of sent adsorbent can be done by either oxidation or reduction of sulfur portion. Depending on the regeneration process selected, elemental sulfur, hydrogen sulfide or sulfur oxides would be generated (Zhou ed., 2007).

The S-Zorb Sulfur Removal Technology (S-Zorb SRT) is a representative reactive adsorption desulfurization process announced by ConocoPhillips Company in 2000. Fuel feedstock is vaporized at 380-420°C in the presence of hydrogen gas and injected to the adsorption reactor. Sulfur portion in the OSCs cleaved from the molecules are adsorbed on the adsorbent, leaving the hydrocarbon portion in the fuel stream.

Hydrogen gas is primarily used to prevent coke building up on the adsorbent only, thus hydrogen consumption is relatively low comparing with HDS. Spent adsorbent is regenerated by an oxidation process, which convert the adsorbed sulfur to sulfur dioxide. S-Zorb SRT can be used to lower the sulfur content in gasoline and diesel fuels to a level of 5 ppm_w with a relatively low capital cost comparing with hydrodesulfurization units.

Several studies have also demonstrated that adsorptive desulfurization can produce desulfurized diesel or gasoline with sulfur content less than 30 ppm_w (Liu et al. 2007 and Tang et al, 2009). However, all these processes require specially prepared or synthesized adsorbents which are not commercially available at this stage.

Commercially available adsorbents such as activated carbon, activated alumina or zeolites are reported to be not applicable on adsorptive desulfurization (Takahashi et al., 2002). Besides, it is predicted that ADS is not a cost effective process to be applied on untreated fuel with high sulfur content. Factors affecting desulfurization including adsorption capacity, durability, regenerability and selectivity on sulfur compounds are also a major concern in developing ADS (Kwon et al., 2008).

1.4.3 Biodesulfurization (BDS)

Biodesulfurization, an enzymatic process involving the use of bacteria as biocatalysts to remove OSCs in fuels, is an innovative technology, which uses bacteria as the catalyst to remove sulfur from the feedstock.

Theoretically, biodesulfurization can be conducted in aerobic or anaerobic conditions. In aerobic conditions, OSCs are stepwise oxidized and eventually forming sulfate salts in the presence of sulfur-specific desulfurization microbes such as *R. Rhodochrous*, *R. erythropolis* D-1, *Gordona* CYKS1 and *Rhodococcus* UM3. OSCs are first oxidized to the corresponding sulfoxide, and then to sulfone, followed by sulfinate, and finally to desulfurized organic portion and inorganic sulfate ions (McFarland, 1999). While OSCs in fuel are converted to water-soluble sulfate which can be easily removed, the desulfurized organic potion would stay in the fuel. Thus, the fuel value would not be degraded. Figure 1.10 shows the general degradation pathway of DBT in the presence of sulfur-specific desulfurization microbes.

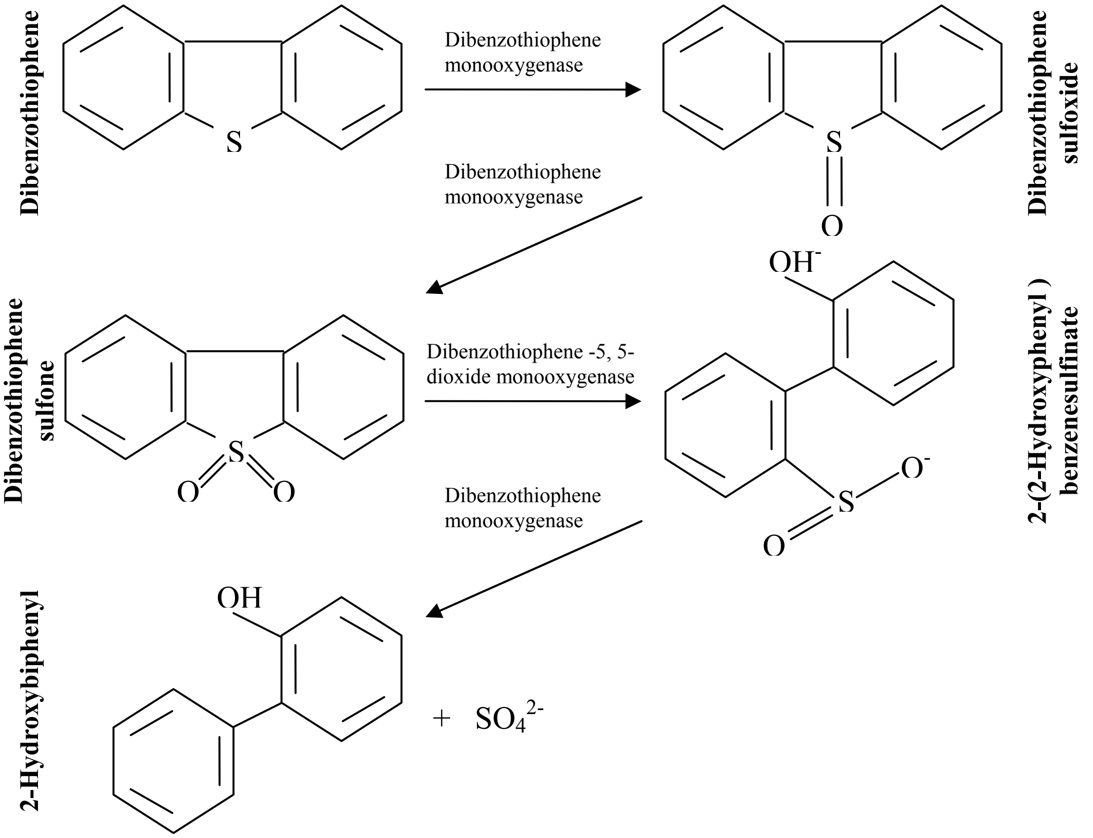


Figure 1.10 Sulfur-specific degradation pathway of DBT

On the other hand, anaerobic biodesulfurization causes the reduction of OSCs to H_2S in the presence of sulfur-reducing bacteria such as *Desulfovibrio sapovorans*. Although it has been demonstrated as a possible desulfurization pathway in model compound studies (Armstrong et al., 1995), no significant reduction in sulfur content in real fuel oil samples is observed under anaerobic biodesulfurization (McFarland, 1999). The industries are therefore more interested in aerobic biodesulfurization, and in most cases, the word “biodesulfurization” refers to aerobic biodesulfurization.

Recent researches have successfully demonstrated that various sulfur-specific desulfurization microbes can achieve 57% reduction in BT content (Kirimura et al., 2002), 90% reduction in DBT content (Li et al., 2006), 50% reduction in some of the alkyl derivatives of DBTs (Rashidi et al., 2006), higher than 80% desulfurization in HDS treated diesel (Li et al., 2003) and higher than 45% desulfurization in heavy oil (Yu et al., 2006).

Nevertheless, there are some factors limiting the applicability of BDS. Biological and enzymatic reactions are highly sensitive to environmental conditions such as operating temperature, solvent used, toxin and nutrient availability. Besides, a pre-HDS treatment is usually required to provide a relatively low sulfur fuel. Up to now, biodesulfurization has only been tested in bench scale study. Pilot-scale tests with more detailed designs and cost estimation have not been developed.

1.4.4 Oxidative Desulfurization (ODS)

Oxidative desulfurization is considered as the latest unconventional desulfurization process which involves chemical oxidation of divalent organic sulfur compounds to the corresponding hexavalent sulfur, also known as sulfone. The physical and chemical properties of sulfones, for instance boiling points, polarity and solubility in various solvents, are significantly different from the original sulfur compounds. In general, sulfones have higher boiling points and increased polarity which leads to higher solubility in polar solvent. Therefore, sulfones can be easily separated from fuels through distillation, solvent extraction or adsorption.

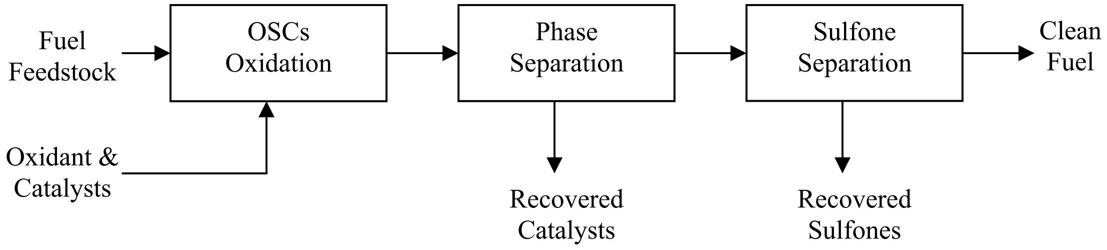


Figure 1.11 General process scheme for ODS

Theoretically, ODS can be performed by various type of oxidants. Nitric acid and nitrogen oxides were two popular oxidants used to remove both organic sulfur compounds and organic nitrogen compounds in 1980s (Tam et al., 1990). Due to poor selectivity, low yield and loss in heating value for the treated oil, these oxidants have not been widely used.

Recently, more studies are focused on hydrogen peroxide and organic peroxides as oxidants in ODS. With application of specific catalysts such as transition metal complexes and also phase transfer catalysts, hydrogen peroxide can be activated to effectively oxidize OSCs to sulfones under mild conditions (Yen et al., 2000; Zapata et al., 2005).

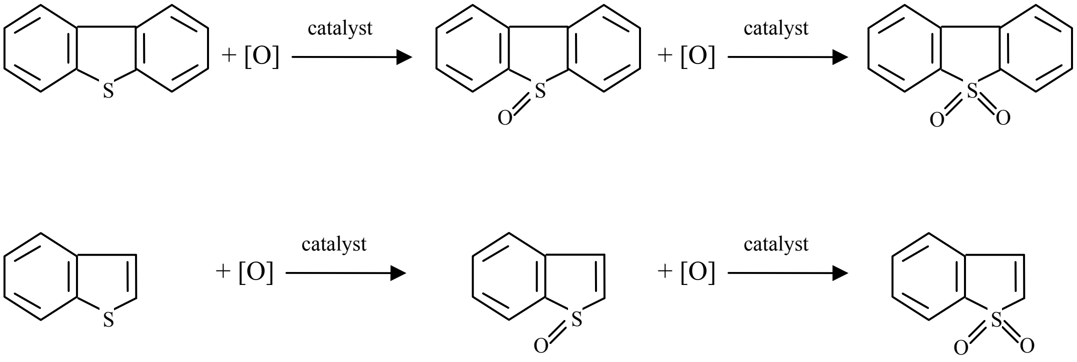


Figure 1.12 General reactions of BT and DBT in ODS (Gatan et al., 2004)

After the oxidation process, sulfones separation can be achieved by liquid-liquid extraction using polar solvents or by adsorption using, for instance, silica gel or alumina. Spent solvent can be purified by distillation so as to obtain clean solvent and concentrated sulfones. N, N-dimethylformamide, dimethyl sulfoxide, sulfolane, methanol and acetonitrile are some of the polar solvents which can be used for liquid-liquid extraction.

Among all the solvents listed, N, N-dimethylformamide is the most effect solvent to remove sulfones. Nevertheless, the oil recovery rate would be significantly lowered when this solvent is used for extraction (Otsuki et al., 2000). It has also been reported that some of the hydrocarbons such as naphthalene would be extracted from fuel during liquid-liquid extraction, resulting in reduction in heating value and fuel quality (Mei et al., 2003).

Instead of liquid-liquid extraction, sulfone adsorption with alumina could be applied to increase selectivity and reduce loss of valuable hydrocarbons (Etemadi et al., 2007). The major advantages of ODS include low capital cost, low reactor temperatures and pressures, short reaction time, no emissions, and no hydrogen requirement. It has been estimated by pilot plant studies that ODS could be operated in less than half of the cost of a new high-pressure hydrotreater (Energy Information Administration, 2001).

The Ultrasound Assisted Oxidative Desulfurization (UAOD) process is one of the most promising ODS systems with greater than 95% oxidation yield of organic sulfur in short period of time under mild conditions (Wan et al., 2007). However, the UAOD process cannot successfully produce ultra-low sulfur diesels. The modified UAOD process with the application of ionic liquids developed later demonstrated a greater than 98% desulfurization on various diesels which can meet the ULSD standards (Cheng et al., 2008).

Nonetheless, both the UAOD and the modified UAOD processes require high dosage of 30% wt. hydrogen peroxide solution and high energy consumptions. Both systems required 100 fold more oxidant than stoichiometic requirements. Lowered oxidant concentration would significantly reduce the OSCs oxidation yield (Wan et al., 2007). On the other hand, a typical 10 minutes ultrasonication using a probe ultrasonic reactor (model number VCX-750) applied in the UAOD and modified UAOD process to desulfurize 20g diesel requires 450 kJ of energy, which is equivalent to approximately 50% of chemical energy in 20g treated diesel, assuming a energy density of 45 MJ/kg in diesel (Gibilisco, 2006).

1.5 Research Objectives

With the tightened environmental regulations on diesel and other fuel oil, traditional HDS alone is not adequate to meet the upcoming sulfur limits. Oxidative desulfurization has been proven to be one of the feasible alternatives. Ultrasound Assisted Oxidative Desulfurization and the modified UAOD system developed recently have demonstrated more than 95% desulfurization on varies diesels which meets the ULSD standards (Wan et al., 2007; Cheng et al., 2008). However, high dosage of 30% wt. hydrogen peroxide solution and high energy consumptions are required in those processes.

In order to improve ODS efficiency and its applicability to heavy oil such as residual oil, this research investigates the use of alternative oxidants such as superoxide of alkali metals. Experiments were carried out to optimize ODS process as well as evaluate the desulfurization effectiveness in different fuel oil including residual oil. Furthermore, studies on an alternative enhancement technology, namely, ultraviolet assisted oxidative desulfurization, has also been performed to evaluate its feasibility and its potential in reducing energy consumption.

CHAPTER 2: THEORETICAL BACKGROUND

2.1 Introduction

In order to improve the Ultrasound Oxidative Desulfurization process so as to develop a technology to produce ultralow sulfur fuels with reasonable chemical consumption, a series of process modifications have to be considered.

The UAOD process includes the application of ultrasonication, hydrogen peroxide as oxidizing agent, acid catalysis, and phase transfer catalysis. Based on the UAOD process, the following elements were considered in the modifications: ultrasonication; oxidant selection; acid catalysis; phase transfer catalysis; application of ionic liquid; and photo-catalysis. The basic concepts of these six elements listed are discussed in this chapter.

2.2 Ultrasonication

2.2.1 Fundamentals of Ultrasound

Sonic wave is periodic vibration with frequency in between 15 Hz to 20 kHz which is audible to the average human. Ultrasound, on the other hand, is the radio wave with frequency higher than 20 kHz but lower than 100 MHz (Berlan et al., 1996). Nowadays, ultrasound is commonly applied to various industries including chemical synthesis, biotechnology and environmental engineering. Ultrasound frequency level is inversely proportional to the power output. Typically, low-power, high frequency ultrasound with frequency higher than 1 MHz is considered as non-destructive ultrasound. Ultrasound in this frequency range does not affect the medium it travels through. Thus, it is commonly used in medical sonography or other medical diagnosis.

On the other hand, high-power, low frequency ultrasound with frequency ranged from 20 kHz to 100 kHz does alter the medium it travels through. This type of ultrasound is mostly applied on sonochemical reactions. It has been demonstrated that ultrasound in this range is applicable to improve mixing, increase rate of chemical reactions, promote emulsification, and others (Thompson et al., 1999). Ultrasound with frequency ranged from 100 kHz to 1 MHz has medium power intensity. It is usually applied on biomedical treatments such as focused ultrasound surgery (FUS) or ultrasound based physical therapy (Baker et al., 2001).

2.2.2 Theory on Sonochemistry

The Chemical and mechanical effects of high-power, low frequency ultrasound were first identified in 1930s from a phenomenon called acoustic cavitation or ultrasonic cavitation (Suslick et al., 1999). Cavitation is a unique phenomenon in which a relatively low energy of an acoustic field is concentrated in very small volumes, resulting in a relatively high energy density locally. It is defined as the pulsation, oscillation, growth, splitting and other motion of bubbles and their interaction due to a first reduced, then an increased pressure produced in a liquid (Margulis, 1995).

When the negative pressure produced at the rarefaction period of a sound wave exceeds the van der Waals force among molecules in the liquid, it would initiate the formation of cavitation bubbles at gas or solid particles (Mason, 1999). These cavitation bubbles would grow to an equilibrium size or resonance size when the resonance frequency of the bubbles equals the ultrasound frequency applied. When the cavitation bubble grows to size greater than the resonance size, the bubble would collapse and generate a local high pressure greater than 1000 atm and high temperature up to 5000K instantaneously (Storey et al., 2001).

Sonochemical activity and occurrence of acoustic cavitation could be affected by factors including ultrasound frequency, ultrasonic power, temperature, reactor pressure, solvent properties and sparge gas applied (Beckett et al., 2000).

Sonoluminesence is another phenomenon happening when ultrasound is applied in a liquid. It is the light emitted when cavitation bubbles collapse, which implies the existence of local high temperature. This phenomenon was first discovered by H. Frenzel and H. Schultes by putting an ultrasound transducer in photographic developer fluid in 1934 (Crum et al., 1994). This discovery was later recognized as multiple-bubble sonoluminescence (MBSL). The concept of sonoluminescence is illustrated in Figure 2.1.

Another type of sonoluminescence, single-bubble sonoluminescence (SBSL), was discovered by F. Gaitan and L. Crum in 1989 (Gaitan et al., 1992). The peak temperature could be ranging from 6000K to approximately 20000K. Production of active chemical species such as hydrogen peroxide and hydroxyl radicals are reported (Didenko et al., 2002).

Different theories, including the electrical theories, the mechanochemical theory, the chemiluminescence theory, the hot spot theory, the shock wave theory and others, have been developed to explain these phenomena caused by ultrasound based on light emission mechanisms. Among all, researchers are more interested in the electrical theories, the hot spot theory and the shock wave theory. It was first proposed that the light emitting phenomenon was a result of charge separation in cavitation bubbles, the charge fluctuations when bubbles collapse and other electrical microdischarge (Levshin et al., 1937). Electrical theories have a common assumption that emitting bubble has asymmetric charge distribution, which is found later to be contradicted with systematic studies on SBSL (Ohl, 2000).

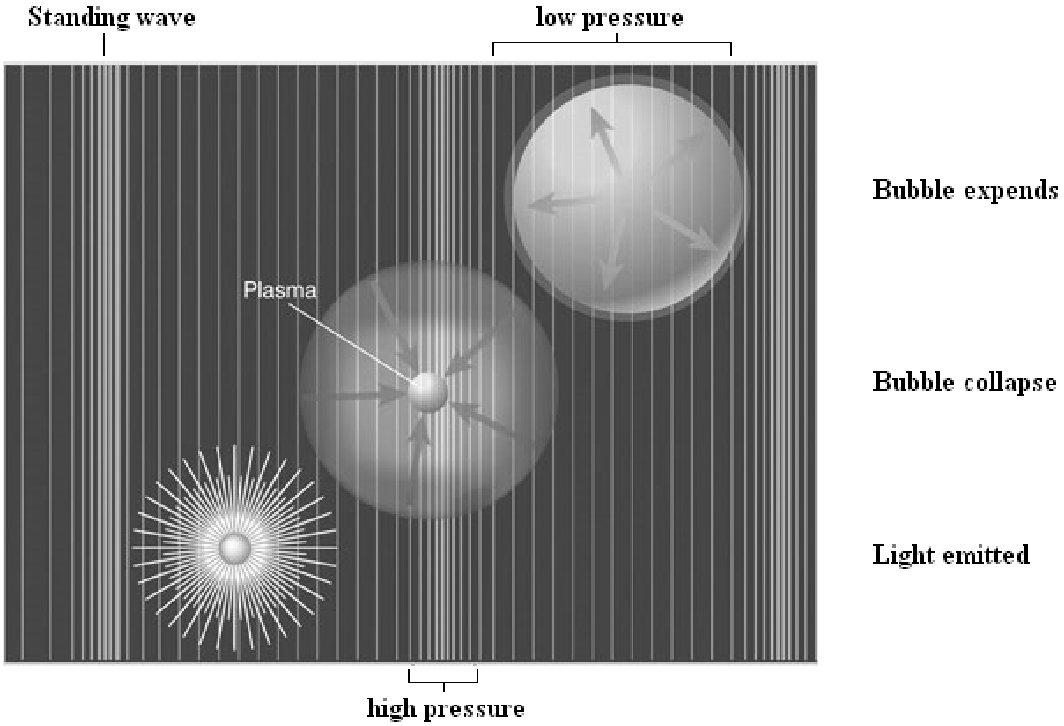


Figure 2.1 The sonoluminescence process (Lohse, 2002)

The hot spot theory is described that the energy for light emission causing sonoluminesence is supplied by thermal energy generated during cavitation bubble collapse. The hot spot is believed either a black body where the radiation and matter are approximately in equilibrium (Noltingk et al., 1950), or Bremsstrahlung, also known as free-free transitions caused by accelerating unbounded electrons (Yasui, 1999). The hot spot theory generally suggested that an instantaneous increase of temperature to a range higher than 10000K, and that of pressure up to 1800 atm would occur during bubble collapse, would be responsible for the sonoluminesence.

The shock wave theory proposed by Jarman in 1960s suggests that mircroshocks propagated within the imploding bubbles induce high temperature and pressure causing sonoluminesence (Taylor et al., 1970). This theory is now considered as an alternative to the hot spot theory, and the possibility of microscale explosive shockwave synthesis at the final stage of bubble collapse has been discussed in various studies (Greenspan et al., 1993; Crum et al., 1998; Young, 2005).

2.2.3 Sonochemistry in Aqueous Phase

Applying high-power low frequency ultrasound to aqueous system would cause the formation of cavitation bubbles and sonoluminescence. Although part of the energy would be released as light and heat, more energy would be involved in chemical reactions. As listed in Table 2.1, it is demonstrated from a single cavitation bubble model in aqueous solution that energy for sonochemical reactions is more than 100 fold of the energy for sonoluminescence (Didenko et al., 2002).

Local high temperature and high pressure generated due to collapse of cavitation would lead to the formation of intermediate radical species including hydroxyl radical ($OH\cdot$), hydrogen radical ($H\cdot$), and hydroperoxyl radical ($HO_2\cdot$). These radicals, especially $OH\cdot$, are highly active and are precursors of many other chemical reactions. Formation of hydrogen peroxide by ultrasonic irradiation is also of particular interests, because it is usually used as an indirect measurement of $OH\cdot$ production.

Table 2.1 Sonochemistry in a cavitation bubble formed in water (Didenko et al., 2002)

Conditions	**3°C**	**22°C**
Number of OH· radicals per cycle	8.2×10^{5}	6.6×10^{5}
Number of NO_2^- ions per cycle	9.9×10^{6}	3.7×10^{6}
Number of photons per cycle	7.5×10^{4}	8.1×10^{3}
Maximum potential energy of bubble (eV)	7.5×10^{10}	6.4×10^{10}
Energy to form OH· radicals (eV per cycle)	4.3×10^{6}	3.4×10^{6}
Energy to form NO_2^- ions (eV per cycle)	4.2×10^{6}	1.6×10^{6}
Energy to form photons (eV per cycle)	2.6×10^{5}	2.7×10^{4}
Energy efficiency of sonochemistry	1.1×10^{-4}	7.8×10^{-5}
Energy efficiency of sonoluminescence	3.5×10^{-6}	4.3×10^{-7}

Ultrasound causes formation of radicals similar to ionizing radiation, which split water molecules into H· and OH· (Yazici et al., 2006). It is also reported that atomic oxygen can be generated from dissolved oxygen in aqueous solution upon ultrasound irradiation (Fang et al., 1995). These radicals and atomic oxygen would further react with dissolved oxygen, water molecules, or other radicals to form hydrogen peroxide and oxygen eventually.

A summary of these chemical reactions according to the initial active species generated from ultrasound is listed in Table 2.2. It has also been reported that the presence of ozone (O_3) would promote generation of free radicals and reactive oxygen species. The presence of inert gas, argon (Ar) for instance, would promote sonoluminescence reactions (Beckett et al., 2001). Figure 2.2 illustrates the chemical reactions during acoustic cavitation with gases including Ar, O_2 and O_3.

Table 2.2 Chemical reactions initiated by ultrasound in water (Mason et al., 2002)

Radiolysis of H_2O	$H_2O \xrightarrow{ultrasound} H\cdot + OH\cdot$ $H\cdot + O_2 \longrightarrow HO_2\cdot$ $HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2$ $OH\cdot + OH\cdot \longrightarrow H_2O_2$
Radiolysis of O_2	$O_2 \xrightarrow{ultrasound} 2O$ $O + H_2O \longrightarrow 2OH\cdot$ $OH\cdot + OH\cdot \longrightarrow H_2O_2$

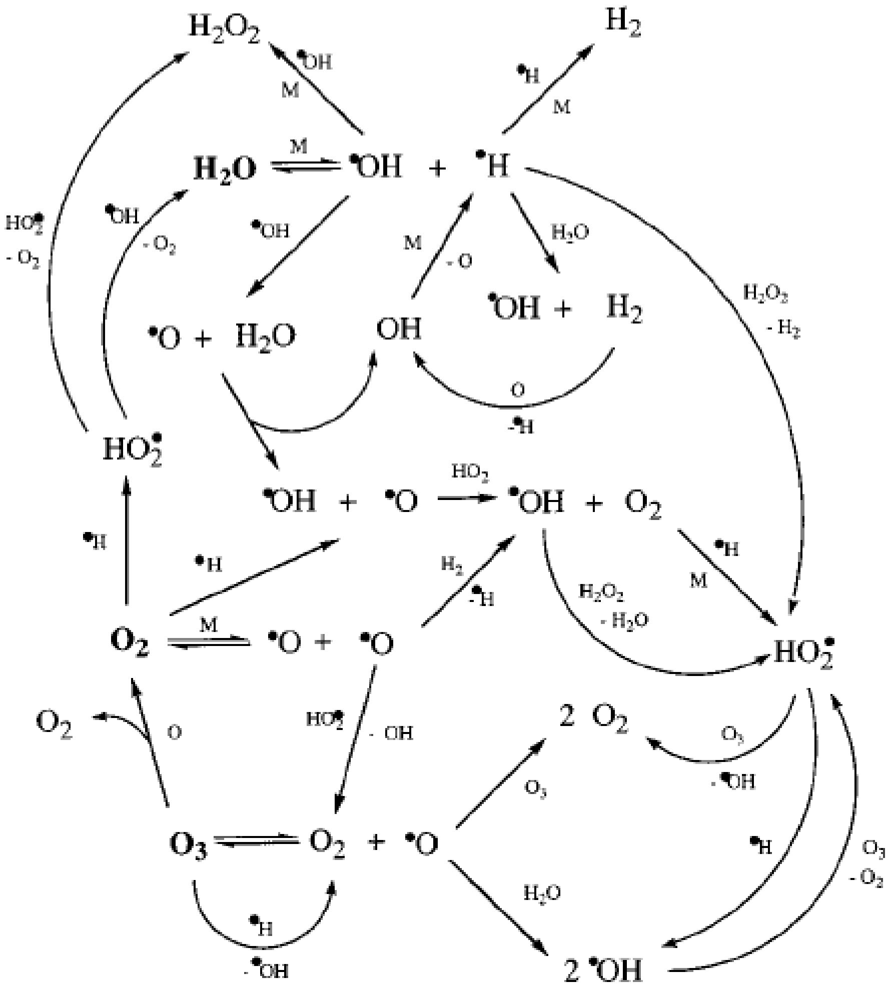


Figure 2.2 Sonochemical reactions in water with Ar, O_2 and O_3 (Beckett et al., 2001)

2.2.4 History of UAOD and Its Modifications

When ultrasound is applied, very fine cavitation bubble would form. This phenomenon can greatly improve emulsification in a system with two or more immiscible liquid phases. This would greatly increase the contact area and thus, the mass transfer of reactants. Combining the effect of local high temperature and pressure produced during collapse of cavitation bubble, ultrasound could greatly increase the rate of reactions, especially in a system involving multiple liquid phases such as UAOD process (Mei et al., 2003).

UAOD process has been under development since 1990s. At the very beginning of the UAOD history, desulfurization was observed by applying a 20 kHz ultrasound to crude oil suspended in basic or acidic conditions. Use of transition metals such as nickel and vanadium as catalysts with hydrogen peroxide as a chemical assisted ultrasound method was developed (Lin et al., 1993; Sadeghi et al., 1994; Yen, 1998).

In the first generation of UAOD, or simply the UAOD process, the Venturella type of transition metal catalysts (TMC), or polyoxometallates with Keggin structure such as phosphotungstic acid ($H_3PW_{12}O_{40}$), and a quaternary ammonium salt, tetraoctylammonium bromide, as phase transfer catalyst (PTC) were introduced so as to produce high effective and selective oxidation with hydrogen peroxide to improve desulfurization (Mei et al., 2003). Structure of phosphotungstic acid is illustrated in Figure 2.3. In the UAOD process, higher than 98% desulfurization on selected diesel samples can be achieved in 10 minutes ultrasonication with 30% wt. hydrogen peroxide as oxidant, together with the selected TMC and PTC. However, it has been demonstrated that the UAOD process has a low conversion on benzothiophene (BT) and its derivatives. Brominated byproducts are also identified in the treated oil samples.

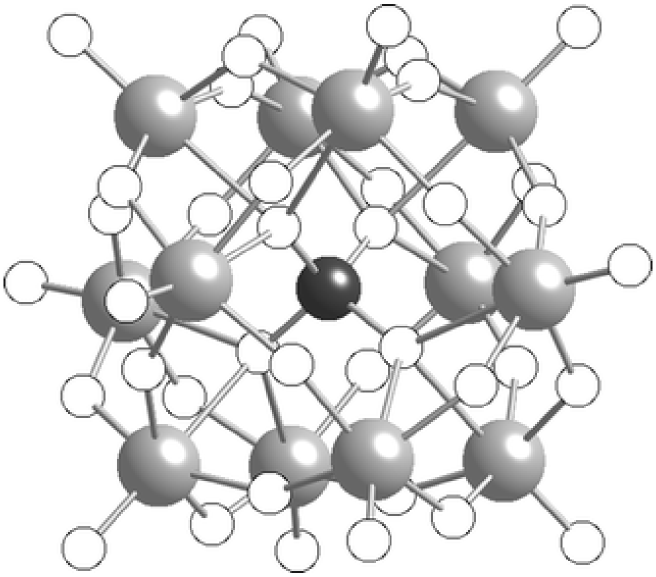


Figure 2.3 The Keggin structure of $[PW_{12}O_{40}]^{3-}$ (Bochet et al., 2009)

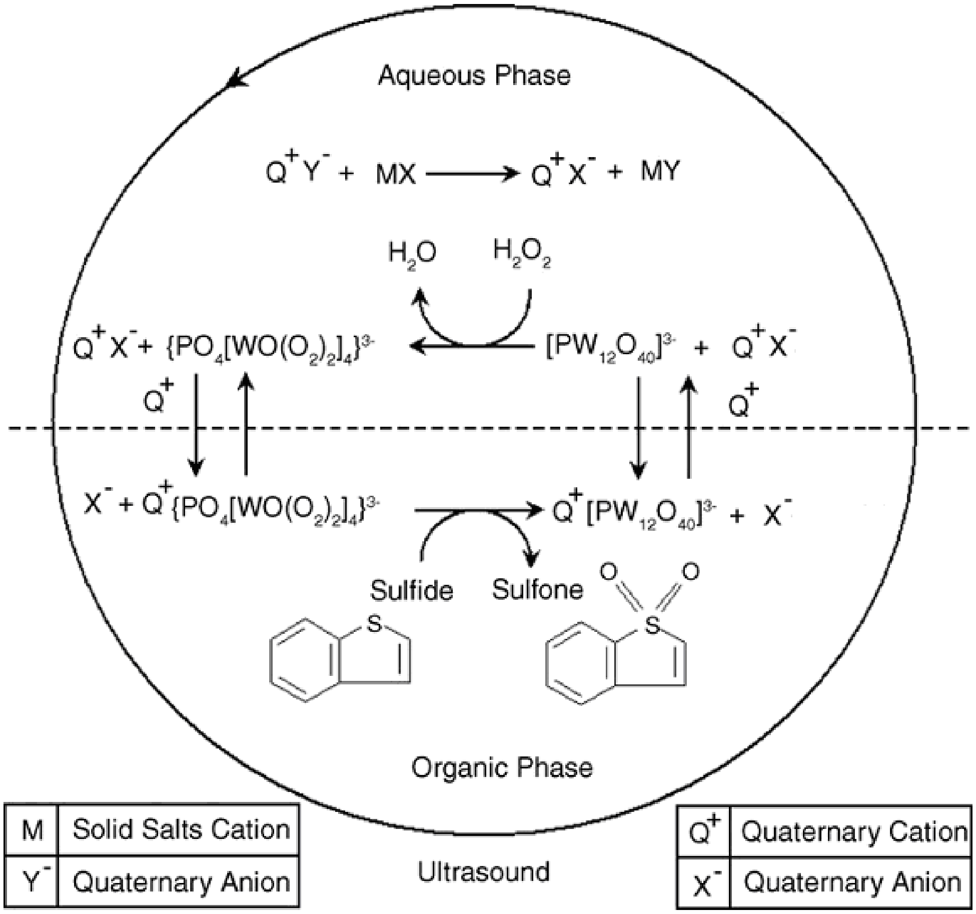


Figure 2.4 Conceptual model of 1st generation of UAOD process (Wan et al., 2007)

Changing phase transfer agent in the second generation of UAOD led to desulfurization without brominated byproduct. Instead of bromide as anion, quaternary ammonium salt with fluoride as anion was used as phase transfer catalyst. This eliminated the formation of byproduct, and also increased the overall desulfurization efficiency (Wan et al., 2007).

The second generation of UAOD demonstrated greater than 95% desulfurization in various diesel samples within 10 to 20 minutes. A portable, continuous flow desulfurization unit was customized based on the second generation UAOD (Wan et al., 2008). The portable UAOD unit can treat a maximum of 52.8 lb diesel per day with 92% desulfurization. In order to reduce hydrocarbon loss, alumina adsorption was applied as a post treatment to remove sulfones instead of liquid-liquid extraction (Etemadi et al., 2007).

The recent development of the third generation of UAOD has included the addition of room temperature ionic liquid (RTIL) and organic acid, into the system. Ionic liquid can serve as both extracting reagent and phase transfer catalysts which would further improve desulfurization efficiency. The third generation of UAOD can achieve greater than 99.9% desulfurization in various diesel samples by mechanical mixing for 3 hours with or without an addition of 10 minutes ultrasonication (Cheng et al., 2008). Ultra-low sulfur diesel with sulfur content less than 15 ppm_w can be produced from various diesels by this process.

A simplified comparison of the UAOD process (1st generation of UAOD), portable UAOD (2nd generation of UAOD) and the Modified UAOD process (3rd generation of UAOD) is summarized in Table 2.3. With the progressive improvement from the UAOD process to the modified UAOD process, ULSD can now be produced under mild conditions. However, energy and oxidant consumption in all three processes are extremely high. These would reduce the applicability of the processes in the industry.

Table 2.3 Comparison of the UAOD process and its modifications

	UAOD	**Portable UAOD**	**Modified UAOD**
Total Reaction Time, min	10	60	120
Sonication Time, min	10	60	10
Power Used, W	750	100	750
Energy Used, kJ	450	360	450
Temperature, ˚C	70	70	70
[S]:[O] ratio, mol:mol	1:200	1:200	1:100
Desulfurization Yield of BT*	50%	95%	> 98%
Desulfurization Yield of MGO	95%	95%	> 98%
Brominated Byproduct?	Yes	No	No
Produce ULSD?	No	No	Yes

* based on model compound (BT) studies

Besides, it is reported that some RTILs, for instance imidazolium type ionic liquid, would undergo thermolysis by ultrasonic irradiation (Oxley et al., 2003). Oxidative degradation of ionic liquid is also demonstrated in the presence of hydrogen peroxide, acetic acid and ultrasonication (Li et al., 2007). Selection on RTIL was studied during the third generation of UAOD. It was found that the typical type of RTIL, 1, 3-dialkylimidazolium hexafluorophosphate would be degraded to reactive gases including hydrogen fluoride (HF), phosphorus pentafluoride (PF_5) and phosphorus oxyfluoride (POF_3), which can severely damage glass and other equipment. Ionic liquids with alkylsulfate as anion have been used in the sixth generation of UAOD instead. Alkylsulfate anion-based ionic liquids are relatively more stable, and produce non-corrosive byproducts upon degradation (Jess et al., 2004).

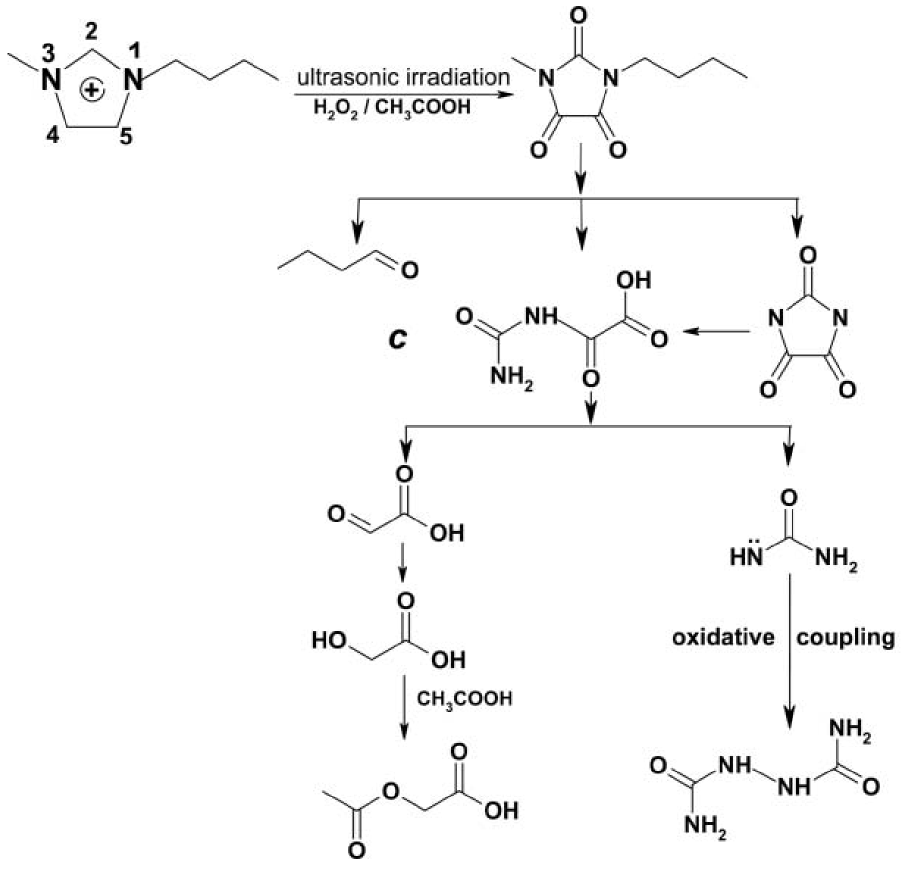


Figure 2.5 Degradation of specific ionic liquid with ultrasound (Li et al., 2007)

2.3 Oxidant Selection

Oxidizing agent is one of the key elements in any oxidative desulfurization process. To achieve oxidative desulfurization, oxidant is required to oxidize organic sulfur compounds into the corresponding sulfoxides or sulfones with higher polarity. With higher polarity than other hydrocarbon, sulfoxides or sulfones can be easily removed from fuel by extraction, adsorption or other post-treatments.

Wide variety of oxidants, such as concentrated nitric acid (Tam et al., 1990), organic hydroperoxides (Boikov et al., 2008), peroxyacids (Tetsuo et al., 1994), hydrogen peroxide (Mei et al., 2003), permanganate (Dehkordi et al., 2008), ozone (Otsuki et al., 1999) and oxygen (Campos-Martin et al., 2004) are considered as possible oxidants for ODS processes. Among all, hydrogen peroxide is considered as the most promising oxidant in terms of selectivity, availability, safety, cost effectiveness and environmental influence (Filippis et al., 2003).

2.3.1 Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is considered as "green" reagent which is commonly used in oxidative desulfurization processes. With the aid of catalysts, hydrogen peroxide can oxidize OSCs to the corresponding sulfones in ambient conditions. During reactions or degradation, water and oxygen are the only by-products which are in general, considered to have no adverse effect on the environment. The degradation of hydrogen peroxide can be illustrated in the following chemical equation:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \text{(Eq. 2.1)}$$

Pure hydrogen peroxide is a pale blue to colorless liquid with density higher than water. Hydrogen peroxide is miscible with water in any portion forming a colorless solution. Nowadays, hydrogen peroxide is widely used as disinfectant, oxidizing agent, and even as a propellant. Due to the high reactivity and oxidizing power, hydrogen peroxide is considered as a reactive oxygen species (Takishima, 1994).

Although dilute (27.5% wt. or lower) hydrogen peroxide are considered stable and safe for storage, concentrated hydrogen peroxide are corrosive and extremely reactive. In fact, solution with higher than 35% wt. hydrogen peroxide are considered as possible cause of spontaneous ignition of combustible materials if contacted. It becomes unstable at elevated temperature and/or pressure. Hydrogen peroxide at 52% wt. solution or above could cause a significantly higher rate of spontaneous ignition if contacted with combustible materials. It could also undergo vigorous self-sustained decomposition or even explosive reaction if it is exposed to heat or contaminants. At 91% wt. or higher, hydrogen peroxide solutions are used as rocket propellant which can undergo explosive reactions.

Due to safety reasons, aqueous solution of 30% wt. of hydrogen peroxide is more commonly used. Although pure hydrogen peroxide has a high active oxygen ratio (Bregeault, 2003), dilution effect should be considered as it would significantly reduce the active oxygen ratio. Active oxygen ratios of some common oxidizing agents are listed in Table 2.4.

Table 2.4 Oxygen-donor Oxidants (Bregeailt, 2003)

Oxidant	**Active Oxygen (% wt.)**	**By-product**
H_2O_2 (pure)	47.1	H_2O
O_3	33.3	O_2
HNO_3	25.4	NO_x
t-BuOOH	17.8	t-BuOH
H_2O_2 (30% wt.)	14.1	H_2O

2.3.2 Superoxide Anions

Superoxide ion, $O_2^- \cdot$, is a free radical with one unpaired electron. Many types of superoxide are considered stable in ambient conditions in the absence of water. Upon contacting with water, it undergoes reaction forming oxygen and hydrogen peroxide, as illustrated in the following equation:

$$2O_2^- \cdot + 2H_2O \rightarrow O_2 + H_2O_2 + 2OH^- \qquad \text{(Eq. 2.2)}$$

Solid state superoxide is available metal superoxides or organic compounds superoxides such as tetraalkylammonium superoxides. The stability of metal superoxides depends on the electropositivity of the metal cation. The electropositivity decreases along the period, and increases down the group of the periodic table. Therefore, alkali metal with higher atomic weight gives a greater stability to its superoxide. Metal superoxides are stable even in high purity at dry ambient conditions. Thus, it can provide a high active oxygen ratio. For instance, potassium superoxide has an active oxygen ratio of 45% wt.

Similar to hydrogen peroxide, superoxide anion is also considered as a reactive oxygen species. In fact, researches have found hydrogen peroxide, the superoxide anion radical, and the hydroxyl radical the most important reactive oxygen species (Callahan et al., 2001). Superoxide can generate other reactive oxygen species including hydrogen peroxide, hydroxyl radical, and perhydroxyl radical by a series of free radical reactions (Foote, 1995).

Although superoxides have not been widely applied to oxidative desulfurization process, chemical reactions between superoxides and organic sulfur compounds were recorded in early 1980s. For instance, thiol, alkyl disulfides and aryl disulfides can be oxidized by superoxide anion to the corresponding sulfinic acids or sulfonic acids (Oae et al., 1981). More complex organic sulfur compounds such as thioamides, thioureas and thiouracils can also be oxidized by superoxides forming amides or other corresponding hydrocarbons, and also elemental sulfur or inorganic sulfate to achieve desulfurization (Chang et al., 1989, Kim et al., 1990). Some of the reactions between OSCs and superoxide are illustrated in Figure 2.6.

Oxidation of Thiols

$$2RSH + 3O_2^{-\cdot} \rightarrow RSO_2^- + RSO_3^- + H_2O$$

Oxidation of Disulfides

$$2RSSR' + 5O_2^{-\cdot} \rightarrow 2RSO_2^- + 2R'SO_3^-$$

Oxidation of N-(2-hydroxy-phenyl)-N-Phenylthioureas

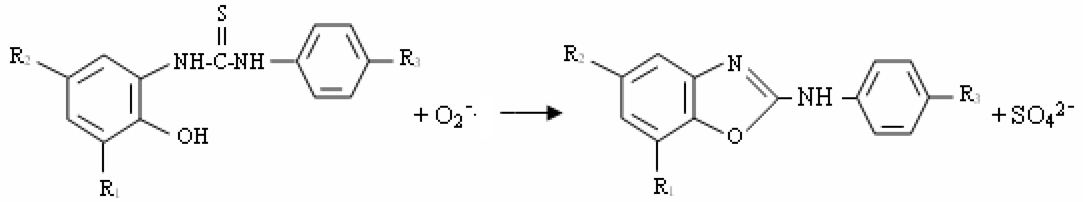


Figure 2.6 Chemical reactions between OSCs and superoxide anion (Afanas’ev, 1989)

2.4 Acid Catalysis

Although oxidative desulfurization can be carried out through noncatalytic oxidation or catalytic oxidation of OSCs, noncatalytic oxidative desulfurization processes requires high temperature of approximately 200°C and high pressure (Paniv et al., 2006). In contrast, catalytic oxidative desulfurization requires relatively mild conditions with temperature ranging from 25°C to less than 100°C under ambient pressure. Various types of ODS catalysts including, aldehydes (Murata et al., 2004), transition metal salts (Chen et al., 2007), polyoxometalate acids (Rosa et al., 2006) and carboxylic acids (Ma et al., 2001), while organic acids and polyoxometalate acids are the most commonly adopted.

Oxidation catalysis with polyoxometalates is considered to be complicated and diverse. Basically, polyoxometalate anions are capable of reversible redox reactions to actively transfer oxygen to the targeting compounds for selective oxidation (Bäckvall, 2004). For instance, active peroxo polyoxometalates can be formed by the interaction between the polyoxometalate anion and hydrogen peroxide. The active peroxo polyoxometalates can be transferred to organic phase easily with the aid of a phase transfer agent.

Polyoxometalates are relatively thermal stable comparing with other transition metal catalysts. Beside, polyoxometalate acids are well known for the high Brönsted acidity. Generally, Brönsted acidity of polyoxometalate acids could be stronger than that of mineral acids such as sulfuric acid by several orders of magnitude. Brönsted acidity of different polyoxometalate acids are in the following sequence: $H_3PW_{12}O_{40}$ > $H_4PVW_{11}O_{40}$ > $H_4SiW_{12}O_{40}$ > $H_3PMo_{12}O_{40}$ > $H_4SiMo_{12}O_{40}$ (Borras-Almenar et al., 2003). Nevertheless, polyoxometalates are not stable towards strong oxidants such as hydrogen peroxide in aqueous solution. Decomposition of polyoxometalates to peroxometalates were observed and thus, causing loss of catalyzing ability (Kozhevnikov, 2002).

Carboxylic acids, or more commonly referred to formic acid and acetic acid, are also applicable in catalytic oxidative desulfurization processes. Coupling with hydrogen peroxide, peroxyl acids could be generated in situ (Greenspan, 1947). It is suggested that peroxyl acids are some of the most possible oxidants for selective oxidation of OSCs (Lanju et al., 2008; Wang et al., 2003).

2.5 Phase Transfer Catalysis

2.5.1 Overview of Phase Transfer Catalysis

Phase transfer catalysis is a major enhancement in many chemical reactions involving multiple phases, especially for those which are immiscible in each other. Generally, reactions could be greatly inhibited due to reactants separation by immiscible phases. Introducing a phase transfer catalyst (PTC) would improve the miscibility of phases, thus increasing chance of reactants contact so as to enhance reaction rate.

One of the most common uses of PTC is to enhance reactions between organic (oil) and inorganic (aqueous) phases. Due to the significant improvement in reaction rate, using PTC would generally increase productivity, improve quality and reduce cost. Phase transfer catalysis has been applied for many applications, including chemicals and pharmaceuticals manufacture, petroleum processing, and other industries (Starks et al., 1994).

2.5.2 Mechanism of Phase Transfer Catalysis

It is known that ionic compounds such as salts and other polar compounds with strong electric dipole are difficult to enter organic phase. Phase transfer catalysis is based on the ability to improve reaction rate of reagents in different phases of a reaction mixture by accelerating interfacial transfer. Depending on the ions required for reaction in organic phase, phase-transfer catalysis can be performed by cation or anion transfer.

Cation transfer is usually related to metallic cation transfer. Neutral complexants such as crown ethers and cryptands for inorganic cation transfer. Crown ethers are considered as some of the most common PTCs for metallic cations transfer. Crown ethers are heterocyclic compounds with several ether groups. Specific crown ether is a strong binding agent for specific cation to form stable complex. Basically, oxygen in the ring structure of crown ether would coordinate with the cation, locating it at the interior of the ring structure and leaving the exterior of the ring as hydrophobic. As a result, the cation would be stabilized and become soluble in organic or nonpolar phase. Affinity of crown ether for a cation depends highly on the structure and denticity. For instance, 15-crown-5 has high affinity for sodium cation, while 18-crown-6 has high affinity for potassium cation (Guida et al., 1980).

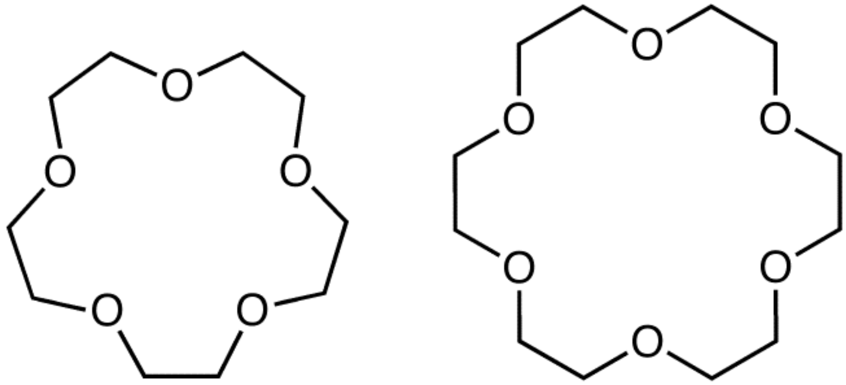


Figure 2.7 Structures of crown ethers: 15-crown-5 and 18-crown-6

Anionic transfer, on the other hand, requires stabilizing the target anion, or in some case neutral molecule, from the polar phase to non-polar phase. PTC is necessary because anions and neutral compounds which are soluble in aqueous phases are generally not soluble in organic phases, whereas the organic reactants in organic phases are not soluble in aqueous phases. These type of phase transfer catalysts are usually referred to as salts of onium cation, including ammonium, phosphonium and arsonium, where quaternary ammonium salts (QASs) are the most common PTCs for anion transfer (Starks, 1971). For example, tetrahexylammonium chloride, $(C_6H_{13})_4N^+Cl^-$, can be used to catalyze the reaction between cyanide in aqueous phase and chlorooctane, a reaction which is theoretically not feasible without PTC. The concept of Starks' extraction is illustrated in Figure 2.8.

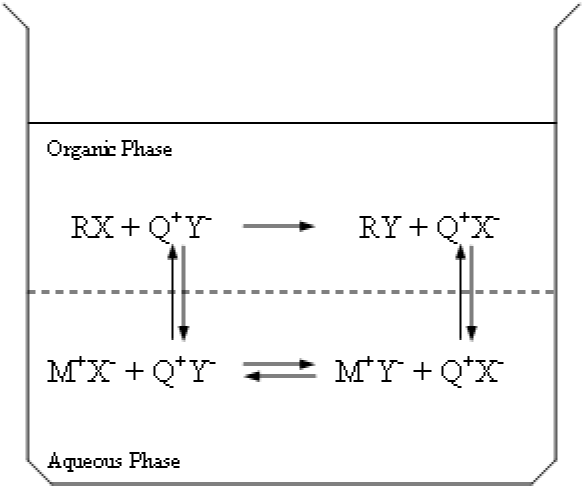


Figure 2.8 Starks' extraction mechanism

Phase transfer catalysts such as QASs are commonly considered as loosen ion pairs comparing with normal salts such as sodium chloride. The looseness of the ion pair is a major reason for enhanced reactivity. According to Starks' extraction mechanism, phase transfer catalysis is applied on nucleophilic substitution reaction:

$$RX + Y^- \rightarrow RY + X^- \quad \text{(Eq. 2.3)}$$

where Y^- is the active nucleophile required to be transferred from aqueous phase into the organic phase. An extraction of the active nucleophile Y^- can be performed by addition of quaternary ammonium cation Q^+, so that an ion pair $[Q^+Y^-]$

would be formed and entering the organic phase for the nucleophilic substitution reaction to happen. Q^+ would recombine with X^- released and reach equilibrium between phases, so as to form a cycle of catalytic reactions.

For successful phase transfer catalysis, it is not only required to transfer the targeting ion to the organic phase, but also activate it or render it to highly active form. QASs can be used for anion activation due to a longer separation between cation and anion in comparison to normal metallic salts (Starks et al., 1994).

Quaternary ammonium salts can also reduce the levels of hydration around the active nucleophile by selecting an appropriate anion (Jones, 2001). The less water of hydration around the active nucleophile, the more reactive it is in most organic phase reactions. Thus, the efficiency of quaternary ammonium catalyst is greatly influenced by the choice of counter anion of the catalyst. The mechanism of nucleophile activation by reducing level of hydration is illustrated in Figure 2.9. Table 2.5 listed the degree of hydration of ionic anions.

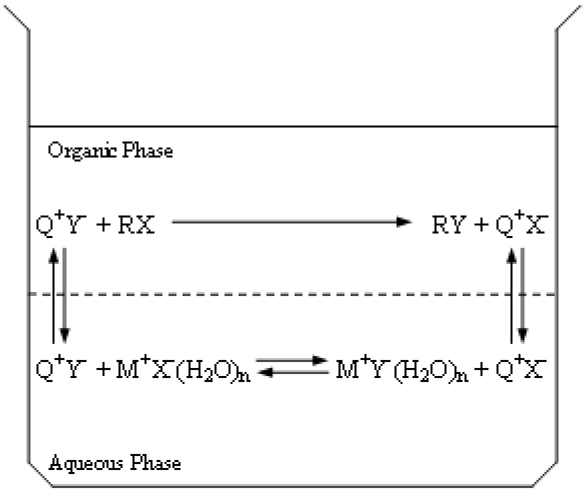


Figure 2.9 Modified Starks' extraction mechanism with water of hydration

Table 2.5 Hydration of anion in chlorobenzene-aqueous system (Jones, 2001)

Anion	**Hydration of Anion in Chlorobenzene**
F^-	8.5
RCO_2^-	4.0
Cl^-	3.0
Br^-	2.0
I^-	1.1

2.5.3 PTC Selection in UAOD Process

In order to enhance organic sulfur oxidation, phase transfer catalysis has been applied in different desulfurization processes. It has been reported that thiophenol, and benzyl mercaptan can be oxidized by chromium trioxide to the corresponding disulfide with 18-Crown-6 as the phase transfer catalyst and dichloromethane as solvent (Juaristi et al., 1984).

In biphasic reactions with a highly polar solvent such as ethyl acetate, methanol or water, ammonium salts are more effective PTC compared with crown ethers. Organic sulfur compounds are generally oxidized to the corresponding sulfoxides or sulfones under these conditions. For example, tetrabutylanunonium bromide is used as a phase transfer agent in the oxidation of organic sulfides to sulfoxides with periodate as oxidant (Venkatachalapathy et al., 1999).

Before the modification of the second generation of the UAOD process, tetraoctylammonium bromide was used as the phase transfer catalyst. However, formation of brominated by-products was observed. Bromine formation during the oxidation process with hydrogen peroxide and acid catalysts could be one of the possible reasons for the formation of by-products. Equation 2.4 illustrates the oxidation of bromide to bromine in acidified hydrogen peroxide solution.

$$H_2O_2 + 2H^+ + 2Br^- \rightarrow 2H_2O + Br_2 \qquad \text{(Eq. 2.4)}$$

According to the standard electrode potentials listed in Table 2.6, the oxidation of bromide by acidified hydrogen peroxide is a spontaneous reaction. This can be proved easily by a simple experimental setup which mixes tetraoctylammonium bromide with acidified hydrogen peroxide solution. A brownish color would be observed instantaneously upon mixing, indicating the oxidation of bromide ion to bromine. Bromine formed could undergo substitution reactions or addition reactions forming brominated by-products.

Table 2.6 Standard electrode potentials for selected half-reactions (Milazzo et al., 1978)

Half-Reaction	**Electrode Protential (V)**
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.76
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$	+1.09

Starting from the second generation of the UAOD process, a specific quaternary ammonium salt, tetraoctylammonium fluoride (TOAF), is used to improve the transfer and reactivity of hydrogen peroxide to oxidize organic sulfur compounds. Because fluoride ion cannot be easily oxidized to fluorine by hydrogen peroxide, no fluorinated by-products would be formed. In addition, fluoride ion has a high degree of hydration, which suppresses the degree of hydration of the active nucleophile. The application of TOAF in the UAOD process has significantly improved the desulfurization efficiency by enabling a better active oxygen transfer from aqueous phase to organic phase, enhancing oxidation of OSCs to the corresponding sulfones (Wan et al., 2007).

Ultrasound serves as a co-agent to lower surface tension and enhance emulsification through micro-bubbles production. Thus, the surface area between reactants would be increased so as to promote reactions (Thompson et al., 1999). With the conjunctive use of ultrasound, acid catalysts and phase transfer catalyst, the desulfurization effectiveness of the UAOD process could be highly increased (Wang et al., 2007). By applying TOAF in the UAOD process to enhance oxidation of organic sulfur compounds in a diesel-hydrogen peroxide emulsion, greater than 95% desulfurization can be achieved on different diesels (Mei et al., 2003; Wan et al., 2007).

2.6 Ionic Liquids (ILs)

2.6.1 Overview of ILs and RTILs

Ionic liquids (ILs), in broad definition, are liquid with ions as the major constituents. In other words, they are the liquid states of any ionic compounds. As defined in early 1940s, ionic liquids include all molten salts such as molten sodium chloride (Barrer, 1943). Development of ionic liquids was initiated in electrochemistry. While most of the electrolytes used were metallic salts in aqueous solution, limitation in conductivity and side reactions from water, or more specifically, hydrogen ions and hydroxide ions, usually suppressed the desired electrochemical reactions (Bockris et al., 1998).

The concept of "zero solvent electrolyte" was developed to eliminate the loss in conductivity and effectiveness. In room conditions, however, pure metallic salts are usually in solid states with a relatively low conductivity and applicability. High temperature was applied to loosen the ionic lattices of salts forming the corresponding ionic liquids. Specific conductivity of the molten salts can be increased by a thousand fold compared to the salt crystals. Specific conductivities of water, aqueous solution of sodium chloride, molten sodium chloride and molten potassium chloride are listed in Table 2.7.

Table 2.7 Specific conductivities (Bockris et al., 1998)

Substance	Temperature (K)	Specific conductivity (s cm^{-1})
H_2O_l	291	4×10^{-8}
$NaCl_{aq}$ (5M)	298	0.25×10^{-3}
$NaCl_l$ melt	1181	3.903
KCl_l melt	1145	2.407

With the rising concerns in pollutions and clean technologies, Montreal Protocol was established to limit the use of volatile organic solvents including chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). These are greatly affected organics synthesis processes in various industries such as petrochemical and pharmaceutical industries (Hough et al., 2007). The use of ionic liquids with relatively low melting points as solvents has been considered as potential substitutes for traditional volatile organic solvents.

Nowadays, ionic liquids are redefined as liquids of fused salts containing only ions with melting point below 100°C (Wasserscheid et al., 2002). Ionic liquids are generally neither flammable, nor explosive (Fox et al., 2008). It is demonstrated that ionic liquids have excellent solvent properties towards various organic and inorganic chemicals. The general properties of ionic liquids are summarized in Table 2.8.

Table 2.8 General properties of modern ionic liquids (Johnson, 2007)

Properties	**Descriptions**
Melting Point	< 100°C
Boiling Point	> 200°C
Thermal Stability	High
Viscosity	< 100 cP
Polarity	Moderate
Specific conductivity	$< 1\times10^{-2}$
Vapor pressure	Negligible

With high boiling points, high thermal stability and negligible vapor pressure, there is almost no solvent emission at room temperature. Emission of volatile organic compounds (VOCs) can be minimized by replacing traditional organic solvents with ionic liquids and thus, ionic liquids are considered as green solvents (Huddleston et al., 1998).

Nevertheless, some ionic liquids are found to be toxic (Zhao et al., 2007). Planning to prevent accidental discharge and design for less toxic ionic liquids could be done to maintain the potential benefits. Table 2.9 shows the toxicity of three ionic liquids, including 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide.

Table 2.9 Toxicity of ionic liquids, expressed as EC_{50} in μM (Matzke et al., 2007)

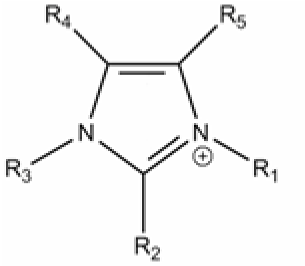
	1-butyl-3-methyl-imidazolium chloride	1-butyl-3-methyl-imidazolium tetrafluoroborate	1-butyl-3-methyl-imidazolium bis(trifluoro-methylsulfonyl)imide
Growth inhibition (duckweed)	660	310	380
Growth inhibition (wheat)	>3000	1700	110
Growth inhibition (cress)	>3000	1900	400
Reproduction inhibition (green algae)	140	130	50
Reproduction inhibition (springtail)	>3000	>4400	30

Because the properties of ionic liquids such as melting point, boiling point, viscosity, and hydrophobicity can be simply adjusted by altering the structures of ions, ionic liquids are also known as designer solvents (Freemantle, 1998). Due to the unique properties and their stabilities, ionic liquids can serve as, not only carrier solvents for organic or inorganic chemical reactions, but also solvents for separation and co-catalysts. It is demonstrated that ionic liquids can be used to separate organic compounds, for instance, olefins from paraffins (Munson et al., 2002).

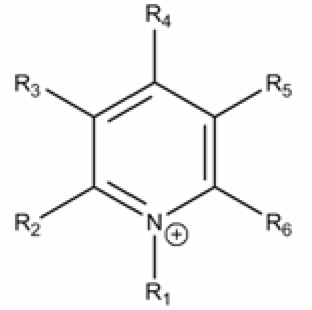
Ionic liquids can also be applied as co-catalysts or catalysts in reactions including hydrogenation of cyclohexene (Suarez et al., 1996); oxidation of 2, 2-dimethylchromene (Song et al., 2000); Knoevenagel condensation of various ketones and aldehydes (Ranu et al., 2006); ethylbenzene production (Rogers et al., 2003); and biocatalytic esterification of carbohydrates (Rantwijk et al., 2003).

Room temperature ionic liquids are ionic liquids which maintain in liquid state at or below room temperature. The first RTIL ethylammonium nitrate, or [$EtNH_3$][NO_3], was discovered early in 1914 (Earle et al., 2000). RTILs usually consist of bulky organic cations such as imidazolium, pyridinium, pyrrolidinium, alkylammonium, alkylsulfonium and alkylphosphonium derivatives, and anions which could be inorganic such as halide, tetrafluoroborate, and hexafluorophosphate, or organic such as fluorinated imide, alkylsulfate and tosylate (Marsh et al., 2002).

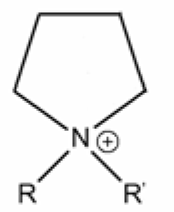
In general, RTILs with halide, nitrate, methylsulfate, or trifluoroacetate anions are miscible in water; RTILs with hexafluorophosphate or bis(trifluoromethylsulfonyl)amide anions are immiscible in water. Nonetheless, miscibility in water of RTILs with tetrafluoroborate and trifluoromethanesulfonate anions depends on the alkyl chain length on the cation (Poole, 2004). Chemical structures of some common cations and anions of RTILs are listed in Figure 2.10.



imidazolium

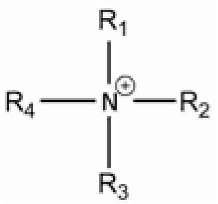


pyridinium

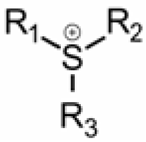


pyrrolidinium

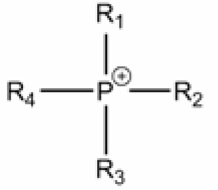
Cations



alkylammonium



alkylsulfonium



alkylphosphonium

$\mathrm{Hal}^{\ominus}$

halide

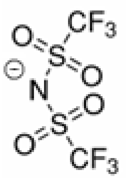
$\mathrm{BF}_4^{\ominus}$

tetrafluoroborate

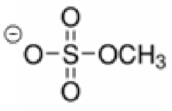
$\mathrm{PF}_6^{\ominus}$

hexafluorophosphate

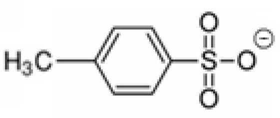
Anions



Bis(trifluoromethyl-
sulfonyl)imide



methylsulfate



tosylate

Figure 2.10 Chemical structures of common cations and anions in RTILs

2.6.2 Applications of ILs in Hydrocarbon Separation

It has been discussed in several publications that hydrocarbons can be separated by extraction using ionic liquids (Huddleston et al., 1998; Munson et al., 2002; Domanska et al., 2007; Arce et al., 2008). Olefins and paraffins have similar physical properties which make them difficult to be separated. With carbon-carbon double bonds, however, olefins show different reactivity to other chemicals and solvents comparing with paraffins.

Separation of olefins from paraffins using ionic liquids can be explained by Prausnitz and Anderson's solution thermodynamics (Lei et al., 2006). Mobility of electron in the functional group of a molecule has great influence on the interaction towards different solvents. With greater electron cloud mobility, the functional group is easier to be polarized resulting in a higher solubility in polar solvent (Safarik et al., 1998).

In general, mobility of electron cloud in C=C bond is greater than in C-C bond, thus olefins would be relatively more soluble in polar solvents. Based on this principle, ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate can be used to extract olefins from paraffins. Similarly, aromatic hydrocarbons such as benzene, toluene and alkylbenzenes can be extracted from hexane, heptane or other paraffins using ionic liquids, for instance, 1-butyl-3-methylimidazolium hexafluorophosphate and ethyl(2-hydroxyethyl)dimethylammonium bis(trifluomethylsulfonyl)imide (Domanska et al., 2007; Meindersma et al., 2006).

2.6.3 Applications of ILs in Desulfurization

It has also been demonstrated that ionic liquids, especially room temperature ionic liquids, could be applicable in desulfurization technologies. Similar to the mechanism in separating olefins from paraffins, selected types of ionic liquids could form relatively strong π complex with OSCs such as thiophene compared with benzene and paraffins (Huang et al., 2004). Thus, OSCs can be extracted from other hydrocarbons so as to obtain desulfurized fuel.

Ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrachloroaluminate have been investigated for this purposed. Extractive desulfurization using ionic liquids are of particular interest due to the simplicity of treatment arrangement which can be applied in ambient conditions. With high ionic liquid to fuel ratio (greater than 5:1), more than 95% desulfurization on various fuels can be achieved in 30 minutes (Zhang et al., 2004).

Another use of RTILs is a combination of oxidative and extractive desulfurization process. With water miscible RTILs, OSCs can be extracted from fuel and become oxidized by oxidant such as hydrogen peroxide to the corresponding sulfones in RTIL phase (Lo et al., 1004). Desulfurization efficiency can be improved even with less ionic liquid consumption. More than 95% desulfurization can be achieved in 3 hours with low ionic liquid to fuel ratio (1:1). Schematic diagram of this concept is illustrated in Figure 2.11.

Some ILs with strong Brönsted acidity or basicity, such as *N*-methylpyrrolidonium tetrafluoroborate, are considered as possible catalysts to generate hydroxyl radicals from hydrogen peroxide, so as to improve the oxidizing power (Parvulescu et al., 2007).

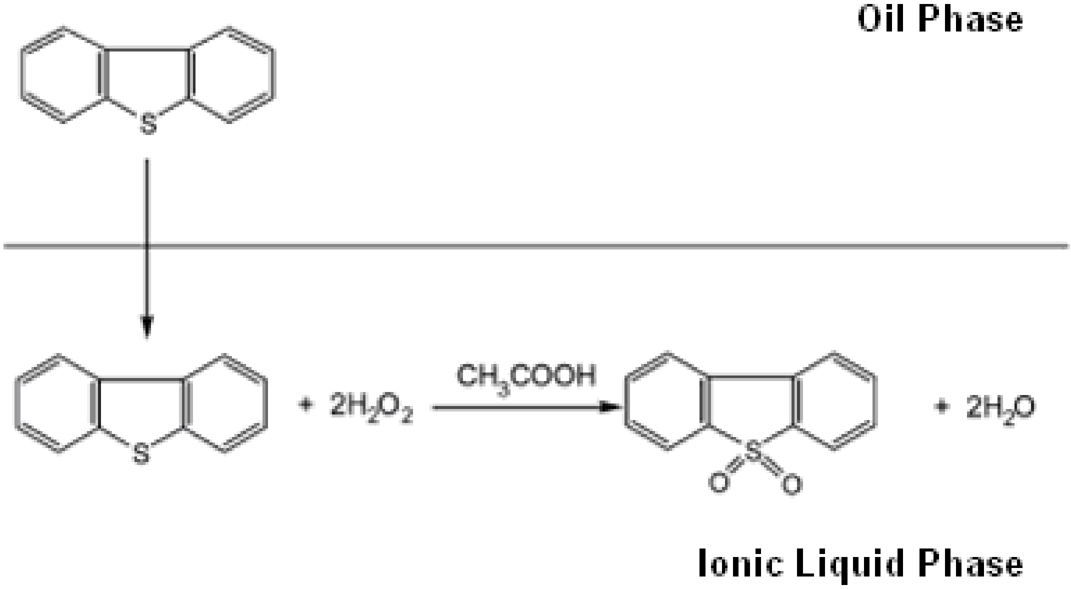


Figure 2.11 Schematic diagram of oxidative extractive desulfurization (Li et al., 2009)

In the third generation of UAOD, or the modified UAOD process, ionic liquid is also utilized for multiple purposes (Cheng et al., 2008). The major mechanism involved in the modified UAOD process is multiple phase-transfer catalysis. A selected type of ionic liquid, imidazolium alkylsulfate, can be used as phase transfer catalyst to transfer active oxygen species from aqueous phase to organic phase as illustrated in Equation 2.5 to Equation 2.7 (Cheng et al., 2008). Ionic liquid could also extract OSCs or oxidized OSCs from the fuel to achieve a lower sulfur fuel. It is demonstrated that the modified UAOD process can achieve more than 99% desulfurization with various type of diesel fuel oils.

$$IM^{+} + RSO_4^{-} \leftrightarrow IM^{+}RSO_4^{-} \qquad \text{(Eq. 2.5)}$$

$$IM^{+}RSO_4^{-} + 2O^{*} \leftrightarrow \left[IM^{+}RSO_6^{-}\right]^{*} \qquad \text{(Eq. 2.6)}$$

$$\left[IM^{+}RO_6^{-}\right]^{*} + RS \rightarrow IM^{+}RSO_4^{-} + RSO_2 \qquad \text{(Eq. 2.7)}$$

2.7 Ultraviolet Irradiation

2.7.1 Fundamentals of Photochemistry and UV Radiation

Photochemistry refers to the study of light induced chemical reactions. Basically, a photochemical reaction is initiated by absorption of light, or photon by an atom, molecule or ion converting to the corresponding excited state species. There are two fundamental principles in photochemistry. The first law, also known as the Grotthus-Draper law, was established by Chiristian J. Grotthus and John W. Draper in early 1800s, stating that only light which is absorbed by a system, such as an atom, molecule or ion, can cause chemical change.

The second law, also known as the Stark-Einstein law, was established by Johannes Stark and Albert Einstein in early 1900s, stating that for one quantum of light, or a photon that is absorbed, only the atom, molecule or ion which absorbs the photon would be excited (Mukherjee, 1978). Due to the complexity of photochemical reactions, not all photo-excited atoms, molecules or ions would be chemically active. Loss of energy from the excited state could happen in unproductive ways. Quantum yield Φ was introduced by Einstein to specify the efficiency of a particular photochemical reaction. Φ is defined as the number of molecules decomposed or formed per number of photon absorbed.

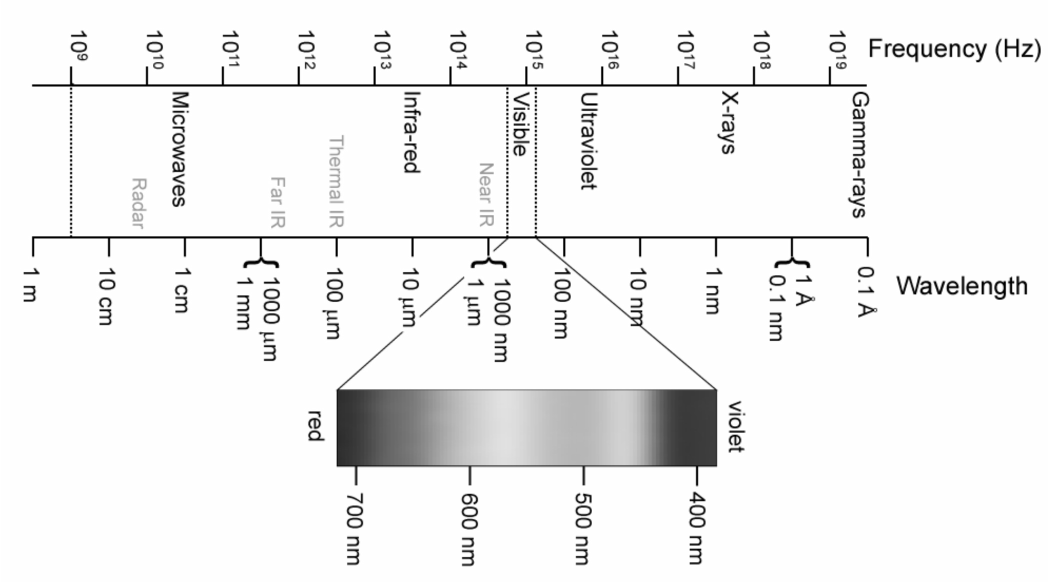


Figure 2.12 Section of Electromagnetic Spectrum (Willis, 2006)

For any chemical reaction, energy is required to overcome the activation energy ΔE_a, and also the enthalpy ΔH. In photochemical reactions, energy is provided by electronic excitation by photon absorption. While the energies of bond dissociation energy per mole of molecules are generally within 150 kJ to 600 kJ, these can be provided by one mole of photons from light with wavelengths between 200nm to 800nm (Mukherjee, 1978). Thus, researches in photochemistry are more focused on a few sections of the light spectrum, or more precisely electromagnetic spectrum including infrared, visible light and ultraviolet (Murov et al., 1993). An excited species could undergo different reactions such as photoionization, photoisomerization, photooxidation, photoreduction, bimolecular quenching and photo substitution (Gold et al., 1987).

Ultraviolet is a type of electromagnetic radiation with wavelength ranging from 10 nm to 400 nm. Depending on the wavelength, UV light can be classified into three major categories as listed in Table 2.10. The most famous photochemical reactions related to UV, perhaps, would be the interaction with ozone generation and decomposition in the stratosphere. The Sun emits UV radiation with a wide range of wavelengths, including UVA, UVB, and UVC. However, UVA is the only major UV radiation reaching the Earth surface. Harmful UVB and UVC would be absorbed in the ozone layer through a series of photochemical reactions:

$$O_2 + hv \rightarrow 2O \qquad \text{(Eq. 2.8)}$$

$$O + O_2 + M \rightarrow O_3 + M \qquad \text{(Eq. 2.9)}$$

$$O_3 + hv \rightarrow O + O_2 \qquad \text{(Eq. 2.10)}$$

$$O_3 + O \rightarrow 2O_2 \qquad \text{(Eq. 2.11)}$$

Due to the high energy per mole of photons as suggested in Table 2.11, ultraviolet is applicable in a wide range of photochemical reactions. While UV light is effective to achieve bond cleavage and other photochemical reactions, UV light has been applied to many areas including air purification, water disinfection, organic destruction, food processing and biomedical applications. UV light has also been used in spectrophotometry and other analytical processes due to UV fluorescence reactions.

Table 2.10 Ultraviolet Classification (ISO, 2007)

Name	**Abbreviation**	**Wavelength (nm)**
Ultraviolet A	UVA	320 – 400
Ultraviolet B	UVB	280 – 320
Ultraviolet C	UVC	100 – 280
Near Ultraviolet	NUV	300 – 400
Middle Ultraviolet	MUV	200 – 300
Far Ultraviolet	FUV	122 – 200
Vacuum Ultraviolet	VUV	10 – 200
Extreme Ultraviolet	EUV	10 – 121

Table 2.11 Energy per mole of photons (Mukherjee, 1978)

Light	Wavelength (nm)	Energy per mole of Photons (kJ)
Ultraviolet	200 – 400	299 – 590
Violet	400 – 450	266 – 299
Blue	450 – 500	239 – 266
Green	500 – 570	209 – 239
Yellow	570 - 590	203 – 209
Orange	590 – 620	192 – 203
Red	620 – 750	159 – 192

2.7.2 UV and Photochemical Reactions in Aqueous System

While water is usually involved in most of the photochemistry studies, the photochemical reactions related to water is particularly important. Although it is suggested that visible light and UVA can dissociate water molecule, significant photolysis of water can only be achieved by UVC or even extreme UV. It has been recorded that the quantum yield Φ of water dissociation to hydrogen radicals and hydroxyl radicals varies from 0.335 to 1, with the corresponding wavelength of UVC applied from 185 nm to 124 nm (Smith, 1970).

$$H_2O + h\nu \rightarrow (H_2O)^* \rightarrow H\cdot + OH\cdot \qquad \text{(Eq. 2.12)}$$

Photolysis of hydrogen peroxide in aqueous solution is another important aspect in aqueous photochemistry. UV irradiation with wavelength ranged from 200 nm to 280 nm, typically 254 nm, can be applied to dissociate hydrogen peroxide into hydroxyl radicals, hydrogen radicals and perhydroxyl radicals (Venkatadri et al., 1993). Instead of ground state hydroxyl radicals ($OH\cdot$), excited state of hydroxyl radicals (OH^*) can also be formed through a series of radical reactions (Smith, 1970).

The excitation of hydrogen peroxide by UV irradiation has been applied in water treatment as one of the advanced oxidation process to destroy organic compounds such as trichloroethylene (TCE), perchloroethylene (PCE) and colored organic compounds. The photochemical reactions of hydrogen peroxide as listed in Figure 2.13.

$$H_2O_2 + hv \rightarrow OH\cdot + OH\cdot$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+$$

$$OH\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O$$

$$OH\cdot + HO_2^- \rightarrow HO_2\cdot + OH^-$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2$$

$$RH + OH\cdot \rightarrow H_2O + R\cdot \rightarrow \text{further oxidation}$$

Figure 2.13 Organic destruction by UV/H_2O_2 system (Venkatadri et al., 1993)

2.7.3 Photocatalysis and Titanium (IV) Oxide

Photocatalysis is, in fact, closely related to photoelectrochemistry. During the development of semiconductor photoelectrochemistry in 1970s, titanium (IV) oxide (TiO_2) was used as semiconductor electrodes for processes such as photoelectrolysis of water and photocell to harvest solar energy. It was found out later that TiO_2 could be applicable for photocatalytic degradation of pollutants such as cyanide (Frank et al., 1977). The interest in photocatalysis and their environmental applications were then realized.

Titanium (IV) oxide is considered as one of the most important photocatalysts due to its high availability, chemically stable structure, high effectiveness with highly oxidizing photogenerated holes on surface, and relatively low cost (Kaneko et al., 2002).

The principle of photocatalysis by TiO_2 or other semiconductors involves the excitation of the semiconductor particles. Under UV irradiation, the energy state of electrons of the semiconductor would change, forming conduction band electrons (e^-_{CB}) and valence band holes (h^+_{VB}) on the surface of the particles (Robert et al., 2002).

Surface with conduction band electrons and valence band holes are the active sites for oxidation or other chemical reactions to generate radicals such as hydroxyl, superoxide, and perhydroxyl radicals from oxygen and water. Radicals generated can be used to oxidize the target pollutants. Direct oxidation of the target pollutants at valence band holes is also possible. The pathways for photogeneration of radicals are illustrated in Figure 2.14.

$$TiO_2 + hv \rightarrow e^-_{CB} + h^+_{VB}$$

$$h^+_{VB} + OH^- \rightarrow OH\cdot$$

$$h^+_{VB} + H_2OH \rightarrow H^+ + OH\cdot$$

$$e^-_{CB} + O_2 \rightarrow O_2^-\cdot$$

$$e^-_{CB} + h^+_{VB} \rightarrow \text{heat}$$

Figure 2.14 Radicals generation in Photocatalysis (Al-Ekabi et al., 1992)

2.7.4 Photolysis and Photo-Oxidation Desulfurization

Desulfurization using photochemical reactions can be separated into two major categories: direct photolysis of OSCs and photo-oxidation of OSCs. Similar to other compounds, organic sulfur compounds can be photo-excited in photochemical reactions. For instance, alkyl radicals and alkanethiyl radicals can be generated from dialkyl sulfides through photolysis to cleave C-S bond.

With the aid of trivalent phosphorus compound, sulfur can be abstracted from alkanethiyl radicals to achieve desulfurization (Coyle, 1991). However, this process is highly dependent on the target compounds and the wavelength of radiation applied. Single wavelength radiation may not be applicable on all OSCs. Besides, instead of C-S bond cleavage, S-H bond or C-H bond cleavage is observed in direct photolysis of thiols and thiophenes (Bianchini et al., 1997). Thus, direct photolysis is not commonly applied on desulfurization.

Photo-oxidation of OSCs is another pathway to achieve desulfurization photochemically. Selected reactants such as water and oxygen could be activated forming reactive oxygen species and radicals which can further react to oxidize OSCs (Baba, 1974). Although photo-oxidation can be improved by the addition of photocatalyst such as TiO_2, low desulfurization efficiency, for instance less than

40% oxidation of DBT in 10 hours, was obtained due to limited reactivity and solubility of oxygen. Aqueous oxidant such as hydrogen peroxide could be used instead to achieve better desulfurization efficiency (Matsuzawa et al., 2001).

CHAPTER 3: MODIFIED OXIDATIVE DESULFURIZATION USING SUPEROXIDE ON MODEL SULFUR COMPOUND STUDY

3.1 Introduction

It is known that organic sulfur compounds are slightly more polar comparing with hydrocarbons with similar structures. In order to separate OSCs from hydrocarbons effectively, however, the slight difference in polarity is not enough. In oxidative desulfurization process, the major goal is to support a highly selective and effective oxidation of organic sulfides to the corresponding sulfones which are significantly more polar comparing with the organic sulfides.

Based on the first two generations of the UAOD process developed, organic sulfur compounds oxidation by hydrogen peroxide with application of transition metal catalysts, or more specifically polyoxometalates (POMs) has been studied (Met et al., 2003, Wan et al., 2007). It has been demonstrated that benzothiophene, dibenzothiophene and their derivatives could be oxidized by the UAOD process in mild conditions with considerably high yield. However, desulfurization efficiencies on thiophene and the derivatives were comparatively low using the TMC/H_2O_2 system.

In the third generation of UAOD system, new components including use of organic acid catalysts such as glacial acetic acid (HAc), and ionic liquids were introduced (Cheng et al., 2008). These modifications were aimed at improving desulfurization efficiency and selectivity. The modified UAOD process had successfully demonstrated high yield to produce various sulfones from the corresponding OSCs by HAc/H_2O_2 oxidation with or without ultrasonication (Cheng et al., 2009).

Although hydrogen peroxide is known as an effective oxidant in oxidative desulfurization (ODS) with minimal pollutants to the environment, only low concentration (< 30% wt.) of hydrogen peroxide solution can be applied due to safety reasons. High concentration (> 50% wt.) of hydrogen peroxide solution is considered as unstable, which could cause spontaneous ignition or even explosion due to vigorous self-sustained decomposition. Low concentration of hydrogen peroxide is relatively safe, but oxidation efficiency would be significantly lowered due to dilution effect (Wan et al., 2008). Weight and volume of oxidant required would also be increased when a low concentration oxidant is used.

Alternative oxidants have been investigated to replace hydrogen peroxide (Chan et al., 2008). In this study, selection of oxidant is based on oxidation effectiveness, availability, cost, safety, and potential by-products or pollutants formation. Similar to the third generation of the UAOD process, complementary techniques including ultrasonication, acid catalyzed oxidation, phase transfer catalysis, mechanical mixing and application of room temperature ionic liquid mentioned in Chapter 2 are employed in this development. Preliminary investigation on utilizing UV irradiation to enhance oxidative desulfurization is also discussed.

A series of experiments based on BT and DBT model sulfur compounds were conducted to accomplish optimum reaction conditions. In this chapter, the effects of type and amount of acid catalyst, phase transfer catalyst, ionic liquid, oxidant, and treatment methods applied are discussed.

3.2 Materials and Experimental Procedures

3.2.1 Chemical Preparation

Model sulfur compounds used in this study including thiophene (T), 2-methyl thiophene (2MT), benzothiophene (BT), 2-methyl benzothiophene (2MBT), dibenzothiophene (DBT), 4, 6-dimethyl dibenzothiophene (4,6DMDBT) were obtained from Sigma-Aldrich Co., Allentown, Pennsylvania. Solvents for model sulphur compounds solutions preparation including toluene and n-decane were obtained from VWR Inc., West Chester, Pennsylvania. Acetonitrile was obtained from VWR Inc. Oxidants used including 30% wt. hydrogen peroxide (H_2O_2) solution was obtained from VWR Inc., while sodium superoxide, potassium superoxide and potassium permanganate were obtained from Sigma-Aldrich Co. Acid catalysts including glacial acetic acid and trifluoroacetic acid were obtained from Sigma-Aldrich Co. Phase transfer catalysts including 18-Crown-6, tetraoctylammonium bromide and tetraoctylammonium chloride were obtained from Sigma-Aldrich Co., while tetraoctylammonium fluoride was synthesized by halogen exchange process (Dermeik et al., 1989). Photocatalyst used including titanium (IV) oxide was obtained from Sigma-Aldrich Co. Ionic liquids including 1-butyl-3-methylimidazolium hexafluoro-phosphate [BMIM][PF_6], 1-ethyl-3-methylimidazolium ethylsulfate [EMIM][$EtSO_4$], 1,2,3-trimethyl-imidazolium methylsulfate [TMIM][$MeSO_4$], and tributylmethyl-phosphonium methyl-sulfate [TMBP][$MeSO_4$] were obtained from Sigma-Aldrich Co.

3.2.2 Ultrasonic Reactor

Similar to the previous generation of the UAOD process, a probe ultrasonic reactor, model number VCX-750, manufactured by Sonic & Materials Inc., Newtown, Connecticut was used in this study. Probe type ultrasonic reactor can provide high intensity (100 watts/cm^2) ultrasound irradiation as a point source, producing ultra-fine emulsion to enhance mixing. This reactor can support variable power output, integrated temperature control and remote processing for different purposes. Specifications of this ultrasonic reactor are listed in Table 3.1.

Table 3.1 Specifications of Ultrasonic Reactor VCX-750 listed in product catalogue

Dimensions	(H×W×D) 235 mm × 190 mm × 340 mm
Power Output	750 Watts
Frequency	20kHz
Sealed Converter	Piezoelectric Lead Zirconate Titanate Crystal (PZT)
Standard Probe Size	Diameter: 13 mm; Length 136 mm
Probe Material	Titanium Alloy Ti-6Al-4V
Processing Capacity	10 ml – 250 ml

3.2.3 Ultraviolet Lamp

An ultraviolet lamp, model number UVLMS-38, manufactured by UVP Ltd., Upland, California was used in this study. This UV lamp can provide UVA, UVB and UVC at the wavelength or 365 nm, 302 nm and 254 nm respectively. Instead of normal glassware, fused quartz glass reactor was used in the UV related experiments to minimize UV light blockage. Specifications of this ultraviolet lamp are listed in Table 3.2.

Table 3.2 Specifications of UV lamp UVLMS-38 listed in product catalogue

Dimensions	(L×W×D) 376 mm × 96 mm × 64 mm
Power Output	8 Watts
Frequency	254nm / 302 nm / 365 nm

3.2.4 Analytical Method

In accordance with ASTM D4294 and ISO 8754, non-dispersive X-ray fluorescence (NDXRF) was used to determine the total sulfur content of the samples. Sulfur-in-Oil Analyzer (SLFA-20), manufactured by Horiba Inc., Irvine, California was used to measure total sulfur content of samples based on this method. Sulfur-in-Oil Analyzer is applicable to measure samples with total sulfur content ranged from 0 to 5 wt%, with a lower detection limit of 20 ppm_w.

Figure 3.1 Sulfur-in-oil analyzer (SLFA-20)

3.3 Experimental Design, Procedure, Results and Discussion

3.3.1 Use of Solid Oxidants in Oxidative Desulfurization

3.3.1.1 Solid Oxidants Selection

As discussed in Chapter 2.3, dilution of oxidants with water would lower the reaction rate and increase the total reactant volume. It usually happens when an aqueous oxidant, such as hydrogen peroxide, is used in the process. Previous work has demonstrated that lowering H_2O_2 concentration would significantly retard the conversion of sulfur to sulfone (Wan et al., 2007). While high concentration of H_2O_2 is unstable and highly reactive, other pure oxidants for instance, solid oxidants, are considered to improve the oxidative desulfurization process.

Selection of solid oxidant was primarily based on the oxidation potential. Three solid oxidants, potassium permanganate, sodium superoxide, and potassium superoxide were selected for this study. Potassium permanganate is known as a strong oxidizing agent, especially in acidified condition. On the other hand, superoxide is highly reactive radical anion. It is also a precursor of other reactive oxygen species such as singlet oxygen, hydrogen peroxide, and hydroxyl radical.

3.3.1.2 Experimental Procedure

Either BT or DBT model sulfur compound was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content. Instead of a pure solvent, a solvent mixture was used to simulate real petroleum products.

Known amount of selected oxidant, either 30% wt. hydrogen peroxide, potassium permanganate, sodium superoxide or potassium superoxide, was first mixed with 5 grams of 1-butyl-3-methylimidazolium hexafluoro-phosphate [BMIM][PF_6], and 0.1 gram of tetraoctylammonium fluoride to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with 3 grams of acetic acid to produce mixture B.

Mixture A was then slowly added to mixture B, and the resulting mixture was heated up to 70°C with continuous magnetic stirring. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected on the top and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.3.1.3 Results and Discussion

Table 3.3 to Table 3.6 show the desulfurization of BT and DBT with selected oxidants: 30% wt. hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), sodium superoxide (NaO_2), and potassium superoxide (KO_2), respectively, at fixed oxidant to sulfur ratios with magnetic stirring at 70°C for 3 hours. In high sulfur to oxidant mole ratio (1:4), greater than 85% desulfurization efficiency for both BT and DBT samples could be achieved for all solid oxidants. In contrast, less than 70% desulfurization for both BT and DBT samples were obtained when 30% wt. hydrogen peroxide was used.

Table 3.3 Desulfurization efficiency with 30% wt. H_2O_2 as oxidant

	Mixing Time	**30% wt. H_2O_2 Applied**		**Initial Sulfur Content**		**Sulfur to Oxidant Ratio**	**Final Sulfur Content**	**Sulfur Removal**
	hr	**g**	**mmol**	**ppm_w**	**mmol**	**mmol : mmol**	**ppm_w**	**%**
BT	3	5.5	48	1012	0.32	1:150	< 20	> 98
	3	3.6	32	1012	0.32	1:100	< 20	> 98
	3	1	9.6	1012	0.32	1:30	98	90
	3	0.36	3.2	1012	0.32	1:10	193	81
	3	0.15	1.28	1012	0.32	1:4	354	65
DBT	3	5.5	48	1006	0.31	1:150	< 20	> 98
	3	3.6	32	1006	0.31	1:100	< 20	> 98
	3	1	9.6	1006	0.31	1:30	81	92
	3	0.36	3.2	1006	0.31	1:10	169	83
	3	0.15	1.28	1006	0.31	1:4	322	68

Table 3.4 Desulfurization efficiency with $KMnO_4$ as oxidant

	Mixing Time	$KMnO_4$ Applied		Initial Sulfur Content		Sulfur to Oxidant Ratio	Final Sulfur Content	Sulfur Removal
	hr	g	mmol	ppm_w	mmol	mmol : mmol	ppm_w	%
BT	3	1.5	9.6	1012	0.32	1:30	< 20	> 98
	3	0.5	3.2	1012	0.32	1:10	85	92
	3	0.2	1.28	1012	0.32	1:4	147	85
DBT	3	1.5	9.6	1006	0.31	1:30	< 20	> 98
	3	0.5	3.2	1006	0.31	1:10	83	91
	3	0.2	1.28	1006	0.31	1:4	139	86

Table 3.5 Desulfurization efficiency with NaO_2 as oxidant

	Mixing Time	NaO_2 Applied		Initial Sulfur Content		Sulfur to Oxidant Ratio	Final Sulfur Content	Sulfur Removal
	hr	g	mmol	ppm_w	mmol	mmol : mmol	ppm_w	%
BT	3	0.55	9.6	1012	0.32	1:30	< 20	> 98
	3	0.18	3.2	1012	0.32	1:10	59	94
	3	0.07	1.28	1012	0.32	1:4	108	90
DBT	3	0.55	9.6	1006	0.31	1:30	< 20	> 98
	3	0.18	3.2	1006	0.31	1:10	58	94
	3	0.07	1.28	1006	0.31	1:4	88	91

Table 3.6 Desulfurization efficiency with KO_2 as oxidant

	Mixing Time	**KO_2 Applied**		**Initial Sulfur Content**		**Sulfur to oxidant Ratio**	**Final Sulfur Content**	**Sulfur Removal**
	hr	**g**	**mmol**	**ppm_w**	**mmol**	**mmol : mmol**	**ppm_w**	**%**
BT	3	0.68	9.6	1012	0.32	1:30	< 20	> 98
	3	0.23	3.2	1012	0.32	1:10	39	96
	3	0.09	1.28	1012	0.32	1:4	73	93
DBT	3	0.68	9.6	1006	0.31	1:30	< 20	> 98
	3	0.23	3.2	1006	0.31	1:10	48	95
	3	0.09	1.28	1006	0.31	1:4	81	92

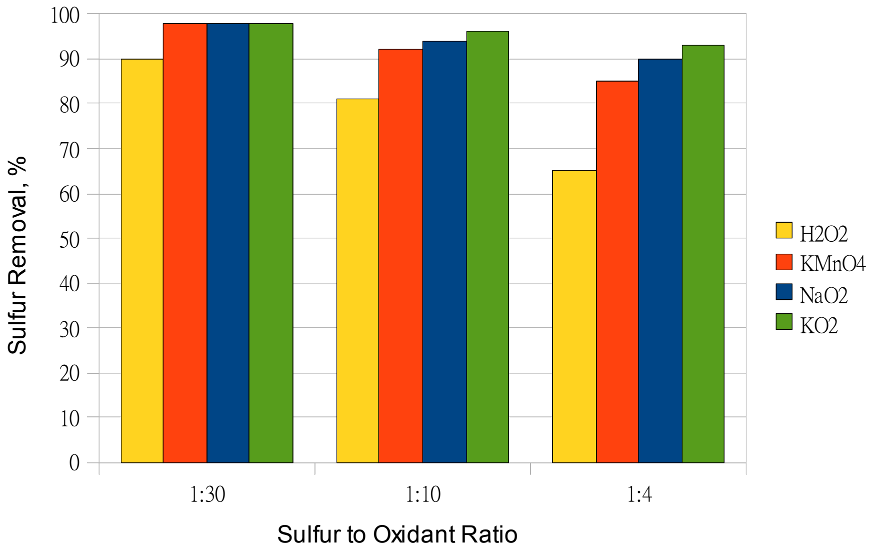


Figure 3.2 Desulfurization efficiencies of BT sample with different oxidants

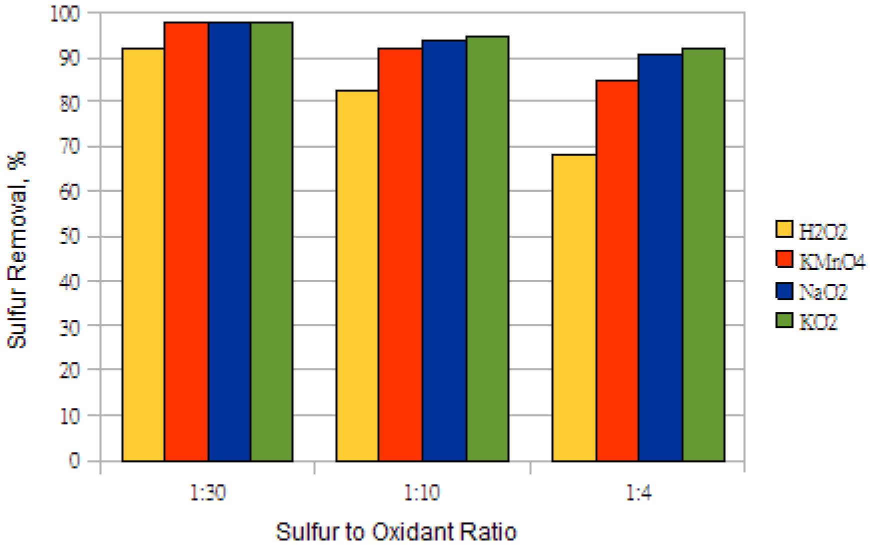


Figure 3.3 Desulfurization efficiencies of DBT sample with different oxidants

Among the three solid oxidants used, relatively low desulfurization efficiencies were obtained when potassium permanganate was used, as illustrated in both Figure 3.2 and 3.3. It was demonstrated that high desulfurization efficiencies could be achieved on both BT and DBT samples when either sodium superoxide or potassium superoxide was used as oxidant, where potassium superoxide demonstrated slightly higher desulfurization efficiencies. Besides, sodium superoxide is relatively unstable comparing with potassium superoxide as discussed in Chapter 2.3. Thus, potassium superoxide was selected as the alternative oxidant to replace hydrogen peroxide used in the UAOD process.

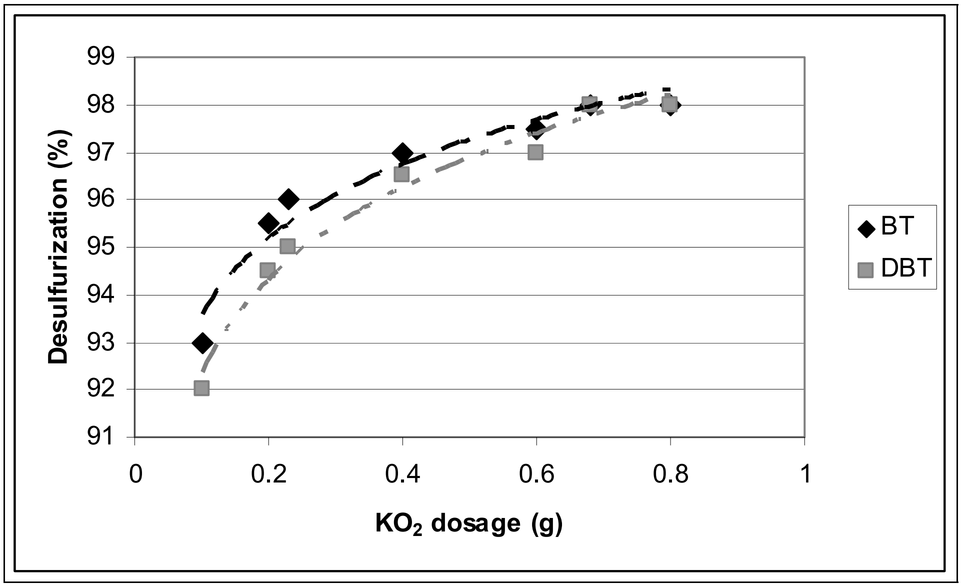


Figure 3.4 Desulfurization efficiencies of BT and DBT with different KO_2 dosage

Under the same conditions, the desulfurization of BT and DBT samples with various amounts of potassium superoxide is illustrated in Figure 3.4. Desulfurization efficiency was optimized by using 0.7 gram of KO_2 to oxidize 10 grams solution with 1000 ppm_w model sulfur compounds, either BT or DBT. The sulfur to oxidant mole ratio at the optimal point was 1:30. Comparing with 30% wt. H_2O_2, using KO_2 as oxidant for oxidative desulfurization process can significantly reduce oxidant consumption, the weight of oxidant requirement, and hence the volume of reactor without losing desulfurization efficiency.

3.3.2 Effect of Different Phase Transfer Catalysts

3.3.2.1 Phase Transfer Catalyst Selection

As discussed in Chapter 2.5, reactions involving reactants in two or more immiscible phases are hindered by inefficient contact and interfacial transfer of reactants. Utilization of phase transfer catalysts can significantly improve interfacial mixing so as to increase rate of reactions. In the UAOD process, QASs are applied as PTCs to increase oxidation rate of OSCs in organic phase by hydrogen peroxide solution. As demonstrated in Table 3.7, only cationic surfactants including QAS are effective PTCs in the UAOD process.

In the conditions with no surfactant, or with either anionic or nonionic surfactants, no or low rate oxidation of OSCs including BT and DBT would be resulted (Wan et al., 2007). Tetraoctylammonium fluoride is identified as the best PTCs in the UAOD process by supporting a high oxidation rate of OSCs with no by-product formation. Thus, TOAF has been used as PTC for the UAOD process.

Table 3.7 Effect of surfactants on the UAOD process (Wan et al., 2007)

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

Note: + indicates the system undergoes reaction in the given conditions
– indicates no or eligible reaction in the given conditions

In the application of solid oxidant in the UAOD process, another type of phase transfer catalyst, crown ether, is also considered due to the ability to stabilize specific metallic cation. For instance, 18-crown-6 shows the ability to form stable complex with potassium cation in organic solvent. Increase in solubility of potassium superoxide in dimethyl sulfoxide has been demonstrated with the application of 18-crown-6. (Suzuki et al., 1979)

3.3.2.2 Experimental Procedure

DBT model sulfur compound was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content.

Using a sulfur to oxidant ratio of 1:30, 0.7 gram of KO_2 was first mixed with 5 grams of $[BMIM][PF_6]$ and known quantity of the selected PTA, either TOAF or 18-crown-6, to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with 3 grams of acetic acid to produce mixture B.

Mixture A was then slowly added to mixture B, and the resulting mixture was heated up to 70˚C with continuous magnetic stirring. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.3.2.3 Results and Discussion

Table 3.8 and Table 3.9 show the desulfurization of DBT with selected phase transfer catalyst, including TOAF and 18-crown-6. Comparing with 18-crown-6, TOAF is a more effective phase transfer catalyst for oxidative desulfurization process using KO_2 as oxidant. Although 18-crown-6 was able to improve the desulfurization process, its effectiveness is considerably lower than TOAF. Formation of tetraalkylammonium superoxide could be a possible pathway to enhance desulfurization with TOAF (Afanas'ev, 1989).

Considering the results using TOAF as PTC with 1 hour reaction time shown in Table 3.9, desulfurization efficiency could be improved from 45% to 80% by adding 0.05 gram of TOAF. Doubling the dosage of TOAF could result in a slight increase of desulfurization efficiency, from 80% to 86%. However, further increasing the dosage of TOAF from 0.1 to 0.5 gram did not show a significant improvement. It suggests that optimal phase transfer condition can be achieved at 0.1 gram of TOAF dosage.

Based on the experimental result, anionic transferrer is a better phase transfer catalyst for this process. Tetraoctylammonium fluoride is considered as an effective PTC due to its stability towards strong oxidizing condition as well as the ability to activate the oxidant in organic phase. Tetraoctylammonium superoxide could possibly be synthesized as an intermediate product. This could help transferring the oxidant to the organic phase so as to achieve oxidative desulfurization. Although higher dosage of PTC is expected to yield better desulfurization efficiency, the difference is not significant when the PTC dosage is greater than 0.1 gram. In this experiment, 0.1 gram of tetraoctylammonium fluoride is considered as the optimum dosage.

Table 3.8 Desulfurization of DBT solution with TOAF as PTC

Mixing Time (hr)	**TOAF Applied (g)**	**Initial Sulfur Content (ppm_w)**	**Final Sulfur Content (ppm_w)**	**Sulfur Removal (%)**
1	0	1006	551	45
2	0	1006	413	59
3	0	1006	372	63
1	0.05	1006	198	80
2	0.05	1006	107	89
3	0.05	1006	58	94
1	0.1	1006	141	86
2	0.1	1006	49	95
3	0.1	1006	< 20	> 98
1	0.5	1006	110	89
2	0.5	1006	38	96
3	0.5	1006	< 20	> 98

Table 3.9 Desulfurization of DBT solution with 18-crown-6 as PTC

Mixing Time (hr)	**18-Crown-6 Applied (g)**	**Initial Sulfur Content (ppm$_w$)**	**Final Sulfur Content (ppm$_w$)**	**Sulfur Removal (%)**
1	0	1006	551	45
2	0	1006	413	59
3	0	1006	372	63
1	0.05	1006	463	54
2	0.05	1006	390	61
3	0.05	1006	333	67
1	0.1	1006	447	56
2	0.1	1006	374	63
3	0.1	1006	314	69
1	0.5	1006	401	59
2	0.5	1006	340	66
3	0.5	1006	298	71

3.3.3 Effect of Acid Catalysts

3.3.3.1 Acid Catalyst Combination

Acetic acid is one of the most common organic acid catalysts used in oxidative desulfurization processes. Recently, it is suggested that trifluoroacetic acid (TFA) could be used as an acid catalyst to improve oxidation of OSCs (Wang et al., 2003; Yazu et al., 2004).

Trifluoroacetic acid is a strong carboxylic acid with more than a thousand folds acidity than acetic acid. In the third generation of the UAOD process, an acid catalyst solution with 20% wt. of TFA and 80% wt. of acetic acid were used to achieve ultralow sulfur diesel with theoretically 0 ppm_w sulfur content (Cheng et al., 2008).

In order to test for the catalytic effect in this oxidative desulfurization process with the application of superoxide, experiments were conducted under different ratios of acetic acid and trifluoroacetic acid combination.

3.3.3.2 Experimental Procedure

DBT model sulfur compound was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content. 0.7 gram of KO_2 was first mixed with 5 grams of $[BMIM][PF_6]$ and 0.1 gram of TOAF to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with known amount of two acid catalysts: acetic acid and TFA to produce mixture B.

Mixture A was then slowly added to mixture B, and the resulting mixture was heated up to 70°C with continuous magnetic stirring. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.3.3.3 Results and Discussion

Table 3.10 shows the desulfurization of DBT solution with different amounts of acetic acid added. Increasing the acid catalyst dosage from 1 gram to 2 grams would result in a slight increase in desulfurization efficiency. However, no significant difference in desulfurization efficiency was observed by further increasing the acid catalyst dosage to 3 grams.

Table 3.10 Desulfurization of DBT solution with respect to acid dosage

Mixing Time (hr)	**Acetic Acid Applied (g)**	**Initial Sulfur Content (ppm$_w$)**	**Final Sulfur Content (ppm$_w$)**	**Sulfur Removal (%)**
1	1	1006	141	86
2	1	1006	49	95
3	1	1006	< 20	> 98
1	2	1006	102	90
2	2	1006	< 20	> 98
3	2	1006	< 20	> 98
1	3	1006	103	90
2	3	1006	< 20	> 98
3	3	1006	< 20	> 98

Table 3.11 Desulfurization of DBT solution with respect to acid catalyst applied

Mixing Time (hr)	**Acetic Acid/ TFA Applied (g)**	**Initial Sulfur Content (ppm_w)**	**Final Sulfur Content (ppm_w)**	**Sulfur Removal (%)**
1	2 / 0	1006	141	90
2	2 / 0	1006	< 20	> 98
1	1.9 / 0.1	1006	59	94
2	1.9 / 0.1	1006	< 20	> 98
1	1.8 / 0.2	1006	53	95
2	1.8 / 0.2	1006	< 20	> 98
1	1.5 / 0.5	1006	47	95
2	1.5 / 0.5	1006	< 20	> 98

Based on the result, 2 grams of acid catalyst was considered as the optimum dosage for the system. Table 3.11 shows the desulfurization of DBT with 2 grams of acid catalyst in various combinations of acetic acid and trifluoroacetic acid.

Addition of 0.1 gram of TFA could result in a slight increase of desulfurization efficiency, from 90% to 94%. However, further increasing the dosage of TFA did not give a significant improvement in desulfurization efficiency. It may be postulated that addition of a small portion, for instance 10% of TFA, in the acid catalyst would be enough for optimization.

3.3.4 Effect of Ionic Liquid

3.3.4.1 Ionic Liquid Dosage

As discussed in Chapter 2, ionic liquid is applicable in oxidative and extractive desulfurization process. Organic sulfur compounds can be extracted from fuel to ionic liquid phase. Especially for water miscible ionic liquid, it provides a better opportunity for the oxidant such as hydrogen peroxide to react with the OSCs forming the corresponding sulfones. More than 95% desulfurization can be achieved in 3 hours with 1:1 ionic liquid to fuel ratio.

Although ionic liquid is known as the new generation of green solvent and catalyst, most of the ionic liquids available are expensive. High dosage of ionic liquid would increase the operating cost of the process, making it less economically feasible.

In order to find the optimal dosage of ionic liquid, experiments were conducted with different dosage of ionic liquids including [BMIM][PF_6] and [EMIM][$EtSO_4$].

3.3.4.2 Experimental Procedure

DBT model sulfur compound was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content. 0.7 gram of KO_2 was first mixed with known amount of the selected ionic liquid and 0.1 gram of TOAF to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with 1.9 grams acetic acid and 0.1 gram of TFA to produce mixture B.

Mixture A was then slowly added to mixture B, and the resulting mixture was heated up to 70°C with continuous magnetic stirring for 3 hours. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.3.4.3 Results and Discussion

The desulfurization efficiency for DBT solution with different dosage of ionic liquid is listed in Table 3.12. The result demonstrated that the desulfurization efficiency increases when the dosage of ion liquid increases. Both ionic liquids exhibited similarity in enhancing the desulfurization process.

Table 3.12 Desulfurization of DBT solution with respect to IL dosage

IL	**IL dosage (g)**	**Initial Sulfur Content (ppm_w)**	**Final Sulfur Content (ppm_w)**	**Sulfur Removal (%)**
[BMIM][PF_6]	0	1006	153	85
	1	1006	36	96
	3	1006	24	98
	5	1006	< 20	> 98
[EMIM][$EtSO_4$]	0	1006	153	85
	1	1006	42	96
	3	1006	23	98
	5	1006	< 20	> 98

By applying 1 gram of the [BMIM][PF_6], the desulfurization efficiency was increased by 11%. Similarly, the desulfurization efficiency was increased by 11% by applying 1 gram of the [EMIM][$EtSO_4$].

It is observed that further increase of ionic liquid dosage could improve the desulfurization efficiency. When the dosage of ionic liquid increased from 1 gram to 3 grams, the desulfurization efficiency increased from 96% to 98%. When the dosage increased to 5 grams, the total sulfur content of the desulfurized sample was less than 20 ppm_w. Although the improvement was marginal, this would nonetheless be applicable to situations where sulfur content less than 20 ppm_w is desired. Therefore, the dosage of ionic liquid was selected to be 5 grams.

3.3.4.4 Ionic Liquid Selection

As discussed in Chapter 2.2, some RTILs would undergo thermolysis by ultrasonic irradiation, or oxidative degradation in the presence of hydrogen peroxide, acetic acid and ultrasonication. One of the mostly employed RTIL, 1,3-dialkylimidazolium hexafluorophosphate [BMIM][PF_6] would be degraded to fluorinated reactive gases which could damage glassware and other equipment.

Ionic liquids with alkylsulfate as anion are relatively more stable and relatively low in toxicity, and thus are considered as possible substitutions of [BMIM][PF_6] used in the previous experiments. Three alternative ionic liquids including 1-ethyl-3-methylimidazolium ethylsulfate [EMIM][$EtSO_4$], 1,2,3-trimethyl-imidazolium methylsulfate [TMIM][$MeSO_4$], and tributylmethylphosphonium methylsulfate [TMBP][$MeSO_4$] were investigated in this study.

3.3.4.5 Experimental Procedure

DBT model sulfur compound was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content. 0.7 gram of KO_2 was first mixed with 5 grams of selected ionic liquid, either [BMIM][PF_6], [EMIM][$EtSO_4$], [TMIM][$MeSO_4$] or [TMBP][$MeSO_4$], together with 0.1 gram of TOAF to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with 1.9 grams acetic acid and 0.1 gram of TFA to produce mixture B.

Mixture A was then slowly added to mixture B, and the resulting mixture was heated up to 70°C with continuous magnetic stirring for 3 hours. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.3.4.6 Results and Discussion

Table 3.13 shows the desulfurization of DBT solution with different ionic liquids applied with 3 hours reaction time. Both systems with ionic liquid [EMIM][EtSO$_4$] and [TMIM][MeSO$_4$], respectively, demonstrated similar desulfurization efficiency comparing with the system using [BMIM][PF$_6$]. With relatively high stability, [EMIM][EtSO$_4$] and [TMIM][MeSO$_4$] are possible substitutes for [BMIM][PF$_6$]. System using [TMBP][MeSO$_4$] has a slightly lower desulfurization efficiency, and thus is not considered as substitute to [BMIM][PF$_6$]. Considering cost and ease of application, [EMIM][EtSO$_4$] will be used in these studies.

Table 3.13 Desulfurization of DBT solution with respect to type of IL

IL	**State at 25°C**	**Initial Sulfur Content (ppm_w)**	**Final Sulfur Content (ppm_w)**	**Sulfur Removal (%)**
[BMIM][PF$_6$]	Liquid	1006	< 20	> 98
[EMIM][EtSO$_4$]	Liquid	1006	< 20	> 98
[TMIM][MeSO$_4$]	Solid	1006	< 20	> 98
[TMBP][MeSO$_4$]	Solid	1006	48	95

3.3.5 Effect of Treatment Methods

3.3.5.1 Time of Ultrasonication

Although it is believed that ultrasonication time would generally increase oxidative desulfurization efficiency, prolonged ultrasonication would also increase energy consumption and cost. Besides, it is suggested that the reaction would generally approach steady state quickly within the first few minutes of ultrasonication (Mei et al., 2003).

A combination of magnetic stirring and ultrasonication was used starting with the third generation of the UAOD system so as to improve desulfurization efficiency and reduce operational cost (Cheng et al., 2008). Based on literature, 10 minutes ultrasonication was applied in the combination of different magnetic stirring time to evaluate the effect of ultrasonication on desulfurization system using KO_2 as oxidant.

3.3.5.2 Experimental Procedure

DBT model sulfur compound was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content. 0.7 gram of KO_2 was first mixed with 5 grams of $[EMIM][EtSO_4]$ and 0.1 gram of TOAF to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with 2 grams acetic acid to produce mixture B.

Mixture A was then slowly added to mixture B, and the resulting mixture was heated up to 70°C with continuous magnetic stirring followed by 10 minutes ultrasonication. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.3.5.3 Results and Discussion

Table 3.14 shows the desulfurization efficiency of DBT solutions with different reaction time under continuous magnetic stirring, followed by ultrasound irradiation. It was observed that 51% desulfurization could be achieved by 10 minutes ultrasonication alone. However, the desulfurization efficiency was increased only from 51% to 53% by doubling ultrasound irradiation to 20 minutes. While ultrasound could enhance OSCs oxidation, it could also increase the rate of degradation of oxidant and other catalysts including ionic liquid. Prolonged ultrasonication would not effectively enhance desulfurization in this system and therefore, the optimum reaction time under ultrasonication was considered as 10 minutes.

Comparing the results from experiment with magnetic mixing alone and that with magnetic mixing followed by 10 minutes ultrasonication, experiments with 10 minutes ultrasonication demonstrated higher desulfurization efficiency, especially in shorter total reaction time. Higher than 98% desulfurization can be achieved in the system with 110 minutes of mixing followed by 10 minutes ultrasound irradiation. However, similar results can be achieved with 180 minutes of mixing alone. Thus, it could be more energy-effective to use magnetic mixing alone.

Table 3.14 Desulfurization of DBT solution under magnetic stirring and ultrasound

Mixing Time (min)	**Ultrasonication (min)**	**Total Reaction Time (min)**	**Initial Sulfur Content (ppm$_w$)**	**Final Sulfur Content (ppm$_w$)**	**Sulfur Removal (%)**
0	0	0	1006	1006	0
30	0	30	1006	368	63
60	0	60	1006	141	86
120	0	120	1006	49	95
180	0	180	1006	< 20	> 98
0	10	10	1006	494	51
20	10	30	1006	274	73
50	10	60	1006	93	91
110	10	120	1006	< 20	> 98
170	10	180	1006	<20	> 98
0	20	20	1006	476	53

In our study, it is demonstrated that it requires 180 minutes to desulfurize 1000 ppm$_w$ DBT solution by mechanical mixing alone. With the aid of 10 minutes ultrasonication, it requires only 120 minutes to achieve the same goal. It is believed that ultrasonication is a possible enhancement method in the new oxidative desulfurization with the application of superoxide. It can provide high local temperature and pressure in microenvironment. As a result, reaction rate is increased and thus improving productivity.

3.4 Desulfurization Efficiency on Various Model Sulfur Compounds

3.4.1 Identification of Experimental Optimum Conditions

It is known that there are various types of organic sulfur compounds in petroleum fuel. Thiophene, benzothiophene, dibenzothiophenes, and their derivatives are the major OSCs in middle distillates such as diesel, and heavier distillates. Among all, 4, 6-dimethyldibenzothiophene is well known for its refractory characteristic in traditional HDS process.

Although the optimal conditions, including the selection of oxidant, catalysts, ionic liquid, and their dosage in our process to desulfurize DBT has been discussed earlier in this chapter, it is important to test if the process can desulfurize other OSCs. In order to investigate the applicability of the process to various OSCs in petroleum products, different model sulfur compounds, including T, 2MT, BT, 2MBT), DBT, and 4,6DMDBT were selected to study their treatability under our process's optimal conditions. Table 3.15 provides a list of the selected optimum desulfurization conditions from this chapter.

Table 3.15 Selected conditions for desulfurization in model compound studies with 10 minutes ultrasonication

Solution of Target Model Sulfur Compound (1000ppm_w)	10 grams
Oxidant: KO_2	0.7 gram
Phase Transfer Catalyst: TOAF	0.1 gram
Acid: 95% HAc and 5% TFA	2 grams
Ionic Liquid: [EMIM][$EtSO_4$]	5 grams
Reaction Temperature	70°C
Magnetic Stirring Time	110 minutes
Ultrasonication Time	10 minutes

3.4.2 Experimental Procedure

The selected model sulfur compound, either T, 2MT, BT, 2MBT, DBT or 4,6DMDBT was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content.

A dosage of 0.7 gram KO_2 was added to 5 grams of selected ionic liquid and 0.1 gram of TOAF to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with 1.9 grams acetic acid and 0.1 gram of TFA to produce mixture B.

Mixture A was slowly added to mixture B, and the resulting mixture was heated up to 70 °C with continuous magnetic stirring for 110 minutes followed by ultrasonication for 10 minutes. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.4.3 Results and Discussion

Table 3.16 shows the desulfurization efficiencies on various model sulfur compounds under the designed conditions. The process demonstrated higher than 97% desulfurization on all model sulfur compounds in this study. Higher than 98% desulfurization on BT, 2MBT, DBT and 4,6DMDBT were achieved, while slightly lower desulfurization efficiencies (97%) on T and 2MT were observed. The high desulfurization efficiencies on various model sulfur compounds suggested that the designed process could be an effective alternative desulfurization process.

Table 3.16 Desulfurization of various model sulfur compounds

Model Sulfur Compounds	**Initial Sulfur Content (ppm_w)**	**Final Sulfur Content (ppm_w)**	**Sulfur Removal (%)**
T	985	23	97
2MT	1010	26	97
BT	1012	< 20	> 98
2MBT	994	< 20	> 98
DBT	1006	< 20	> 98
4,6DMDBT	1007	< 20	> 98

3.5 Kinetic Studies of Desulfurization on Model Sulfur Compounds

Kinetic studies of oxidative desulfurization of model sulfur compounds in carboxylic acid / H_2O_2 have been demonstrated in recent research articles (Dhir et al., 2009; Huang et al., 2007; Te et al., 2001; Yan et al., 2007). The reaction rates depend on various factors, including concentration of organic sulfur compounds, concentration of oxidant and concentration of catalysts. Micro-kinetic pathway of OSC oxidation could include multiple reactions as illustrated in Figure 3.5. In general, the reaction could be written as

Activation of Catalyst: $H_2O_2 + M \leftrightarrow MO + H_2O$ (Eq. 3.1)

Oxidation of OSC: $RS + 2MO \leftrightarrow RSO_2 + 2M$ (Eq. 3.2)

Overall Reaction: $RS + 2H_2O_2 \xleftrightarrow{M} RSO_2 + 2H_2O$ (Eq. 3.3)

where M is the catalyst applied. In such a case, the overall rate equation can be expressed as

$$r = -\frac{dC}{dt} = kC^{\alpha}[H_2O_2]^{\beta} \quad \text{(Eq. 3.4)}$$

where r is the rate of desulfurization of the selected OSC, k is the reaction rate constant, C is the concentration of the selected OSC. In cases with highly excess amount of hydrogen peroxide, change in concentration of oxidant would not be significant and thus, $[H_2O_2]$ can be considered as a constant. Putting $k' = k[H_2O_2]^{\beta}$, the rate equation can be simplified to

$$r = -\frac{dC}{dt} = k'C^{\alpha} \qquad \text{(Eq. 3.5)}$$

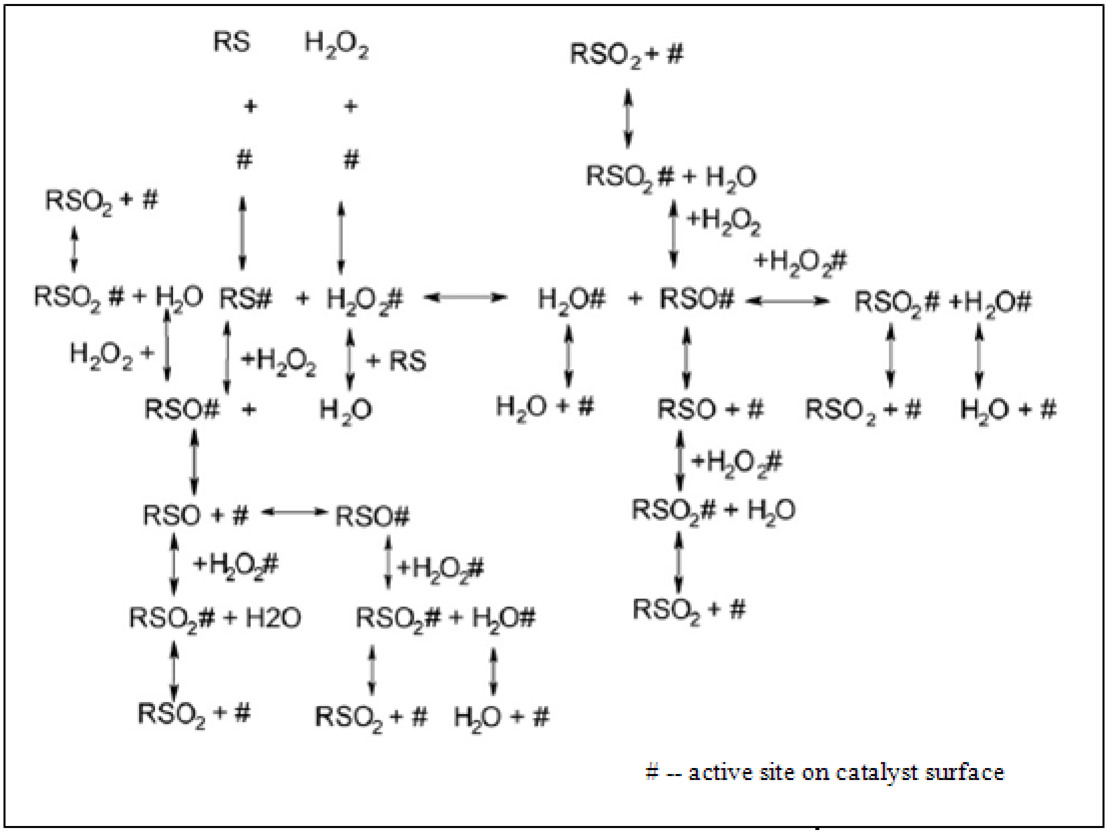


Figure 3.5 Superstructure of alternate reaction micro-kinetic pathway (Dhir et al., 2009)

Because desulfurization using potassium superoxide is not yet widely applied, very limited information on its reaction pathway and kinetics can be found in the literature. With excessive dosage of KO_2, OSC oxidation should follow the pseudo first order reaction kinetics. Thus, the rate equation could be rewritten as

$$r = -\frac{dC}{dt} = k'C \qquad \text{(Eq. 3.6)}$$

Upon integration,

$$\ln\frac{C_t}{C_o} = -k't \qquad \text{(Eq. 3.7)}$$

where C_o is the initial OSC concentration, C_t is the OSCs concentration at time t. The effect of temperature on the reaction rate constant can be expressed by the Arrhenius Equation listed below:

$$k' = Ae^{-E_a/RT} \qquad \text{(Eq. 3.8)}$$

$$\ln k' = \ln A - \frac{E_a}{RT} \qquad \text{(Eq. 3.9)}$$

where A is the Arrhenius frequency factor, E_a is the activation energy of the reaction, R is the ideal gas constant and T is the temperature in K.

In the previous section, studies on various model sulfur compounds including T, 2MT, BT, 2MBT, DBT, 4,6DMDBT under optimum conditions have been discussed.

In this section, desulfurization kinetic studies are performed on the model sulfur compounds in carboxylic acid / KO_2 mixture to estimate the rate constant k'. Effect of temperature on reaction rate for two model compounds, BT and DBT are also studied. Ultrasonication was not applied in this study. Table 3.17 provides a list of the selected desulfurization conditions.

Table 3.17 Selected conditions for desulfurization in model compound studies without ultrasonication

Solution of Target Model Sulfur Compound (1000ppm$_w$)	10 grams
Oxidant: KO_2	0.7 gram
Phase Transfer Catalyst: TOAF	0.1 gram
Acid: 95% Acetic Acid and 5% TFA	2 grams
Ionic Liquid: [EMIM][$EtSO_4$]	5 grams
Reaction Temperature	30 to 70°C
Magnetic Stirring Time	0 to 180 minutes

3.5.1 Experimental Procedure

The selected model sulfur compound, either T, 2MT, BT, 2MBT, DBT or 4,6DMDBT was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content.

A dosage of 0.7 gram KO_2 was added to 5 grams of selected ionic liquid and 0.1 gram of TOAF to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with 1.9 grams acetic acid and 0.1 gram of TFA to produce mixture B.

Mixture A was slowly added to mixture B, and the resulting mixture was heated up to the designated temperature with continuous magnetic stirring up to 180 minutes. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.5.2 Results and Discussion

Table 3.18 and Figure 3.6 show the desulfurization efficiencies on various model sulfur compounds as a function of time under the selected conditions listed in Table 3.17. With high dosage of KO_2, it is assumed that the desulfurization of the model sulfur compounds follow the pseudo first order reaction kinetics. Thus, linear relation should be demonstrated by plotting $-\ln(C_t/C_o)$ versus t with the slope equals to the reaction rate constant k', as illustrated in Figure 3.7 to Figure 3.9. The reaction rate constants for each model sulfur compounds are summarized in Table 3.19. The reaction rate constants using 30% H_2O_2 as oxidant are listed in Table 3.20 for comparison.

Table 3.18 Desulfurization efficiencies with respect to reaction time

	Mixing Time (min)	**T (°C)**	**Initial Sulfur Content (ppm_w)**	**Final Sulfur Content (ppm_w)**	**Sulfur Removal (%)**
T	0	70	985	985	0
	30	70	985	380	61.4
	60	70	985	178	81.9
	120	70	985	71	92.8
	180	70	985	28	97.2

Table 3.18 (continued)

	Mixing Time (min)	**T (˚C)**	**Initial Sulfur Content (ppm$_w$)**	**Final Sulfur Content (ppm$_w$)**	**Sulfur Removal (%)**
2MT	0	70	1010	1010	0
	30	70	1010	411	59.3
	60	70	1010	187	81.5
	120	70	1010	88	91.3
	180	70	1010	31	96.9
BT	0	70	1012	1012	0
	30	70	1012	341	66.3
	60	70	1012	112	88.9
	120	70	1012	35	96.5
	180	70	1012	<20	> 98
2MBT	0	70	994	994	0
	30	70	994	358	64
	60	70	994	151	84.8
	120	70	994	42	95.8
	180	70	994	21	97.9
DBT	0	70	1006	1006	0
	30	70	1006	368	63.4
	60	70	1006	141	86
	120	70	1006	49	95.1
	180	70	1006	< 20	> 98
4, 6 DMDBT	0	70	1007	1007	0
	30	70	1007	388	61.5
	60	70	1007	167	83.4
	120	70	1007	58	94.2
	180	70	1007	27	97.3

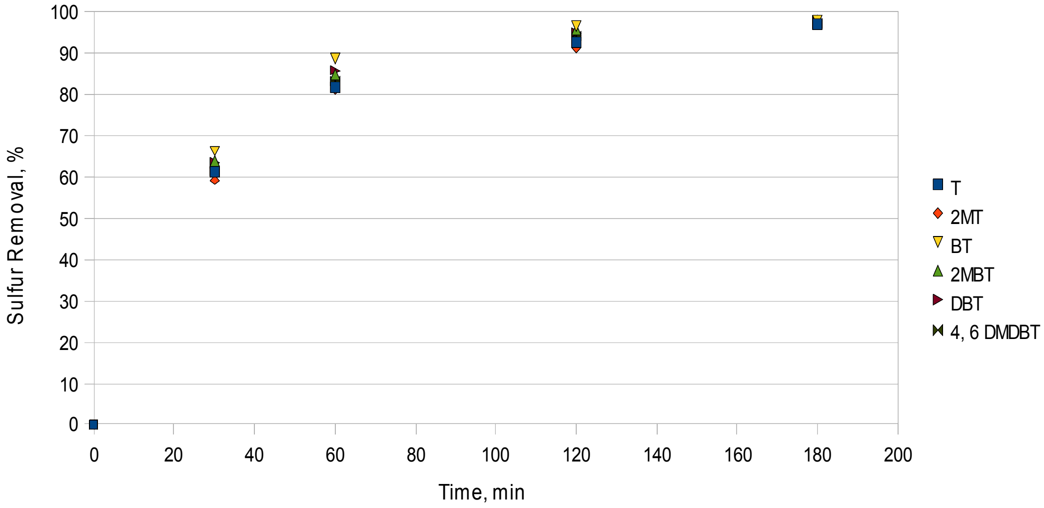


Figure 3.6 Desulfurization efficiencies of various model sulfur compounds for KO_2 process

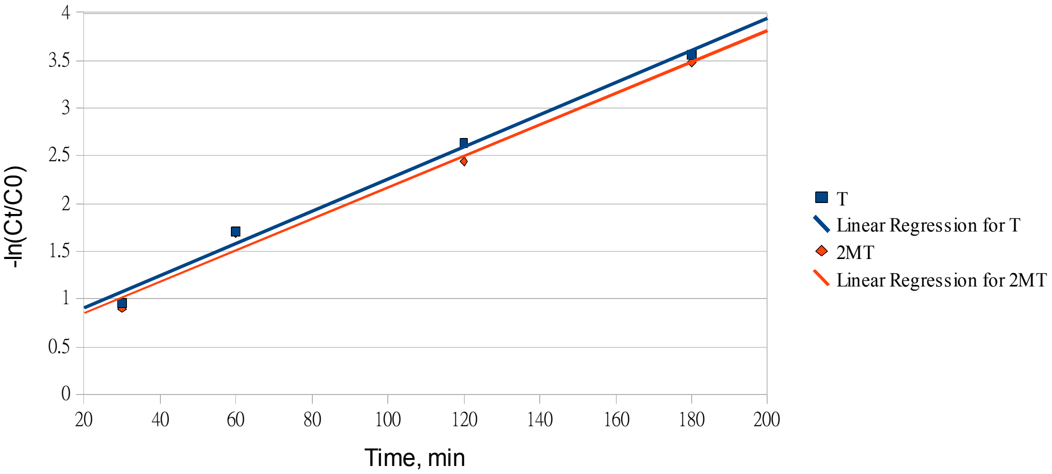


Figure 3.7 Linear regression of $-\ln(C_t/C_o)$ vs time for T and 2MT for KO_2 process

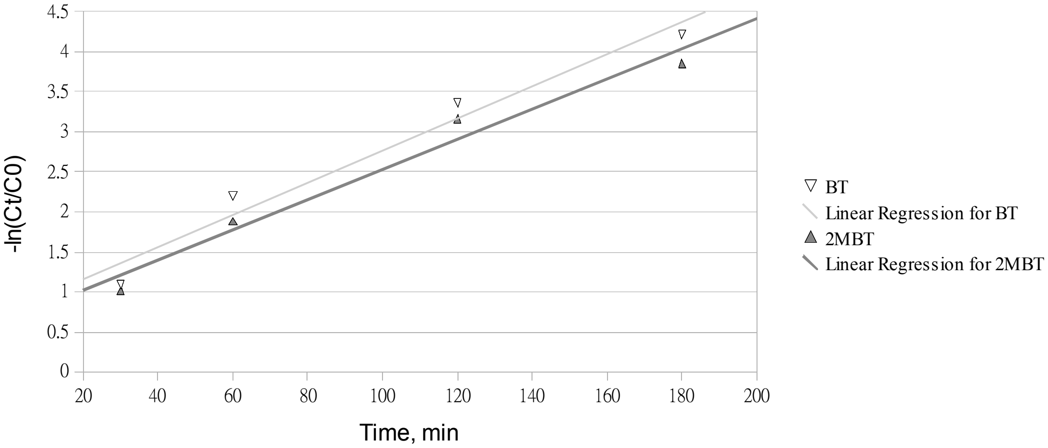


Figure 3.8 Linear regression of –ln(C_t/C_o) vs time for BT and 2MBT for KO_2 process

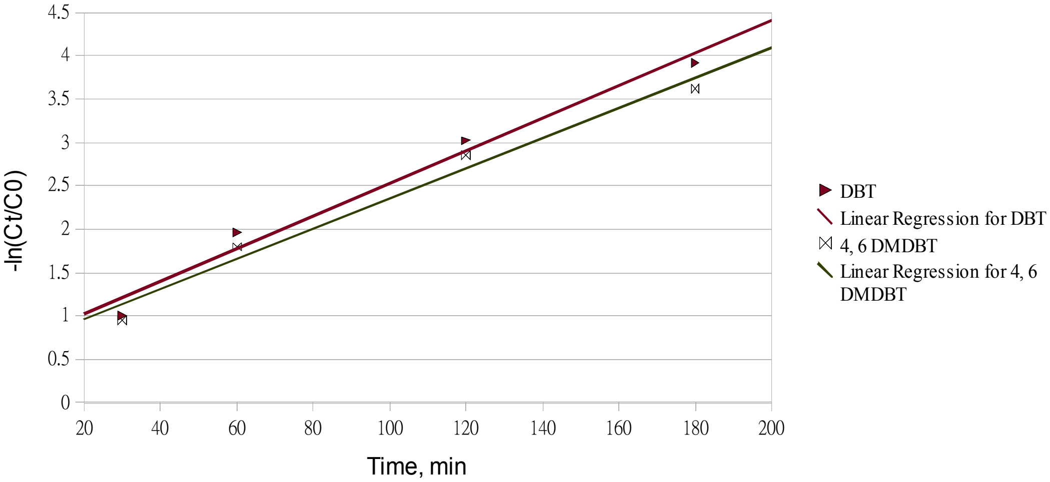


Figure 3.9 Linear regression of –ln(C_t/C_o) vs time for DBT and 4,6DMDBT for KO_2 process

Table 3.19 Rate constants for various model sulfur compounds using KO_2

Model Sulfur Compound	**k', min^{-1}**	**R^2**
T	0.0190	0.991
2MT	0.0184	0.987
BT	0.0229	0.935
2MBT	0.0212	0.970
DBT	0.0211	0.978
4,6 DMDBT	0.0197	0.978

The reaction rate constants are within the range of 0.018 to 0.022 min^{-1} for all 6 model sulfur compounds tested. The reaction rate constants indicate the oxidation efficiencies of the tested model sulfur compounds marginally diminish in following order: BT > 2MBT > DBT > 4, 6DMDBT > T > 2MT.

Table 3.20 Rate constants for various model sulfur compounds using H_2O_2 (Cheng, 2007)

Model Sulfur Compound	**k', min^{-1}**	**R^2**
T	0.0196	0.997
2MT	0.0199	0.995
BT	0.0276	0.998
2MBT	0.0218	0.997
DBT	0.0228	0.997
4,6 DMDBT	0.0230	0.979

From Table 3.19 and 3.20, the reaction rate constants using KO_2 as oxidant are comparable to those using 30% H_2O_2 as oxidant. With all R^2 values greater than 0.93, the plots demonstrate good linear relation and thus, it is valid to assume that the reactions follow the pseudo first order reaction kinetics. However, R^2 value for the linear regression of $-\ln(C_t/C_o)$ versus time in the experiments using KO_2 as oxidant are relatively lower than the those using 30% H_2O_2 as oxidant.

The reaction rate constants for BT and DBT at different temperatures can be found by conducting the same experimental conditions listed in Table 3.17. Linear regression of $–\ln(C_t/C_o)$ versus time at different temperature for the desulfurization of BT and DBT are illustrated in Figure 3.10 and Figure 3.11, respectively. Using the reaction rate constants at different temperature, the activation energy E_a and the Arrhenius frequency factor A can be estimated from the Arrhenius equation by plotting $-\ln(k')$ versus 1/T, as illustrated in Figure 3.12. The value of E_a and A for BT and DBT are summarized in Table 3.21. The apparent activation energies also demonstrated that BT with lower activation energy has a higher reactivity as compared to DBT.

Table 3.21 Apparent activation energies for oxidation of BT and DBT

	k', min^{-1}			**E_a, kJ/mol**	**A, min^{-1}**
Temperature, K	**303**	**323**	**343**		
BT	0.0061	0.0155	0.0229	28.77	601.85
DBT	0.0050	0.0098	0.0211	31.01	1085.72

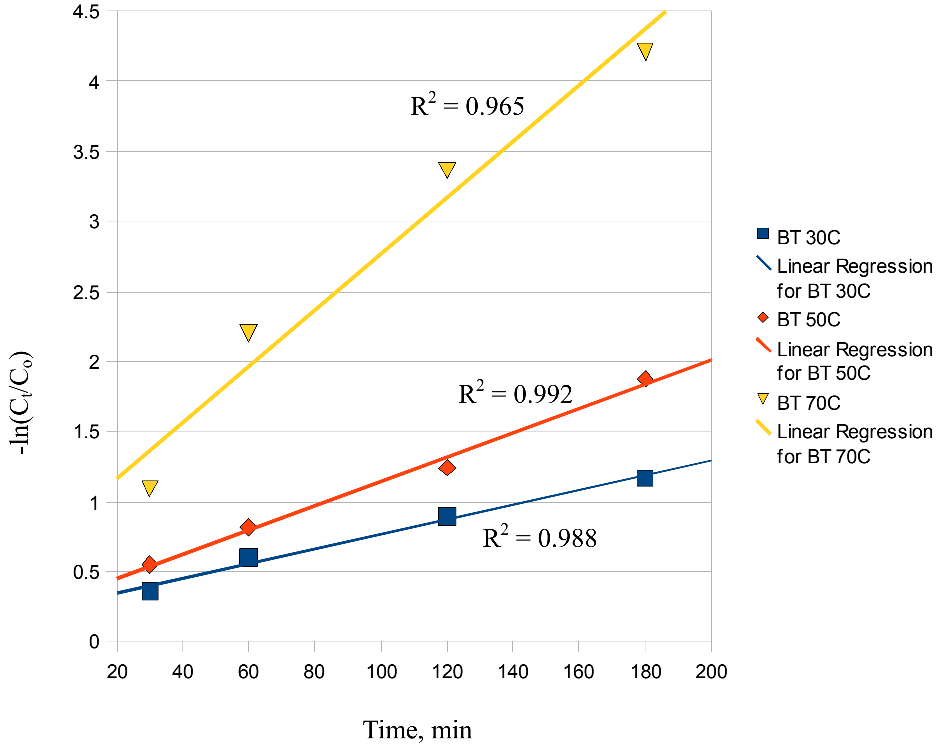


Figure 3.10 Linear regression of –ln(C_t/C_o) vs time at different temperature for BT

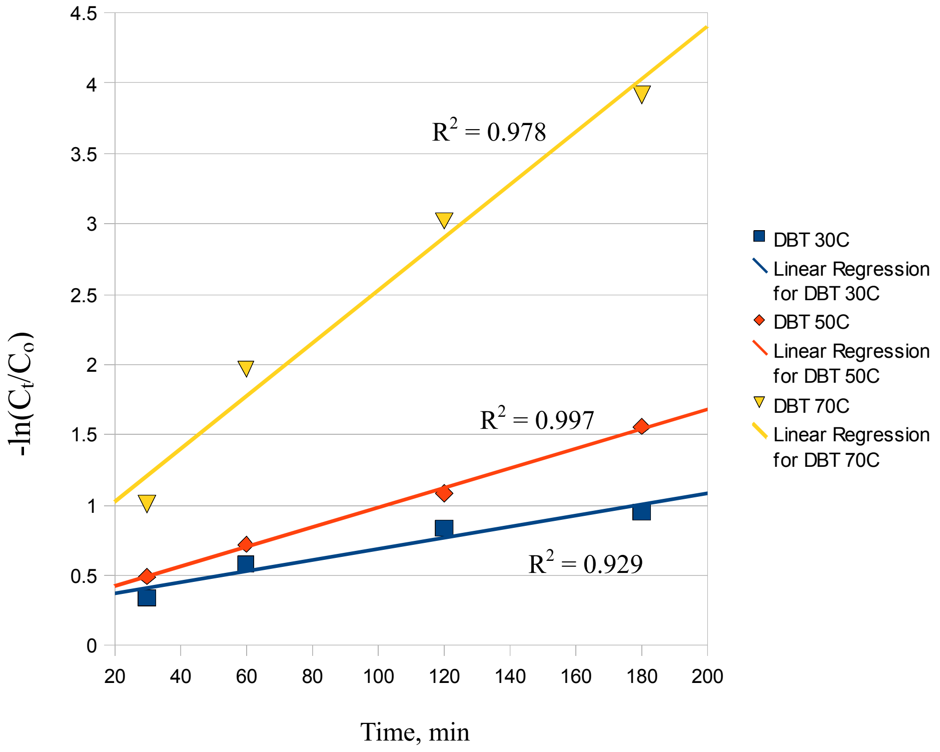


Figure 3.11 Linear regression of $-\ln(C_t/C_o)$ vs time at different temperature for DBT

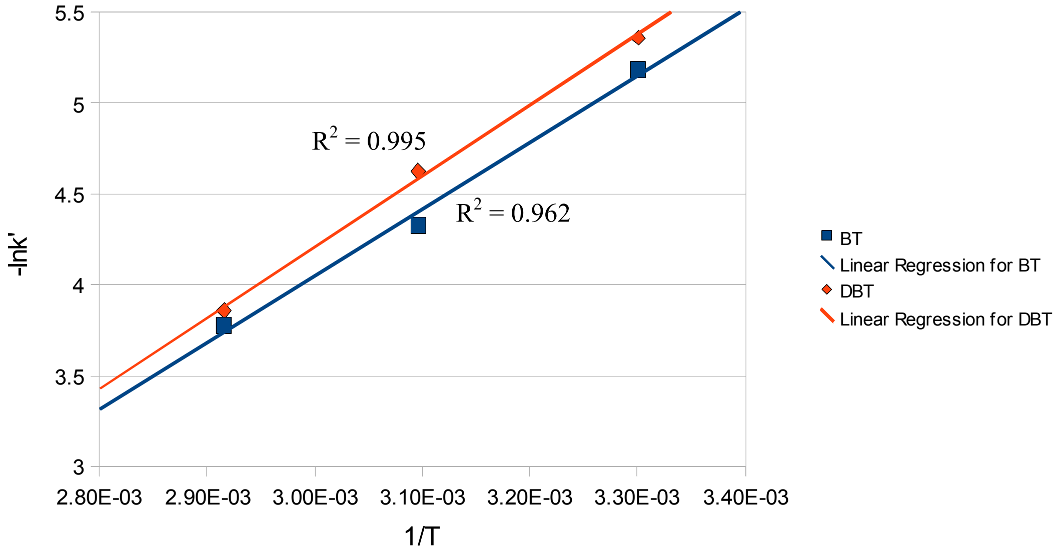


Figure 3.12 -ln(k') versus 1/T for model sulfur compounds BT and DBT

3.6 Preliminary Study on UV Assisted Desulfurization Process

3.6.1 Challenge in UAOD Processes

It has been demonstrated that different generation of UAOD processes can achieve high oxidation rates with various OSCs, and thus, yielding high desulfurization efficiencies. However, power consumption in ultrasonication is considerably high. For instance, power output for ultrasound reactor VCX-750 is 750 watts. This could be the major drawback of UAOD systems. Besides, ultrasonication could cause decomposition of various catalysts including phase transfer catalyst, trifluoroacetic acid, and ionic liquids. Therefore, alternative activation methods with lower energy consumption are of particular interest.

UV irradiation is known to improve oxidation in water treatment systems. Recent researches have also demonstrated the feasibility in utilizing UV to enhance oxidative desulfurization. However, most UV related desulfurization processes require use of high pressure mercury UV lamp with energy output greater than 200 watts, with irradiation time longer than 1 hour (Matsuzawa et al., 2001). This would result in even higher energy consumption comparing with ultrasonication. Therefore, a low power UV lamp with power output at 8 watts was used in this preliminary study to illustrate the feasibility of UV assisted desulfurization process with low energy consumption. 30% wt. hydrogen peroxide was used in this point of the study for better comparison.

3.6.2 Experimental Procedure

Selected model sulfur compound, either BT or DBT, was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content. 1 gram of H_2O_2 was first mixed with 1 gram of selected ionic liquid and 0.1 gram of TOAF to produce mixture A; 10 grams of stock solution of model sulfur compound were mixed with 1.9 grams acetic acid and 0.1 gram of TFA to produce mixture B.

Mixture A was then slowly added to mixture B, and 0.1 gram of a photo-catalyst, titanium (IV) oxide was added to the mixture. The resulting mixture was kept at ambient condition using continuous magnetic stirring for 60 minutes with or without UV irradiation.

The experiments were performed in dark to eliminate the interference by other light sources. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and was extracted with acetonitrile to remove sulfones. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

3.6.3 Results and Discussion

Table 3.22 shows that desulfurization for BT and DBT were not significant in 60 minutes mixing alone. In contrast, higher than 50% desulfurization can be achieved for both BT and DBT solutions by applying UV irradiation. The result is comparable to system with 10 minutes ultrasonication.

Table 3.22 Desulfurization of model sulfur compounds with UV

	Mixing (min)	**UV**	**Ultrasound (min)**	**$S_{initial}$ (ppm_w)**	**S_{final} (ppm_w)**	**S Removal (%)**
BT	60	Off	0	1012	971	4
DBT	60	Off	0	1006	968	4
BT	60	On	0	1012	461	54
DBT	60	On	0	1006	418	58
BT	50	Off	10	1012	384	62
DBT	50	Off	10	1006	360	64

The power output of the ultrasound device used is 750W and the power output used of UV lamp is 8W. Considering the energy consumption, 10 minutes ultrasonication requires more than 15 times energy comparing with 60 minutes UV irradiation. More experiments are required to test for the applicability of the system on other model compounds and fuel samples.

3.7 Summary and Conclusion

This study aimed at developing alternative oxidation processes to achieve high desulfurization. Use of solid type oxidant can significantly reduce the volume and weight of required oxidant as compared with systems using 30% wt. hydrogen peroxide solution as oxidant.

Potassium superoxide is found to be effective as the alternative oxidant due to the high effectiveness in oxidizing OSCs, high purity, high stability for storage under ambient conditions and relatively low adverse environmental impacts comparing with other solid oxidants. By using potassium superoxide, the weight of oxidant required can be reduced to one-fifth of the weight when hydrogen peroxide is used.

In the reaction system with multiphase, phase transfer catalyst was demonstrated to promote reaction as a result of interfacial exchange. With the application of tetraalkylammonium salts, an intermediate product tetraalkylammonium superoxide could be formed so as to transfer superoxide radical to organic phase. PTC counter ion selection is also important for successful phase transfer catalysis. It is suggested that fluoride should be used as the PTC counter ion to maximize the efficiency.

Acid catalysts including acetic acid and trifluoroacetic acid are also used to improve reaction rate and selectivity. It has been demonstrated that higher acidity of acid catalysts can promote oxidative reactions using hydrogen peroxide as oxidant, but it is relatively not significant in system using superoxide as oxidant. Trifluoroacetic acid could be decomposed forming acid fumes upon ultrasonication, and explosive reaction may also occur in extreme cases. Thus, minimum amount of trifluoroacetic acid should be used in the system. Trifluoroacetic acid would only be used up to 5% of the total weight of acid catalyst to enhance oxidative desulfurization in this system.

Addition of ionic liquids can improve desulfurization efficiency of the system. Although 1-butyl-3-methylimidazolium hexafluorophosphate is known as the most common ionic liquid used in oxidative desulfurization, its instability in ultrasonication and oxidants systems could cause operational problems. Corrosive gases including hydrogen fluoride, phosphorus pentafluoride and phosphorus oxyfluoride could be generated as decomposition byproducts of this ionic liquid. High stability ionic liquids such as 1-ethyl-3-methylimidazolium ethylsulfate and 1,2,3-trimethylimidazolium methylsulfate could be used to alleviate formation of decomposition byproduct.

It is demonstrated that the modified process with solid oxidant is applicable to desulfurize various model sulfur compounds. Higher than 98% oxidation and desulfurization can be achieved on benzothiophene, 2-methyl benzothiophene, dibenzothiophene, and 4, 6-dimethyl dibenzothiophene, while 97% oxidation and desulfurization can be achieved on thiophene and 2-methyl thiophene. As shown in the kinetic studies, the oxidation efficiencies of the model sulfur compounds decrease in the following order: BT > 2MBT > DBT > 4, 6DMDBT > T > 2MT.

A preliminary investigation on UV assisted oxidative desulfurization conducted in this study demonstrated a possible way to lower the power consumption in UAOD processes. Higher than 50% desulfurization on both BT and DBT can be achieved in 1 hour under UV irradiation with application of 30% wt. hydrogen peroxide, phase transfer catalyst, acid catalysts, photo-catalyst, and ionic liquid. This result is comparable to a system with same reactants under ultrasonication for 10 minutes. It was demonstrated that energy consumption can be lowered by roughly 95% by using low power UV irradiation instead of ultrasonication. Further studies could be conducted to investigate the applicability of UV irradiation in desulfurization other OSCs and fuel samples.

CHAPTER 4: MODIFIED OXIDATIVE DESULFURIZATION USING KO_2 AND H_2O_2 ON PETROLEUM FUEL

4.1 Introduction

As discussed in Chapter 1, alkyl benzothiophene derivatives and alkyl dibenzothiophene derivates are the major organic sulfur compounds found in mid-distillates such as diesel, and also heavy distillates such as residual oil. These two groups of OSCs, especially with alkyl substituent at 4- and/or 6-postion are considered refractory to traditional hydrodesulfurization process. Thus, these groups of OSCs are the major sulfur compounds found in hydrodesulfurized fuels.

In previous generations of the UAOD processes, high desulfurization efficiencies have been demonstrated on benzothiophene and dibenzothiophene using 30% wt. hydrogen peroxide as oxidant under mild conditions (Wan et al., 2007; Etemadi et al., 2007). The third generation of the UAOD process, or the modified UAOD process, has successfully demonstrated the production of ultra-low sulfur diesel using 30% wt. H_2O_2 as oxidant. However, this process is found not to be applicable to heavy oil desulfurization mainly due to heavy deposition of asphaltenes.

Besides, concentrated hydrogen peroxide is a potential hazard due to its spontaneous ignition and explosive properties. Diluted hydrogen peroxide solutions are commonly used in the oxidative desulfurization process. However, dilution would increase the volume and weight of oxidant required together with a reduction of the reaction efficiency. These effects would increase the overall cost of the process.

The modification using potassium superoxide (KO_2) as oxidant, discussed in Chapter 3, has demonstrated high desulfurization efficiencies for thiophene, benzothiophene, dibenzothiophene and their derivatives. The results are comparable to the third generation of the UAOD process (modified UAOD process). In this study, modified desulfurization process using KO_2 as oxidant was applied to petroleum fuels including diesel and residual oil. The process can be operated under mild conditions with the enhancement from phase transfer catalysis and acid catalysis (Chan et al., 2009). The process consists of two steps: selective oxidation of OSCs in fuel with or without ultrasound irradiation followed by separation of oxidized OSCs from fuels by solvent extraction or solid adsorption.

In this chapter, modified desulfurization process using KO_2 as oxidant was applied to some of the commercial fuels including marine gas oil (MGO), jet propellant 8 (JP-8), sour diesel and also residual fuel oils to investigate the feasibility of desulfurizing commercial fuels.

4.2 Materials

Three diesel fuels, including jet propellant 8 (JP-8) with 782 ppm_w sulfur content received from U.S. Army Research Laboratory, Adelphi, Maryland; marine gas oil (MGO) with sulfur 1631 ppm_w content received from Navy Station, Long Beach, California; and sour diesel with 8117 ppm_w sulfur content received from Golden Eagle Oil Refinery Inc., Woods Cross, Utah; were used as the mid-distillate feedstock. Two residual oil samples, including residual oil no. 6 (RO-6) received from Eco Energy Solutions Inc., Reno, Nevada; and intermediate fuel oil (IFO) received from Intelligent Energy Inc., Long Beach, California; were used as the heavy-distillate feedstock.

Oxidants used including 30% wt. H_2O_2 solution was obtained from VWR Inc., while potassium superoxide, acid catalysts (glacial acetic acid and trifluoroacetic acid), and phase transfer catalysts (tetraoctylammonium bromide and tetraoctylammonium chloride) were obtained from Sigma-Aldrich Co., while tetraoctylammonium fluoride was synthesized by halogen exchange process (Dermeik et al., 1989). Ionic liquids including 1-butyl-3-methyl-imidazolium hexafluorophosphate [BMIM][PF_6], 1-ethyl-3-methylimidazolium ethylsulfate [EMIM][$EtSO_4$], and 1,2,3-trimethyl-imidazolium methylsulfate [TMIM][$MeSO_4$] were obtained from Sigma-Aldrich Co. Acetonitrile, solvent used for sulfones extraction, was obtained from VWR Inc.

4.3 Experimental Procedure and Analytical Method

Known amount of oxidant, either potassium superoxide or 30% wt. hydrogen peroxide, was first mixed with 5 grams of selected ionic liquid, either 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6], 1-ethyl-3-methyl-imidazolium ethylsulfate [EMIM][$EtSO_4$] or 1,2,3-trimethylimidazolium methyl-sulfate [TMIM][$MeSO_4$], and 0.1 gram of tetraoctylammonium fluoride to produce mixture A; 10 grams of the selected mid-distillate feedstock, either JP-8, MGO or sour diesel; or heavy-distillate feedstock, either RO-6 or IFO, were mixed with 2 grams of acetic acid to produce mixture B.

Mixture A was slowly added to mixture B, and the resulting mixture was heated up to 70° C with continuous mixing for desired time period. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and extracted with acetonitrile. The acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

The total sulfur concentration of the fuel samples was determined according to ASTM D4294 and ISO 8754. Sulfur-in-Oil Analyzer (SLFA-20), manufactured by Horiba Inc. was used to measure total sulfur content of samples based on non-dispersive X-ray fluorescence (NDXRF). Sulfur-in-Oil Analyzer is applicable to samples with total sulfur as high as 5% wt., with a lower detection limit of 20ppm_w.

4.4 Results and Discussion

4.4.1 Desulfurization of JP-8

Table 4.1 shows the desulfurization of JP-8 using potassium superoxide with the application of different ionic liquids. Table 4.2 shows the desulfurization of JP-8 using 30% wt. hydrogen peroxide using different ionic liquids for comparison. The weight of oxidant used was fixed at 0.5 gram. The reaction time was 180 minutes.

Table 4.1 Desulfurization of JP-8 using KO_2 as oxidant

Ionic Liquid	**KO_2**		**$[S]_{Initial}$**		**$[S] : [KO_2]$**	**$[S]_{Final}$**	**[S] Removal**
	g	**mmol**	**ppm_w**	**mmol**	**mol : mol**	**ppm_w**	**%**
[BMIM][PF_6]	0.5	9.6	782	0.24	1 : 29	< 20	> 98
[EMIM][$EtSO_4$]	0.5	9.6	782	0.24	1 : 29	< 20	> 98
[TMIM][$MeSO_4$]	0.5	9.6	782	0.24	1 : 29	< 20	> 98

As shown in Table 4.1, higher than 98% desulfurization efficiencies for JP-8 were achieved by using potassium superoxide as oxidant, regardless of the type of ionic liquid used. Thus, all ionic liquids including [BMIM][PF_6], [EMIM][$EtSO_4$], and [TMIM][$MeSO_4$] were considered applicable to this desulfurization process. As discussed in Chapters 2 and 3, [BMIM][PF_6] could decompose to corrosive gases under ultrasonication and/or oxidation conditions. Therefore, [EMIM][$EtSO_4$], and [TMIM][$MeSO_4$] would be considered as better options of ionic liquids applied to this desulfurization process.

Table 4.2 Desulfurization of JP-8 using 30% wt. H_2O_2 as oxidant

Ionic Liquid	**H_2O_2 (30%)**		**$[S]_{Initial}$**		**[S] : [H_2O_2]**	**$[S]_{Final}$**	**[S] Removal**
	g	**H_2O_2 mmol**	**ppm_w**	**mmol**	**mol : mol**	**ppm_w**	**%**
[BMIM][PF_6]	0.5	4.4	782	0.24	1 : 18	101	87
[EMIM][$EtSO_4$]	0.5	4.4	782	0.24	1 : 18	92	90
[TMIM][$MeSO_4$]	0.5	4.4	782	0.24	1 : 18	112	86

Comparing with systems using 30% wt. hydrogen peroxide (Figure 4.2), systems using potassium superoxide afforded higher desulfurization efficiencies. One of the possible reasons could be a higher availability of oxidant per mass of potassium superoxide as compared to 30% wt. hydrogen peroxide system.

Another set of experiments were conducted using 0.5 gram of potassium superoxide as oxidant and [EMIM][$EtSO_4$] as the ionic liquid. Desulfurization efficiencies as a function of reaction time are shown in Figure 4.1. It is demonstrated that the desulfurization efficiency approached to 100% at 100 minutes.

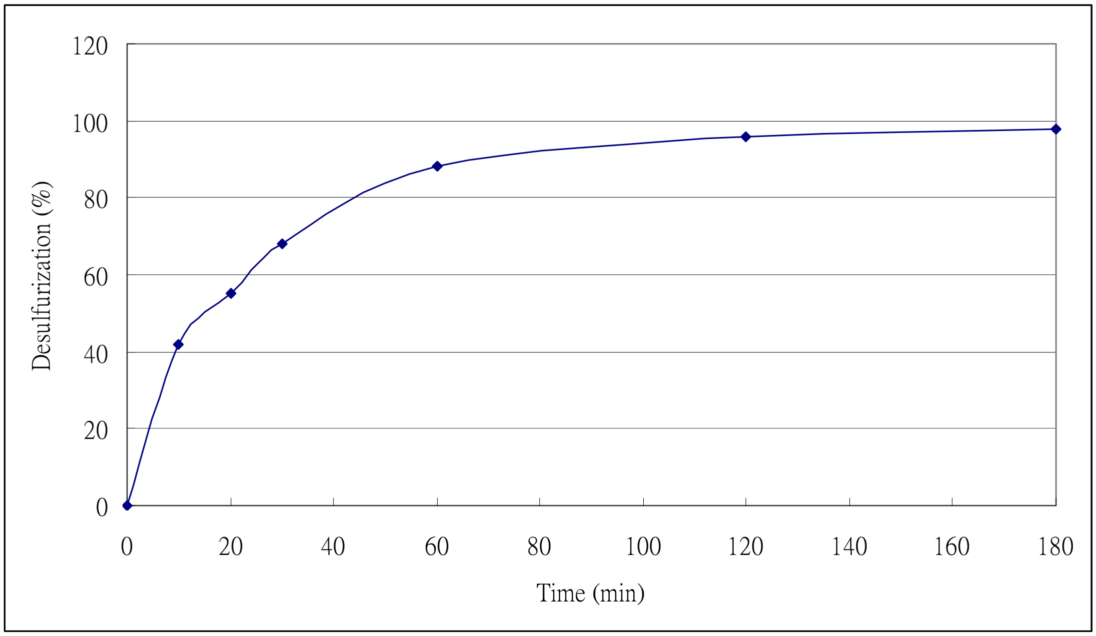


Figure 4.1 Desulfurization of JP-8 with respect to total reaction time

4.4.2 Desulfurization of MGO

Table 4.3 shows the desulfurization of MGO using potassium superoxide with using different ionic liquids. Table 4.4 shows the desulfurization of MGO with 30% wt. hydrogen peroxide using different ionic liquids. The weight of oxidant used was 0.5 gram for both systems. The reaction took place at 70°C with reaction time of 180 minutes.

Similar to desulfurization of JP-8, higher than 98% desulfurization efficiencies was achieved for MGO by using potassium superoxide as oxidant, regardless of the type of ionic liquid used. However, under the same conditions, the maximum desulfurization efficiency achieved ffor 30% wt. H_2O_2 was only 82%. A possible explanation could be the availability of 1.5 times more oxidant in the superoxide system as compared to hydrogen peroxide system.

As described in the previous chapters, corrosive gases could be generated from [BMIM][PF_6] under strong oxidizing condition. Without losing desulfurization efficiency, alternative ionic liquids such as [EMIM][$EtSO_4$] and [TMIM][$MeSO_4$] should be considered for application to this desulfurization process.

Table 4.3 Desulfurization of MGO using KO_2 as oxidant

Ionic Liquid	**KO_2**		**$[S]_{Initial}$**		**[S] : [KO_2]**	**$[S]_{Final}$**	**[S] Removal**
	g	**mmol**	**ppm_w**	**mmol**	**mol : mol**	**ppm_w**	**%**
[BMIM][PF_6]	0.5	9.6	1600	0.5	1 : 14	< 20	> 99
[EMIM][$EtSO_4$]	0.5	9.6	1600	0.5	1 : 14	< 20	> 99
[TMIM][$MeSO_4$]	0.5	9.6	1600	0.5	1 : 14	< 20	> 99

Table 4.4 Desulfurization of MGO using 30% wt. H_2O_2 as oxidant

Ionic Liquid	**H_2O_2 (30%)**		**$[S]_{Initial}$**		**[S] : [H_2O_2]**	**$[S]_{Final}$**	**[S] Removal**
	g	**H_2O_2 mmol**	**ppm_w**	**mmol**	**mol : mol**	**ppm_w**	**%**
[BMIM][PF_6]	0.5	4.4	1600	0.5	1 : 8.8	358	77
[EMIM][$EtSO_4$]	0.5	4.4	1600	0.5	1 : 8.8	294	82
[TMIM][$MeSO_4$]	0.5	4.4	1600	0.5	1 : 8.8	309	81

4.4.3 Desulfurization of Sour Diesel

Tables 4.5 and 4.6 show the desulfurization of sour diesel using potassium superoxide and 30% wt hydrogen peroxide, respectively, using different ionic liquids. The weight of oxidant used was fixed at 0.5 gram for both systems. The reaction temperature was maintained at 70°C with a reaction time of 180 minutes.

Table 4.5 Desulfurization of sour diesel using KO_2 as oxidant

Ionic Liquid	**KO_2**		**$[S]_{Initial}$**		**[S] : [KO_2]**	**$[S]_{Final}$**	**[S] Removal**
	g	**mmol**	**ppm_w**	**mmol**	**mol : mol**	**ppm_w**	**%**
[BMIM][PF_6]	0.5	9.6	8100	2.53	1 : 2.8	491	94
[EMIM][$EtSO_4$]	0.5	9.6	8100	2.53	1 : 2.8	428	95
[TMIM][$MeSO_4$]	0.5	9.6	8100	2.53	1 : 2.8	432	95

Table 4.6 Desulfurization of sour diesel using 30% wt. H_2O_2 as oxidant

Ionic Liquid	**H_2O_2 (30%)**		**$[S]_{Initial}$**		**[S] : [H_2O_2]**	**$[S]_{Final}$**	**[S] Removal**
	g	**H_2O_2 mmol**	**ppm_w**	**mmol**	**mol : mol**	**ppm_w**	**%**
[BMIM][PF_6]	0.5	4.4	8100	2.53	1 : 1.7	4733	42
[EMIM][$EtSO_4$]	0.5	4.4	8100	2.53	1 : 1.7	4348	46
[TMIM][$MeSO_4$]	0.5	4.4	8100	2.53	1 : 1.7	4197	48

As can be seen in Table 4.5, a maximum of 95% desulfurization efficiency can be achieved by using potassium superoxide as oxidant, with either [EMIM][EtSO$_4$], or [TMIM][MeSO$_4$]. Lower desulfurization efficiency (42%) was obtained in the system using [BMIM][PF$_6$] as ionic liquid.

In comparison, for the system using 30% wt. hydrogen peroxide (Table 4.6), the maximum efficiency was only 48%. It is thus shown that superoxide is highly superior to hydrogen peroxide in desulfurization of sour diesel.

These studies indicate that superoxide results in higher desulfurization efficiency as compared to hydrogen peroxide. Two major reasons can be advanced: 1) with the equal mass consideration, the number of moles of oxidant provided by 30% wt. H_2O_2 is 55% less than number of mole of oxidant provided by pure KO_2; and 2) water molecules in H_2O_2 solution could hinder the reaction rate due to dilution effect (Wypych, 2001). Among the three diesel fuels; i.e., JP-8, MGO, and sour diesel, the greatest difference in desulfurization efficiencies between the two oxidants (superoxide versus hydrogen peroxide) occurred for sour diesel.

4.4.4 Kinetic Studies of Desulfurization on Various Diesel Samples

Kinetic studies of oxidative desulfurization reported by different research groups (Tam et al., 1990, Te et al., 2001; Huang et al., 2007; Yan et al., 2007; Dhir et al., 2009) indicate that oxidation rate using excess amount of oxidant follows pseudo first order reaction kinetics. In the studies reported herein, desulfurization of model sulfur compounds reported in Chapter 3, section 3.5, using excess amount of potassium superoxide follows pseudo first order reaction kinetics. The experimental rate constants were obtained from the rate equations previously applied to model sulfur compounds including T, 2MT, BT, 2MBT, DBT and 4,6DMDBT.

While sulfur content in diesel is mainly composed of thiophenes, benzothiophenes, and dibenzothiophenes and their derivatives, it is expected that the desulfurization of JP-8, MGO and sour diesel would also follow the pseudo first order reaction kinetics.

Desulfurization kinetic studies were conducted for the three diesel fuels including JP-8, MGO and sour diesel, using KO_2 oxidant with sulfur to oxidant ratios of 1:29, 1:14 and 1:2.7, respectively. Figure 4.2 illustrates the desulfurization efficiencies as a function of reaction time for the three diesel fuels using 0.5 gram of potassium superoxide as oxidant and [EMIM][$EtSO_4$] as ionic liquid. The linearized plots of -

$\ln(C_t/C_o)$ versus time are shown in Figure 4.3 and the reaction rate constants are summarized in Table 4.7.

Table 4.7 Rate constants for various diesel samples using KO_2 as oxidant

Diesel	**k', min^{-1}**	**R^2**
JP-8	0.0231	0.970
MGO	0.0202	0.949
Sour Diesel	0.0151	0.815

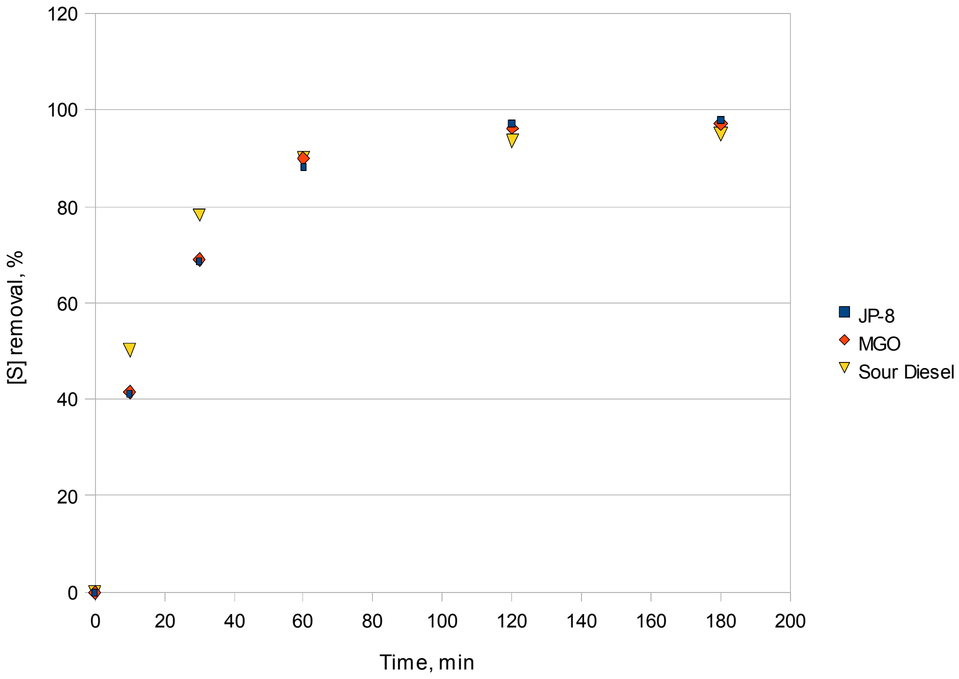


Figure 4.2 Desulfurization removal efficiencies of different diesel fuels as a function of reaction time

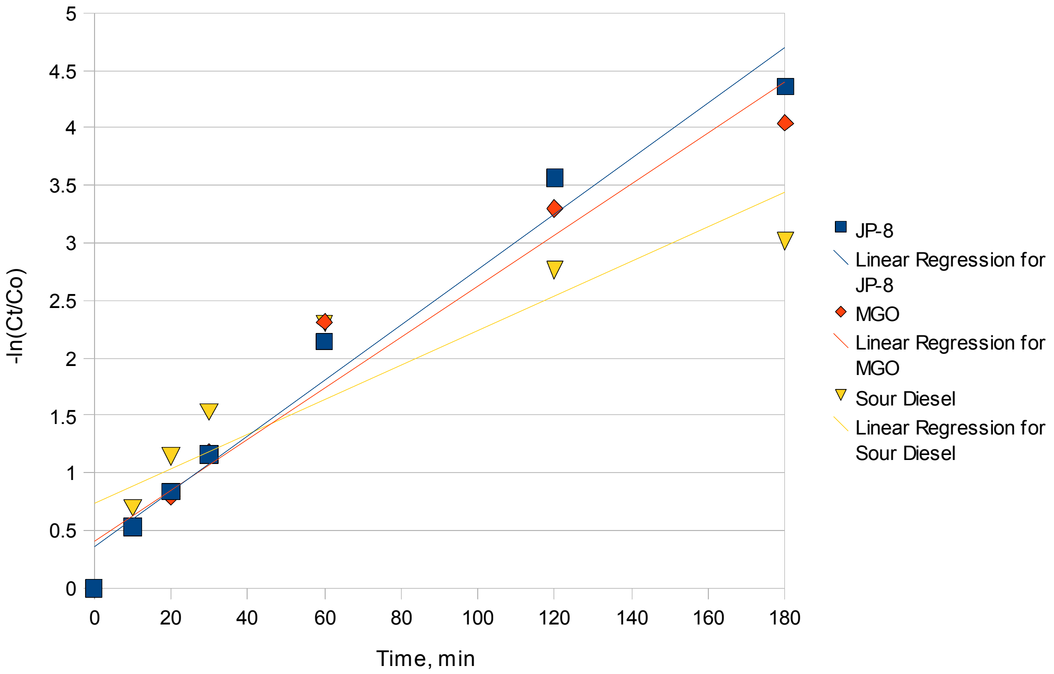


Figure 4.3 Desulfurization rates of different diesel fuels as a function of reaction time

The apparent first order rate constant, k’, for JP-8, MGO and sour diesel were 0.0231 min^{-1}, 0.0212 min^{-1} and 0.0151 min^{-1}, respectively. The correlation coefficient, R^2, for JP-8 and MGO were 0.970 and 0.949, respectively while R^2 for sour diesel was significantly lower (0.815).

As can be observed in Figure 4.3, the reaction rate for sour diesel is significantly lower as compared to those for JP-8 and MGO. A possible explanation for this phenomenon is the comparatively lower oxidant to sulfur ratio in the sour diesel system, in which the concentration KO_2 became significantly low at longer reaction time. As a result, the assumption of pseudo first order kinetics was no longer valid.

Future studies should consider the determination of superoxide concentration during the reaction process. Chemiluminescence determination and direct spectrophotometrical determination of superoxide concentration are some of the possible methods (Afanas’ev, 1989; Endo et al., 2002; Rose et al., 2008; Wali et al., 2002). Also, more tests should be conducted to understand the actual reaction pathway of KO_2 is also required.

4.4.5 Desulfurization of Heavy-Distillates

Table 4.8 shows the desulfurization of heavy-distillates, RO-6, and IFO using potassium superoxide with a fixed “sulfur to oxidant” mole ratio and different ionic liquids. The reaction took place in 3 hours mechanical mixing.

Further, a series of experiments using 30% wt. H_2O_2 were also conducted to desulfurize the two heavy-distillates. It was observed, however, that the phases could not be easily separated after treatment by the modified UAOD process due to heavy precipitation and conglomeration. It was thus decided that the modified UAOD process using 30% wt. H_2O_2 is not applicable to desulfurize these heavy-distillates.

Table 4.8 Desulfurization of different heavy-distillates using KO_2 as oxidant

	Ionic Liquid	**KO_2**		**$[S]_{Initial}$**		**[S] : [KO_2]**	**$[S]_{Final}$**	**[S] Removal**
		g	**mmol**	**ppm_w**	**mmol**	**mol : mol**	**ppm_w**	**%**
RO-6	[BMIM][PF_6]	0.7	9.9	12187	3.8	1 : 2.6	6037	51
	[EMIM][$EtSO_4$]	0.7	9.9	12187	3.8	1 : 2.6	5578	54
	[TMIM][$MeSO_4$]	0.7	9.9	12187	3.8	1 : 2.6	5711	53
IFO	[BMIM][PF_6]	1.6	22.1	27223	8.5	1 : 2.6	6479	76
	[EMIM][$EtSO_4$]	1.6	22.1	27223	8.5	1 : 2.6	5710	78
	[TMIM][$MeSO_4$]	1.6	22.1	27223	8.5	1 : 2.6	5358	80

4.5 Summary and Conclusion

This study aimed as developing alternative oxidation processes to achieve high desulfurization efficiencies on various commercial fuels including diesels and residual oils with relatively low consumption of oxidant.

Use of solid type oxidant can significantly reduce the volume and weight of required oxidant comparing with systems using 30% wt. hydrogen peroxide solution as oxidant. In low oxidant to sulfur ratio, potassium superoxide showed significantly more effective comparing with 30% wt. hydrogen peroxide.

As illustrated in Table 4.3, higher desulfurization efficiencies could be observed in systems using [EMIM][EtSO$_4$] and [TMIM][MeSO$_4$] instead of [BMIM][PF$_6$]. Therefore, [EMIM][EtSO$_4$] and [TMIM][MeSO$_4$] are considered as better ionic liquid for this system.

It was demonstrated that high desulfurization efficiencies on commercial diesels including JP-8, MGO and sour diesel could be achieved. Greater than 98% desulfurization efficiencies were observed for JP-8 and MGO. 95% desulfurization was achieved on sour diesel using potassium superoxide as oxidant. This is possibly due to the high initial sulfur content of sour diesel. With lower oxidant to sulfur ratio, the desulfurization efficiency on sour diesel was relatively low.

The pseudo first order rate constant for JP-8, MGO and sour diesel obtained from the kinetic studies are 0.0231 min^{-1}, 0.0212 min^{-1} and 0.0151 min^{-1}, respectively. Lower reaction rate for sour diesel was possibly due to low oxidant to sulfur ratio applied.

In this study, it was also demonstrated that 50% to 75% desulfurization efficiencies could be achieved with heavy-distillates by using potassium superoxide as oxidant. The process could yield residual oil with sulfur content of less than 1%, satisfying the 2010 sulfur cap of 1% regulated by MARPOL. Nonetheless, in order to meet the 5000ppm_w surfur cap goal in 2020, further desulfurization of the heavy distillates is still required.

Desulfurization efficiencies of RO-6 and IFO were relatively low compared to the diesel fuels and the model compound including T, 2MT, BT, 2MBT, DBT and 4,6DMDBT. This could be caused by the complex structure of RO-6 and IFO hindering the desulfurization efficiency. Furthermore, there could be other refractory sulfur compounds which are not susceptible to oxidation or difficult to be extracted.

CHAPTER 5: QUALITATIVE ANALYSIS USING GC-SCD

5.1 Introduction

As previously discussed, it is widely accepted that organic sulfur compounds in petroleum products can cause serious pollution to the environment. Upon combustion, OSCs would be transformed to sulfur oxides, which are known to be the key contaminant causing acid rain and health hazards. Some of the polycyclic aromatic sulfur compounds could also be possible mutagens or carcinogens. Thus, desulfurization technologies are expected to significantly lower the sulfur concentration in various petroleum products.

In order to investigate the reactivity and understand the oxidation pathway of organic sulfur compounds, identification of OSCs in petroleum products is of great importance in the industry. Also, understanding the distribution of OSCs and identifying the refractory compounds are highly desirable for the development of desulfurization technologies.

Gas chromatography (GC) equipped with appropriate detectors is one of the most common methods to measure and characterize volatile sulfur, nitrogen and phosphorus compounds. There are several detectors which can be used to detect sulfur containing compounds, including Atomic Emission Detector (AED), Hall Electroconductivity Detector (HECD), Flame Photometric Detector (FPD), Pulse Flame Photometric Detector (PFPD), Flame Ionization Detector (FID) and Mass Spectroscopy Detector (MS). These detectors are applicable to identify a wide range of elements and compounds (Lee, 1991; Mistry et al., 1994; Ellzy et al., 1998). However, most of these detectors are not able to provide accurate results or a linear response to the concentration of sulfur containing compounds (Andari et al., 1996). Although AED shows a higher linear dynamic range comparing with other detectors, it is much more expensive and difficult to operate. Besides, its selectivity towards different elements is questionable (Mistry et al., 1994).

Sulfur Chemiluminescence Detector (SCD) is a more recent detector which can serve better for both qualitative and quantitative analyses of organic sulfur compounds. SCD is based on a two-step process (Benner, 1989). Sulfur containing compounds are first reacted in a high temperature furnace (> 800°C) with hydrogen rich hydrogen/air mixture forming sulfur monoxide. Sulfur monoxide formed is transferred to a reaction chamber where sulfur monoxide is oxidized by ozone forming sulfur dioxide (SO_2*) in an excited state. Upon decay, the exited state of SO_2 emits UV radiation with a peak wavelength of 350 nm. The chemiluminescent emission is detected by a photomultiplier tube. Because the intensity of light emitted is proportional to the concentration of sulfur, SCD can be used to measure sulfur both quantitatively and qualitatively. A block diagram of GC-SCD with the major chemical reactions involved is illustrated in Figure 5.1.

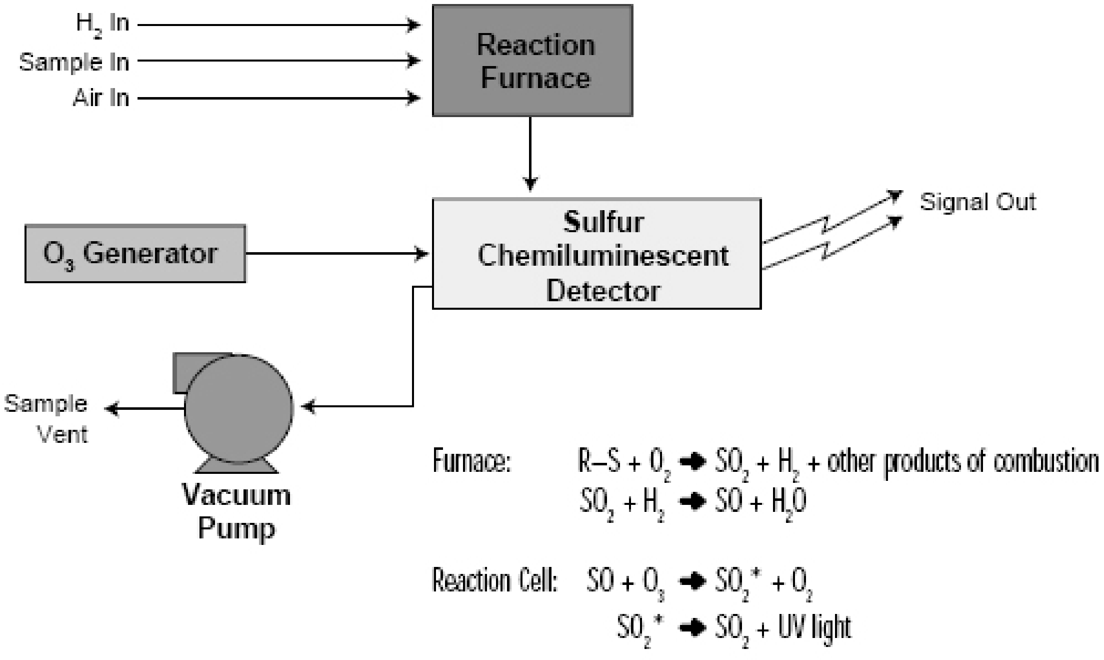
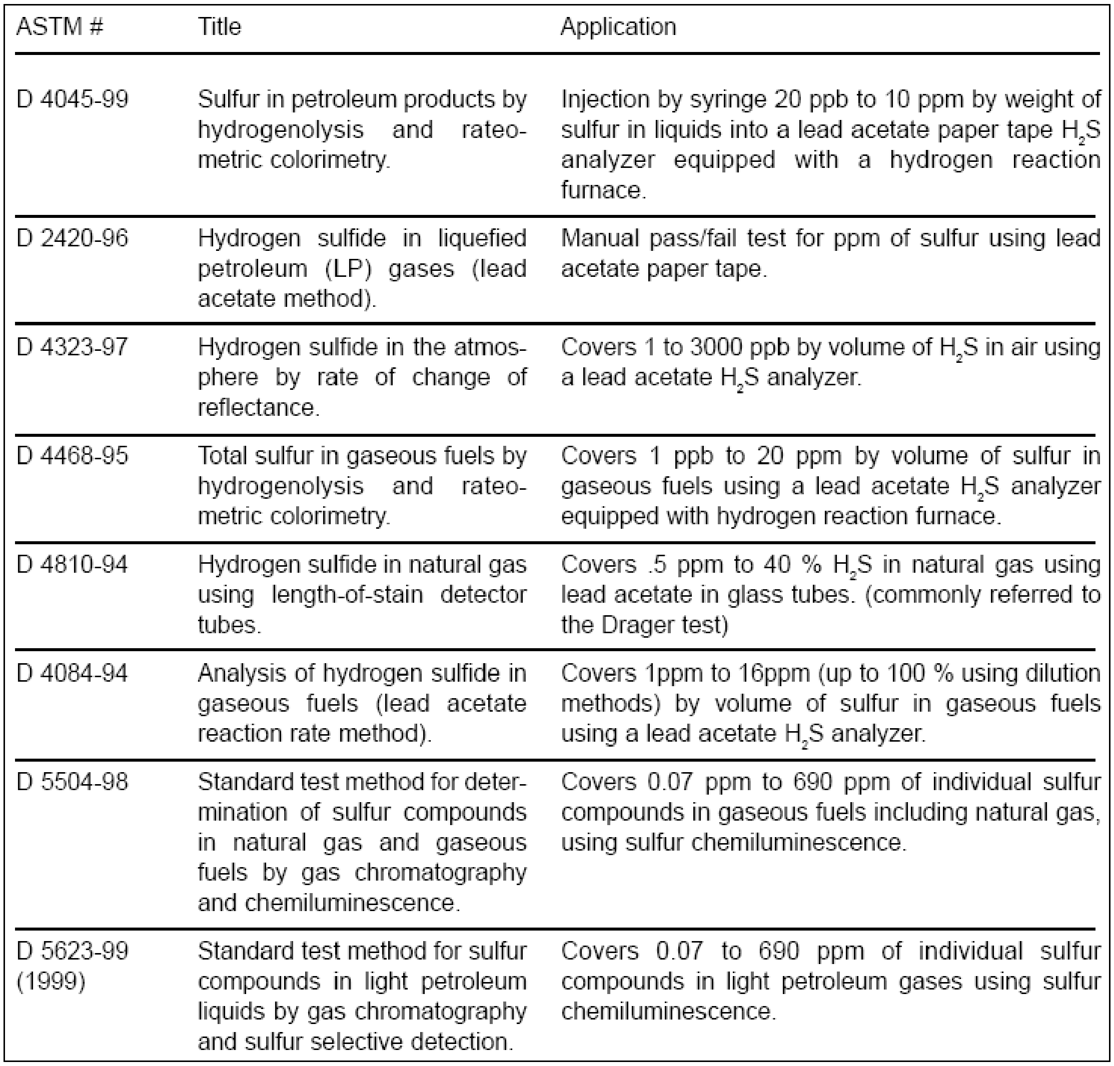


Figure 5.1 Major reactions in SCD (GAS Inc., 2004)

Sulfur chemiluminescence detector provides higher sensitivity for any organic sulfur compounds with the lower detection limit in ppb level. It provides linear response with respect to concentration, which can be used to measure sulfur concentration. While SCD is specified to detect sulfur only, there is no interference by co-eluting species of other hydrocarbons and thus, providing a better chromatograph to identify sulfur compounds. High stability, selectivity and absence of quenching are also some of the advantage of SCD. GC-SCD is one of the standard test methods to characterize organic sulfur compounds approved by ASTM as stated in ASTM D 5504, ASTM D 5623, and ASTM D 7011.



ASTM #	Title	Application
D 4045-99	Sulfur in petroleum products by hydrogenolysis and rateometric colorimetry.	Injection by syringe 20 ppb to 10 ppm by weight of sulfur in liquids into a lead acetate paper tape H_2S analyzer equipped with a hydrogen reaction furnace.
D 2420-96	Hydrogen sulfide in liquefied petroleum (LP) gases (lead acetate method).	Manual pass/fail test for ppm of sulfur using lead acetate paper tape.
D 4323-97	Hydrogen sulfide in the atmosphere by rate of change of reflectance.	Covers 1 to 3000 ppb by volume of H_2S in air using a lead acetate H_2S analyzer.
D 4468-95	Total sulfur in gaseous fuels by hydrogenolysis and rateometric colorimetry.	Covers 1 ppb to 20 ppm by volume of sulfur in gaseous fuels using a lead acetate H_2S analyzer equipped with hydrogen reaction furnace.
D 4810-94	Hydrogen sulfide in natural gas using length-of-stain detector tubes.	Covers .5 ppm to 40 % H_2S in natural gas using lead acetate in glass tubes. (commonly referred to the Drager test)
D 4084-94	Analysis of hydrogen sulfide in gaseous fuels (lead acetate reaction rate method).	Covers 1ppm to 16ppm (up to 100 % using dilution methods) by volume of sulfur in gaseous fuels using a lead acetate H_2S analyzer.
D 5504-98	Standard test method for determination of sulfur compounds in natural gas and gaseous fuels by gas chromatography and chemiluminescence.	Covers 0.07 ppm to 690 ppm of individual sulfur compounds in gaseous fuels including natural gas, using sulfur chemiluminescence.
D 5623-99 (1999)	Standard test method for sulfur compounds in light petroleum liquids by gas chromatography and sulfur selective detection.	Covers 0.07 to 690 ppm of individual sulfur compounds in light petroleum gases using sulfur chemiluminescence.

Figure 5.2 Some of the standard sulfur measurement methods adopted by ASTM (GAS Inc., 2004)

In order to investigate the oxidation pathway of organic sulfur compounds in the new system, a series of experiments were conducted using the modified desulfurization process with KO_2 as oxidant on different samples, including a premixed solution of model sulfur compounds including benzothiophene, dibenzothiophene, and 4, 6-dimethyl dibenzothiophene; a solution of benzothiophene sulfone; a solution of dibenzothiophene sulfone; and also some of the commercial fuels including JP-8, MGO, sour diesel and also residual fuel oils.

During the experiment, it was found that the intensity of model sulfur compounds were significantly reduced after the oxidation process even if the total sulfur concentration did not change. A test was done to examine if there was inorganic sulfur compounds, for instance, sulfate in the sample after oxidation. Based on the results, it is believed that sulfate could be one of the products. While sulfate is not detectable by GC-SCD and could deposit on the GC column, samples after oxidation process were washed with water to lower down sulfate and other ions concentrations.

In this chapter, qualitative analyses on the sulfur species using HP-6890 Series gas chromatograph equipped with Sievers model 355B Sulfur Chemiluminescence Detector purchased from Agilent Technologies Inc., Santa Clara, California are discussed. Also, the oxidation mechanism of organic sulfur compounds using potassium superoxide is proposed.

5.2 Materials

Model sulfur compounds used in this study including benzothiophene, benzothiophene sulfone (BTO), dibenzothiophene, dibenzothiophene sulfone (DBTO), 4, 6-dimethyl dibenzothiophene were obtained from Sigma-Aldrich Co. Solvents for model sulfur compounds solutions preparation (toluene and n-decane) and solvent used for sulfones extraction (acetonitrile) were obtained from VWR Inc. Oxidant potassium superoxide, acid catalysts including glacial acetic acid and trifluoroacetic acid, and phase transfer catalyst tetraoctylammonium bromide were obtained from Sigma-Aldrich Co., while tetraoctylammonium fluoride was synthesized by halogen exchange process (Dermeik et al., 1989). Ionic liquid 1-butyl-3-methylimidazolium hexafluoro-phosphate [BMIM][PF_6], was obtained from Sigma-Aldrich Co.

Three diesel fuels, including JP-8 with 780 ppm_w sulfur content received from Army Research Laboratory; MGO with sulfur 1600 ppm_w content received from Navy Station; and sour diesel with 8100 ppm_w sulfur content received from Golden Eagle Oil Refinery Inc., were used as the mid-distillate feedstock. Two residual oil samples, RO-6 received from Eco Energy Solutions Inc.; and IFO received from Intelligent Energy Inc., were used as the heavy-distillate feedstock.

5.3 Experimental Procedure

5.3.1 Preparation of Model Sulfur Compound Solutions

Sample 1: Known amount of BT, DBT and 4, 6 DMDBT model sulfur compounds were dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 300 ppm_w BT, 300 ppm_w DBT, and 400 ppm_w 4, 6DMDBT, giving a total of 1000 ppm_w sulfur content.

Sample 2: Known amount of BTO model sulfur compound was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content.

Sample 3: Known amount of DBTO model sulfur compound was dissolved into a solvent mixture with 30% wt. toluene and 70% wt. n-decane to make a stock solution with approximately 1000 ppm_w sulfur content.

5.3.2 Desulfurization of Feedstock

To avoid potential contamination of sulfur compounds from other reactants, sulfur containing ionic liquids including 1-ethyl-3-methyl-imidazolium ethylsulfate [EMIM][$EtSO_4$] and 1,2,3-trimethylimidazolium methyl-sulfate [TMIM][$MeSO_4$] were not used in this study. Instead, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] was employed. It is known that ionic liquid can extract a portion of sulfone from oil samples. To minimize the extraction effect of sulfur compounds by ionic liquid, the dosage of ionic liquid is reduced to 1 gram without significant loss of desulfurization efficiency with a 180 minutes reaction time.

Based on the optimal condition discussed in Chapter 3, Section 3.4, 0.7 gram of potassium superoxide was first mixed with 1 gram of selected ionic liquid [BMIM][PF_6] and 0.1 gram of tetraoctyl-ammonium fluoride (TOAF) to produce mixture A; 10 grams of the selected model sulfur compounds solution as described in Chapter 5, Section 5.3.1, or selected fuel sample such as JP-8, MGO, sour diesel, RO-6 or IFO, were mixed with 2 grams of acetic acid to produce mixture B. Mixture A was then slowly added to mixture B, and the resulting mixture was heated up to 70°C and stirred for 180 minutes. Emulsion formed after the treatment process was separated by centrifugation. Oil phase was collected and extracted with acetonitrile. Total sulfur content of acetonitrile-extracted oil phase was analyzed by the Sulfur-in-Oil Analyzer.

5.3.3 Analytical Method

The total sulfur concentration of the fuel samples was determined according to ASTM D4294 and ISO 8754. Sulfur-in-Oil Analyzer (SLFA-20), manufactured by Horiba Inc. was used to measure total sulfur content of samples based on non-dispersive X-ray fluorescence. Sulfur-in-Oil Analyzer is applicable for samples with total sulfur as high as 5% wt., with a detection limit of 20ppm$_w$.

Identification of organic sulfur compounds was carried out by HP-6890 Series GC equipped with Sievers 355B SCD (GC-SCD). The GC capillary column was equipped with a 30m × 0.32mm HP-5 fused silica column with 0.25μm film thickness.

To separate different compounds, a specified column temperature profile based on Andari et al. (1996) was applied. The column temperature started at 35°C and was gradually increased to 70°C at a rate of 10°C per minute. Then, the temperature was increased to 280°C at a rate of 3°C per minute. The column temperature was kept at 280°C for another 2.5 minutes to vaporize the remaining hydrocarbon. Ultra high purity helium (carrier gas) was supplied at a constant pressure of 60 psig. Ultra high purity hydrogen (fuel) was supplied at constant pressures of 40 psig.

The SCD furnace temperature was set at 800°C with air flow of 5.8mL per minute and hydrogen flow of 100mL per min. Ultra high purity oxygen was supplied to the ozone generator with flow rate of 60 mL/min with a constant pressure of 60 psig at 25°C. The injected volume of sample was 1 μL with appropriate dilution to 50 ppm_w to 100 ppm_w total sulfur concentrations.

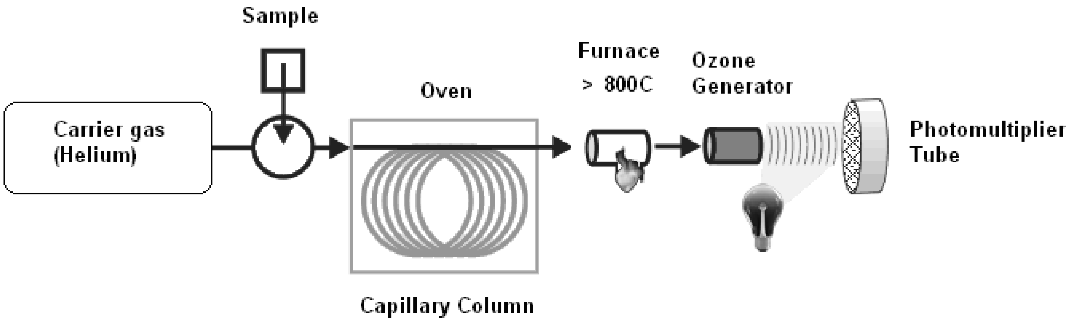


Figure 5.3 Block diagram of GC-SCD setup

5.3.4 Estimation of Retention Time of Different OSCs

An initial test was conducted to illustrate the retention time of three model compounds namely BT, DBT and 4, 6 DMDBT. Although similar operating conditions were used as reported by Andari et al. (1996), the retention times of the model sulfur compounds reported in this study (Table 5.2) were of significantly different. Andari et al. used an earlier GC model HP 5890 series II using a methyl silicon fused capillary column, while this study used a HP-6890 Series GC with HP-5 fused silica capillary column. Both columns are very similar except for their polarities, which could explain the difference in retention time.

Based on Cheng et al. (2005), it would be reasonable to assume that the retention times for different columns with similar properties follow a linear regression. A plot of experimental retention time from this study versus a retention time reported by Andari et al for the three model sulfur compounds is shown in Figure 5.4. The estimated retention time for several organic sulfur compounds are presented in Tables 5.1 and 5.2.

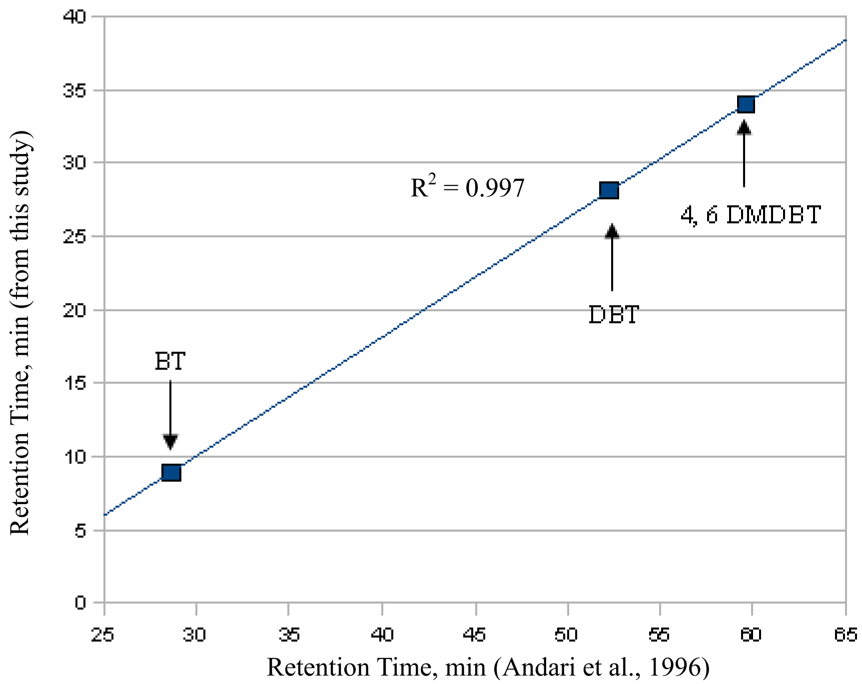


Figure 5.4 Experimental retention time versus reference retention time of model sulfur compounds BT, DBT and 4, 6 DMDBT

Table 5.1 Calculated retention time of various BT and DBT derivatives

	Retention Time, min	
	Andari et al., 1996	Estimated
C2 benzothiophenes	37.68 – 39.45	16.27 – 17.70
C3 benzothiophenes	41.11 – 43.45	19.05 – 20.94
C4 benzothiophenes	43.83 – 48.73	21.25 – 25.22
C5 benzothiophenes	49.25 – 51.33	25.64 – 27.32
C6 benzothiophenes	51.79 – 55.80	27.69 – 30.94
C7 benzothiophenes	56.31 – 57.78	31.35 – 32.54
C8 benzothiophenes	58.18 – 59.87	32.86 – 34.23
C1 di-benzothiophene	56.09 – 57.52	31.17 – 32.33
C2 di-benzothiophene	59.52 – 61.64	33.73 – 35.67
C3 di-benzothiophene	62.17 – 64.95	36.09 – 38.34
C4 di-benzothiophene	65.47 – 68.27	38.77 – 41.03
C5 di-benzothiophene	69.44 – 69.78	41.98 – 42.25

Table 5.2 Calculated retention time of various OSCs

	Retention Time, min		
	Andari et al., 1996	From this study	Estimated
thiophene	5.52	1.12	1.06
2-methyl thiophene	9.06	2.20	2.26
2-ethyl thiophene	22.29		3.37
2, 5-dimethyl thiophene	23.47		3.47
3-tert-butyl thiophene	25.75		3.60
2, 3, 4-tri-methyl thiophene	25.99		3.73
1, 3-dithiacyclopentane	26.73		3.89
1-heptane thiol	26.99		4.05
1, 4-butane dithiol	28.58		4.24
2-methyl 5-propyl thiophene	30.28		4.48
2-n-butyl thiophene	31.31		4.57
2, 5-diethyl thiophene	33.85		4.66
3-n-butyl thiophene	34.16		4.75
3, 4-diethyl thiophene	35.16		4.96
2, 3, 4, 5 tetra-methyl thiophene	39.45		5.29
n-butyl sulfide	45.68		5.96
ethyl phenyl thiophene	25.75		6.62
1, 5-pentane dithiol	25.99		6.81
1-octane thiol	26.73		7.41
benzyl methyl sulfide	26.99		7.62
benzothiophene	28.58	8.89	8.91
1-nonane thiol	30.28		10.28
1, 6-hexane dithiol	31.31		11.12
5-methyl benzothiophene	33.85		13.17
3-methyl benzothiophene	34.16		13.42
1-decane thiol	35.16		14.23
3, 5-dimethyl benzothiophene	39.45		17.70
di-phenyl sulfide	45.68		22.75
benzyl phenyl sulfide	50.11		26.33
di-benzothiophene	52.25	28.08	28.06
di-benzyl sulfide	54.54		29.92
4, 6-dimethyl dibenzothiophene	59.61	34.01	34.02
thianthrene	59.72		34.11
2, 8-dimethyl dibenzothiophene	61.1		35.23

5.4 Results and Discussion

5.4.1 Model Sulfur Compounds Identification

Figures 5.5 and 5.6 depict the GC-SCD chromatograms of BT, DBT and 4, 6 DMDBT before and after the oxidative desulfurization treatment using KO_2 as oxidant. It can be observed that the retention times for the oxidized products of BT, DBT and 4,6DMDBT identified as BTO, DBTO, and 4, 6 DMDBTO, respectively, shifted to the right.

Nevertheless, the intensity of the peaks are significantly reduced even the total sulfur concentration measured by Sulfur-in-Oil Analyzer did not show significant difference. One of the hypotheses is that superoxide might be able to oxidize organic sulfur compounds to inorganic sulfate.

Due to the fact that GC-SCD is not capable of identifying sulfate ion, experiments were conducted to examine if there was inorganic sulfate present in the sample after oxidation. The sample was extracted with deionized water (DW) to possibly partition sulfate ion. Addition of 0.5 gram barium chloride and precipitation of barium sulfate indicated the presence of sulfate ion. Measurement of total sulfur concentration before (1037 ppm_w) and after water extraction (568 ppm_w) indicate that nearly 54% of total sulfur was extracted.

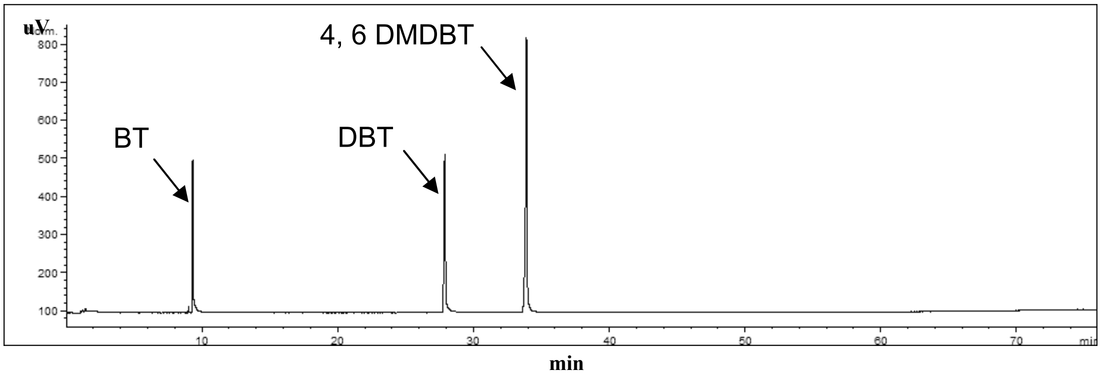


Figure 5.5 GC-SCD chromatogram of sample with BT, DBT and 4, 6 DMDBT before oxidation process

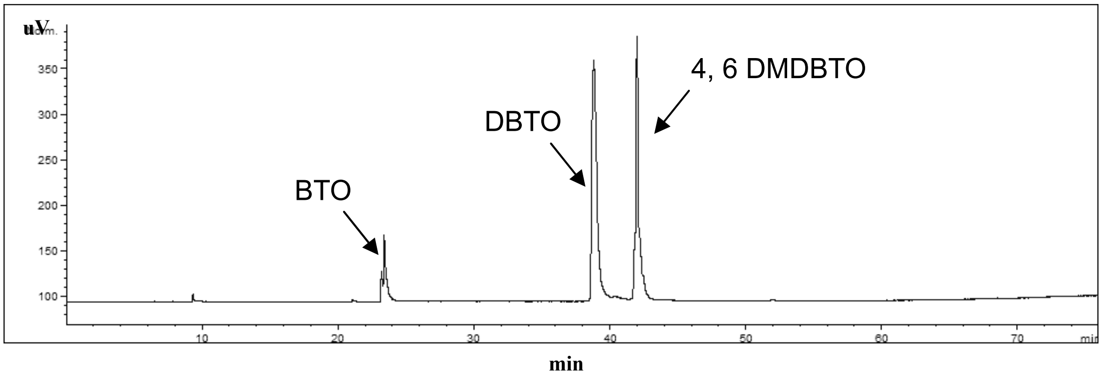


Figure 5.6 GC-SCD chromatogram of sample with BT, DBT and 4, 6 DMDBT after oxidation process

To determine the possible oxidation of sulfones, oxidation studies were conducted for BTO and DBTO separately. The chromatograms BTO and DBTO before and after the oxidation process are shown in Figure 5.7 through Figure 5.10.

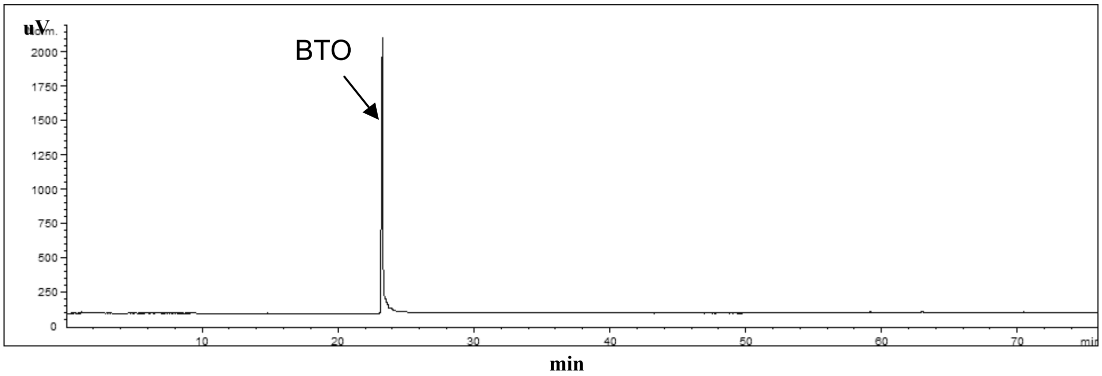


Figure 5.7 GC-SCD chromatogram of sample with BTO before oxidation process

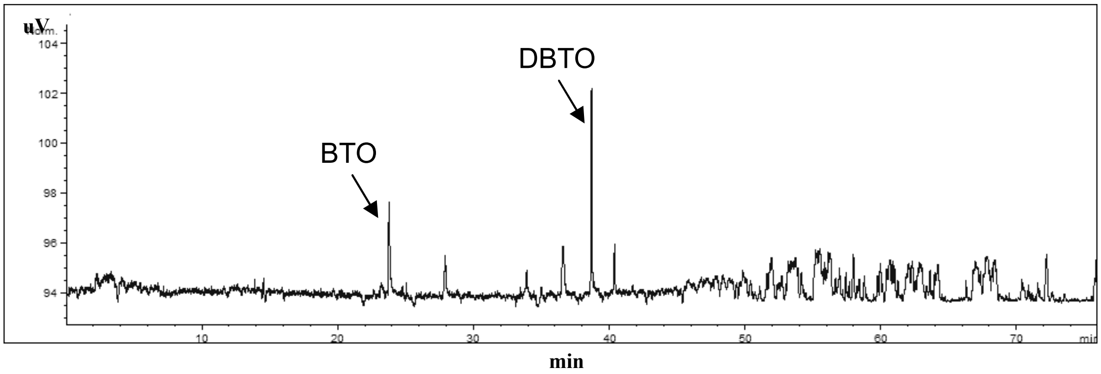


Figure 5.8 GC-SCD chromatogram of sample with BTO after oxidation process

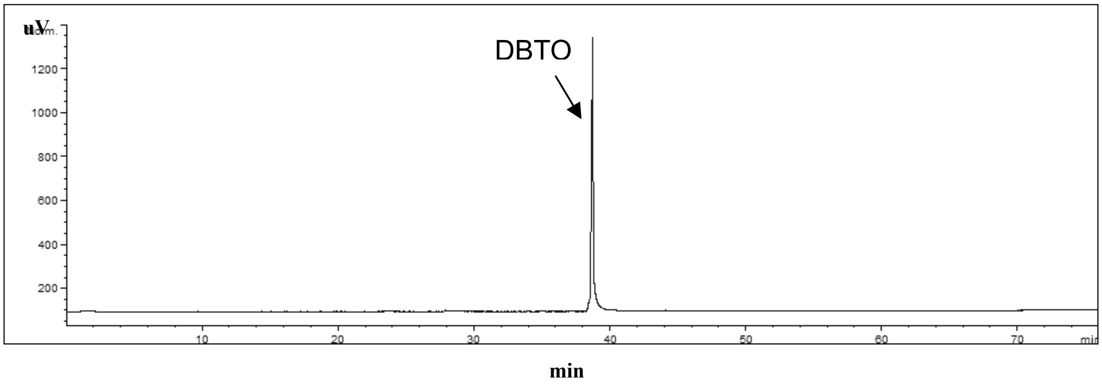


Figure 5.9 GC-SCD chromatogram of sample with DBTO before oxidation process

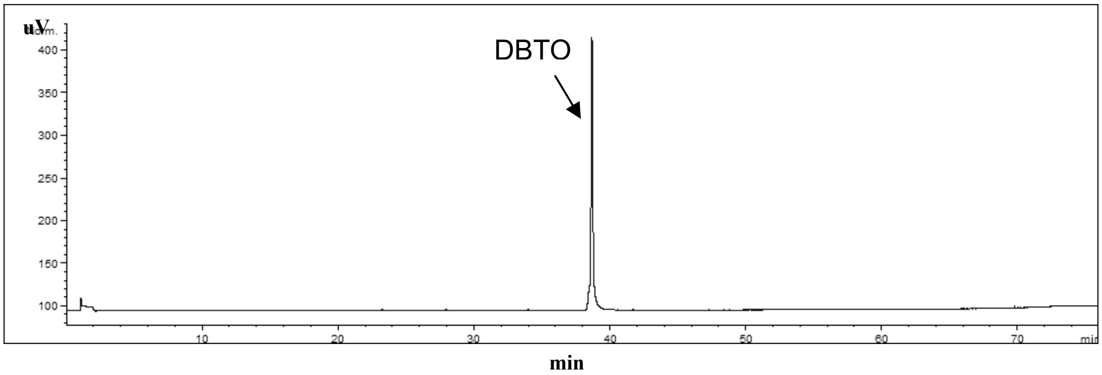


Figure 5.10 GC-SCD chromatogram of sample with DBTO after oxidation process

Figure 5.8 shows that the BTO peak was significantly reduced after oxidation. Furthermore, the chromatogram shows the presence of other organic sulfur compounds. The major peak was identified as DBTO. Some other smaller peaks could be alkyl benzothiophenes, alkyl dibenzothiophenes, or other higher molecular weight OSCs.

It was also observed that the peak intensity of DBTO after oxidation (Figure 5.10) is much lower compared to that before oxidation (Figure 5.9). However, the total sulfur content measured by the Sulfur-in-Oil Analyser did not show significant change. Therefore, each sample was extracted with water and precipitated with barium chloride. The total sulfur concentration of each sample was measure before and after water extraction. The results indicate that the total sulfur concentration for BTO was reduced from 983 ppm_w to 129 ppm_w (87%) and for DBTO from 1080 ppm_w to 393 ppm_w (64%). It can thus be postulated that the oxidation process bas relatively less impact on DBTO than BTO.

As suggested by Oae et al. (1981), Chang et al. (1989), Afanas'ev (1989) and Kim et al. (1990), superoxides could oxidize organic sulfur compounds to sulfonic acids, amides, and also inorganic sulfate. Figure 5.11 illustrates some of the chemical reactions between OSCs and superoxide suggested by Afanas'ev (1989).

In either the UAOD system or the modified UAOD system, OSCs are stoichiometrically converted to sulfones as the final oxidized products. However, in this study, 13% of BT and 36% of DBT were converted to correcponding sulfones, and the rest (87% and 64%, respectively) were converted to sulfate which can be extracted by DW.

Oxidation of Thiols

$$2RSH + 3O_2^{-\cdot} \rightarrow RSO_2^- + RSO_3^- + H_2O$$

Oxidation of Disulfides

$$2RSSR' + 5O_2^{-\cdot} \rightarrow 2RSO_2^- + 2R'SO_3^-$$

Oxidation of N-(2-hydroxy-phenyl)-N-Phenylthioureas

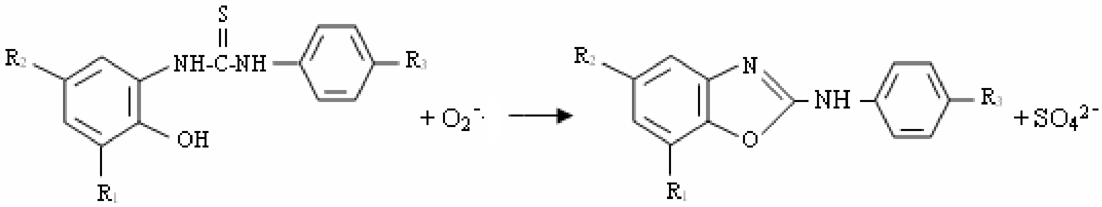


Figure 5.11 Chemical reactions between OSCs and superoxide anion (Afanas'ev, 1989)

5.4.2 Characterization of Untreated Diesel Samples

As discussed in Chapter 5.3.4 and Chapter 5.4.1, some of the model sulfur compounds and their retention times were identified by GC-SCD analysis or estimated through linear regression. The calculated retention time listed on Table 5.1 and Table 5.2 were used to predict the possible species of unknown organic sulfur compounds presented in the samples. This is especially important to identify the refractory compounds in the oxidative desulfurization process with the application of superoxide. Those compounds are some of the most common OSCs found in diesel and other petroleum fuel oil. By identifying the retention times of different OSCs in the fuel samples through GC-SCD analysis, it is possible to characterize the sulfur content in the samples.

Figure 5.12 shows the GC-SCD chromatogram of various model sulfur compounds including thiophene, 2-methyl thiophene, benzothiophene, benzothiophene sulfone, dibenzothiophene, 4, 6-dimethyl dibenzothiophene and dibenzothiophene sulfone. From the chromatograph, the retention times of different OSCs are listed as follow: T at 1.06 minutes, 2MT at 2.26 minutes, BT at 8.89 minutes, BTO at 23.31 minutes, DBT at 28.08 minutes, 4,6-DMDBT at 34.01 minutes, and DBTO at 38.92 minutes.

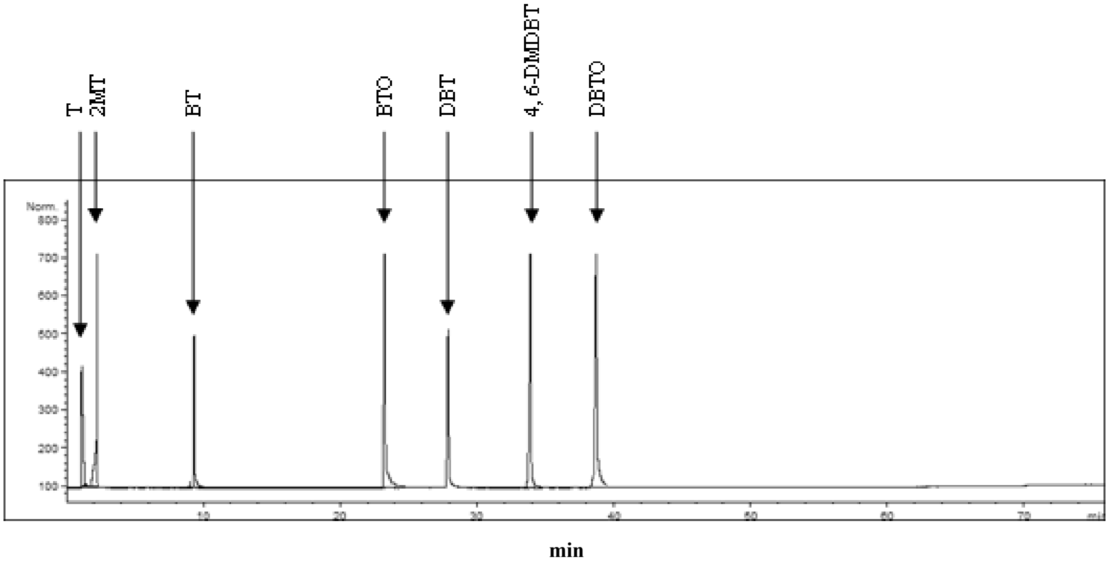


Figure 5.12 GC-SCD chromatogram of various model sulfur compounds

The OSCs compositions of different diesel fuels, including JP-8, MGO and sour diesel were separated, as illustrated in the GC-SCD chromatograms (Figure 5.13). As discussed in Chapter 1, the OSCs in diesel samples are primarily comprised of cyclic sulfide derivates, thiophene derivates, benzothiophene derivates and dibenzothiophene derivates. The OSCs constituents shown in these chromatograms may be identified with reference to Tables 5.1 and 5.2.

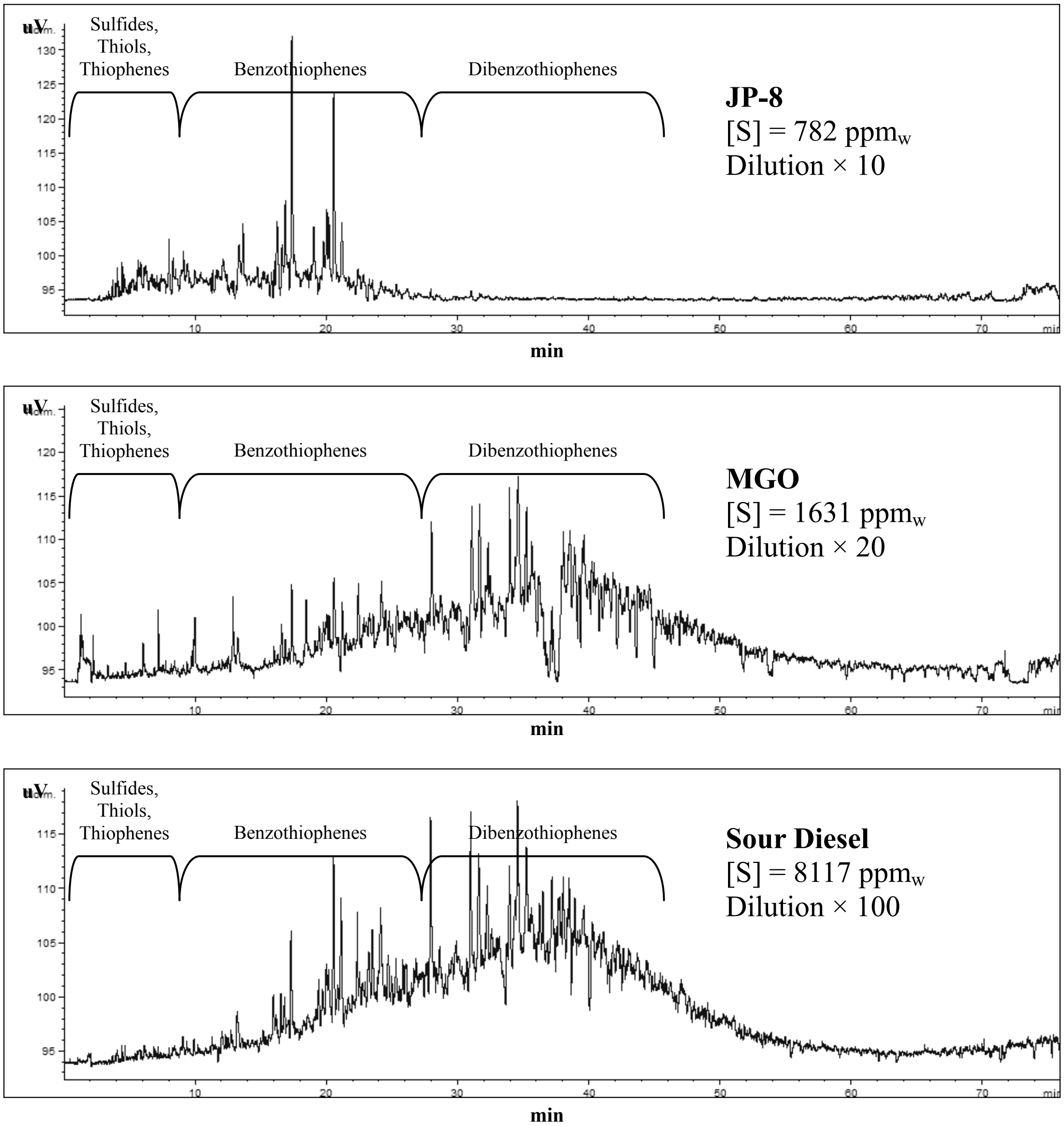


Figure 5.13 GC-SCD chromatogram of various diesel samples

It can be observed in Figure 5.13, JP-8 contains mainly BT and its derivates, together with a small fraction of sulfides, thiols and thiophenes; MGO contains mainly DBTs, some BTs, and a small fraction of sulfides, thiols and thiophenes; and sour diesel contains mainly DBTs and some BTs.

5.4.3 Characterization of Desulfurized Diesel Samples

Oxidative desulfurization with the application of potassium superoxide was applied to each of the diesel sample including JP-8, MGO and sour diesel as stated in Chapter 5.3.2. The sulfur to oxidant ratios applied for JP-8, MGO, and sour diesel were 1:29, 1:14 and 1:2.7 respectively.

To prevent damaging the GC-SCD by acids, salts and other ions, the samples were washed with DW after oxidation, so as to remove ions and other water soluble compounds from the sample. The samples were then injected into the GC-SCD to determine the change in sulfur species composition after oxidation. The oxidized diesel samples were extracted with acetonitrile to remove sulfone formed. The extracted diesel samples were injected into the GC-SCD again to show the remaining sulfur species.

The GC-SCD chromatograms for JP-8, MGO and sour diesel at different stages are illustrated in Figures 5.14, 5.15 and 5.16, respectively. Total sulfur contents in each stage were measured by the Sulfur-in-Oil Analyser, as recorded in Table 5.3.

Table 5.3 Total sulfur content for various diesel samples in different stages

	Original	**After Oxidation**		**After Washing (with DW)**		**After Extraction (with acetonitrile)**	
	[S], ppm_w	[S], ppm_w	Δ[S], %*	[S], ppm_w	Δ[S], %*	[S], ppm_w	Δ[S], %*
JP-8	782	724	7.4	358	54.2	< 20	> 98
MGO	1631	1547	5.1	1252	23.2	28	98.3
Sour Diesel	8117	7869	3.1	7166	6.8	554	93.2

* Δ[S] represents percentage change in sulfur content

As can be seen in Table 5.3, the total sulfur content in all three diesel samples were significantly reduced by washing with DW after oxidation. This indicates the formation of water soluble sulfur compounds after oxidation. Among the three diesel fuels, JP-8 exhibited the highest removal of sulfur content, while sour diesel showed the lowest. There are two possible reasons for this result. The applied oxidant to sulfur ratio for JP-8 was the highest, thus further oxidation would have been possible. Furthermore, it was demonstrated in the model sulfur compound studies that higher percentage of BT can be oxidized to sulfone as compared with DBT under identical treatment conditions. The sulfur contents in JP-8 are mostly BT derivatives, while in sour diesel there are mostly DBT derivatives and thus more water soluble sulfur compounds (sulfate) could be formed from JP-8. Thus, higher degree of sulfur removal can be achieved by washing the oxidized JP-8.

As illustrated in the GC-SCD chromatogram (Figure 5.14-a), the major OSCs in original JP-8 are benzothiophene derivates (C1BT to C4BT) such as 3-methyl benzothiophene and 3, 5-dimethyl benzothiophene, together with sulfides, thiols, and thiophenes derivates. As observed in Figure 5.14-b, the chromatogram peaks for oxidized JP-8 are shifted to the right showing that OSCs are oxidized to molecules with longer retention time, which are expected to be the corresponding sulfones of the original OSCs.

Two major peaks can be seen in the chromatogram of extracted JP-8. They are identified as DBT and 4, 6DMDBT. In the chromatogram of untreated JP-8 (Figure 5.14-a), these two peaks were practically non-existent, however, it seems that these two compounds are formed during the oxidation process (Figure 5.14-b), and are not removed during the extraction process.

In our studies, ultralow sulfur diesel can be produced from JP-8 by a single desulfurization process with the application of superoxide. A further polished product, theoretically "zero sulfur" diesel, could possibly be achieved by a post treatment. Due to the fact that the amount of ionic liquid applied is less than the optimal condition (Table 3.17), the desulfurization efficiency could be further improved by simply increasing the dosage of ionic liquid.

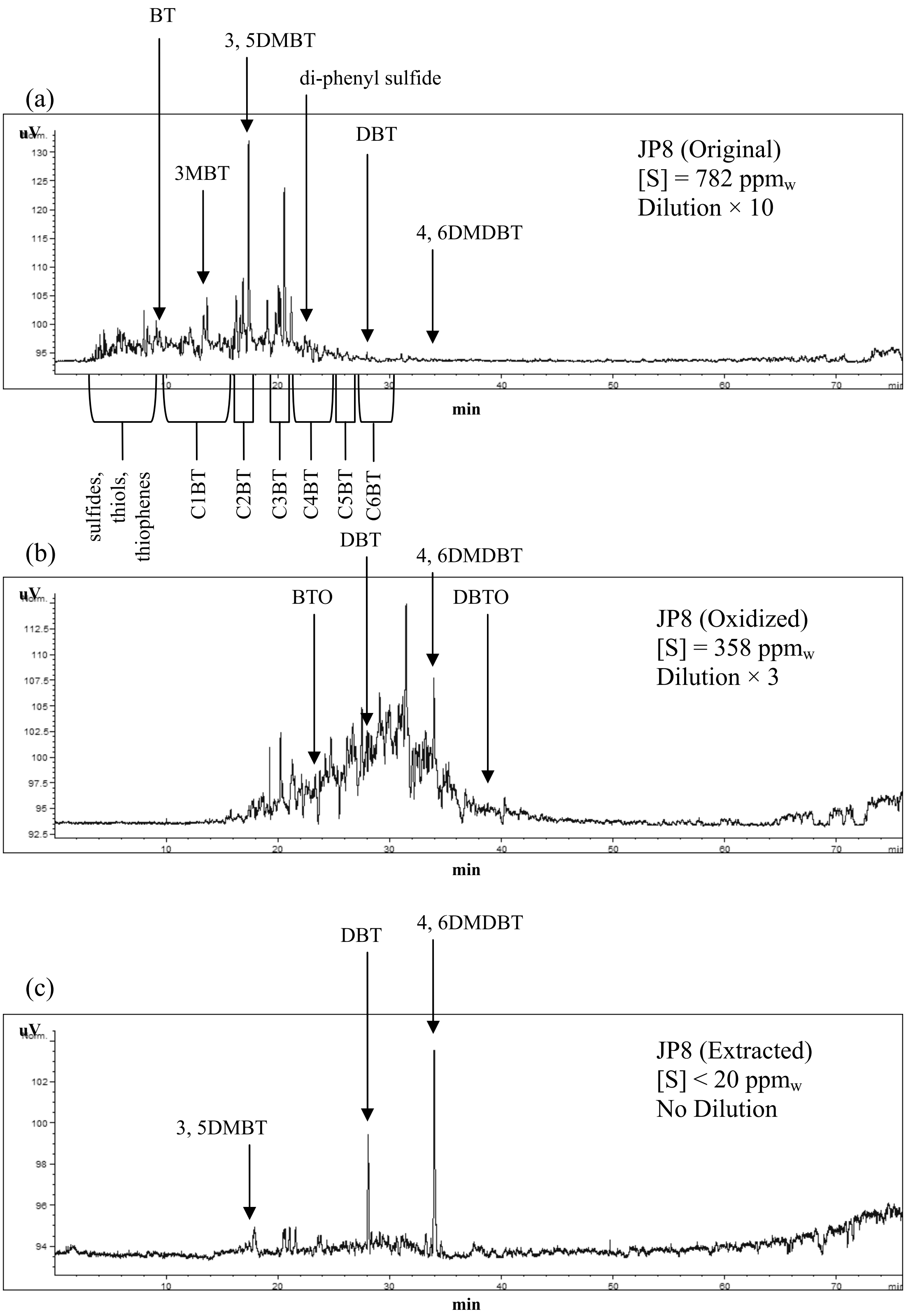


Figure 5.14 GC-SCD chromatogram of JP-8 at different stages of the process

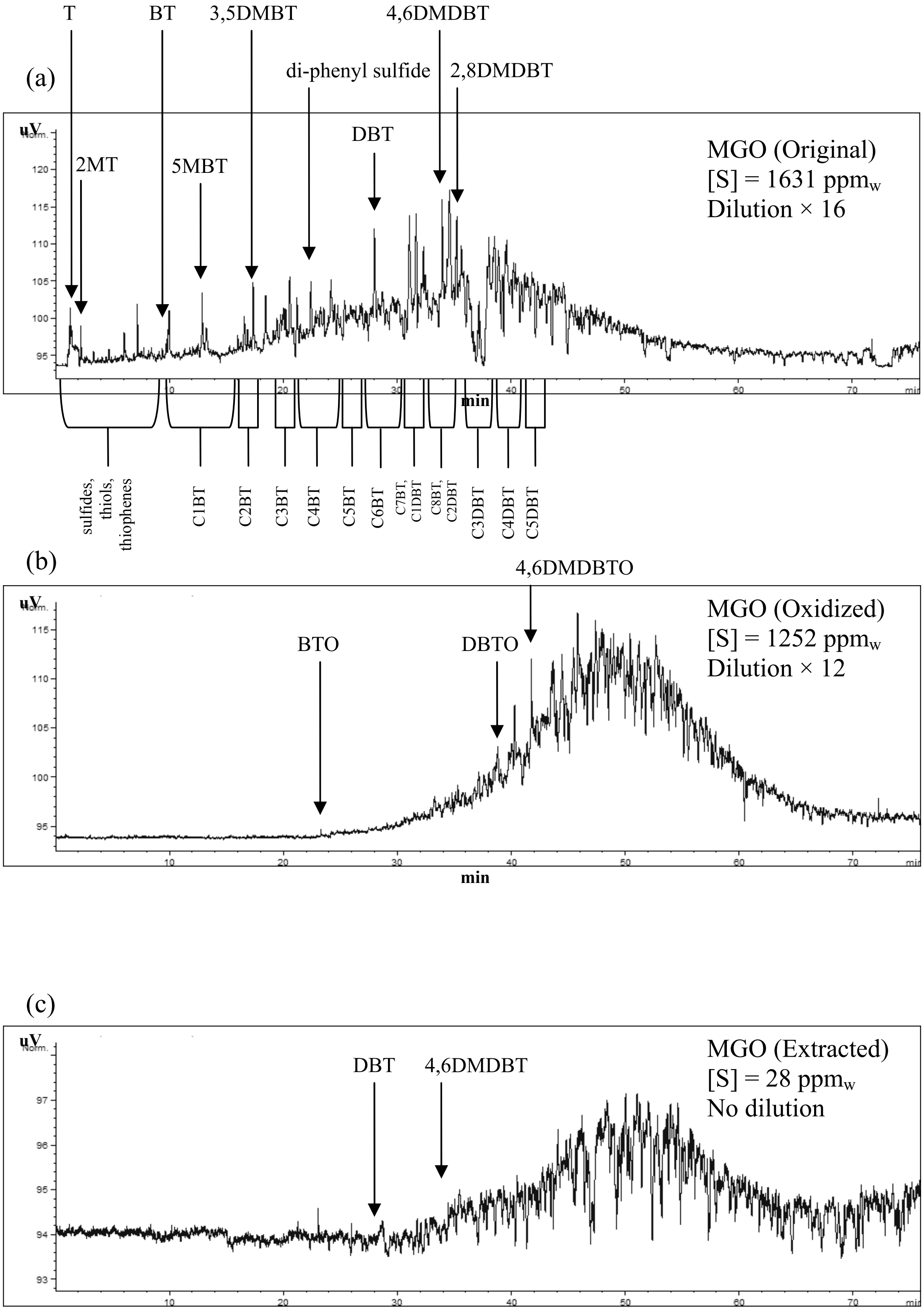


Figure 5.15 GC-SCD chromatogram of MGO at different stages of the process

MGO contains a variety of sulfur species, from thiophenes to dibenzothiophene derivates, as illustrated in its GC-SCD chromatogram shown in Figure 5.15-a. The majority of OSCs in original MGO are dibenzothiophene derivates (C1DBT to C5DBT), together with benzothiophene derivates (C1BT to C8BT).

The peaks of the chromatogram for oxidized MGO (Figure 5.15-b) are shifted to the right showing that OSCs are oxidized to molecules with longer retention time, and are expected to be the corresponding sulfones of the original OSCs. However, the peaks' intensities of the smaller sulfones, such as thiophene sulfone and benzothiophene sulfones, are much lower than expected. This observation concurs with the chromatograms in the model sulfur compound studies and the JP-8 diesel study shown in Figure 5.6 and Figure 5.14-b, respectively, can be hypothesized that smaller OSCs such as thiophenes and benzothiophenes can be oxidized to inorganic sulfur compounds such as sulfate ion, which can simply be removed by washing with water.

It is observed that the sulfur species remaining the extracted MGO (Figure 5.15-c) are mainly substituted DBT derivates. The total sulfur content in the extracted MGO is 28 ppm_w (Figure 5.15-c). Although this amount is higher than the ULSD requirement, the desulfurization efficiency can be improved by increasing ionic liquid dosage, as demonstrated in Chapter 3, Section 3.3.4, so as to achieve the ULSD standard.

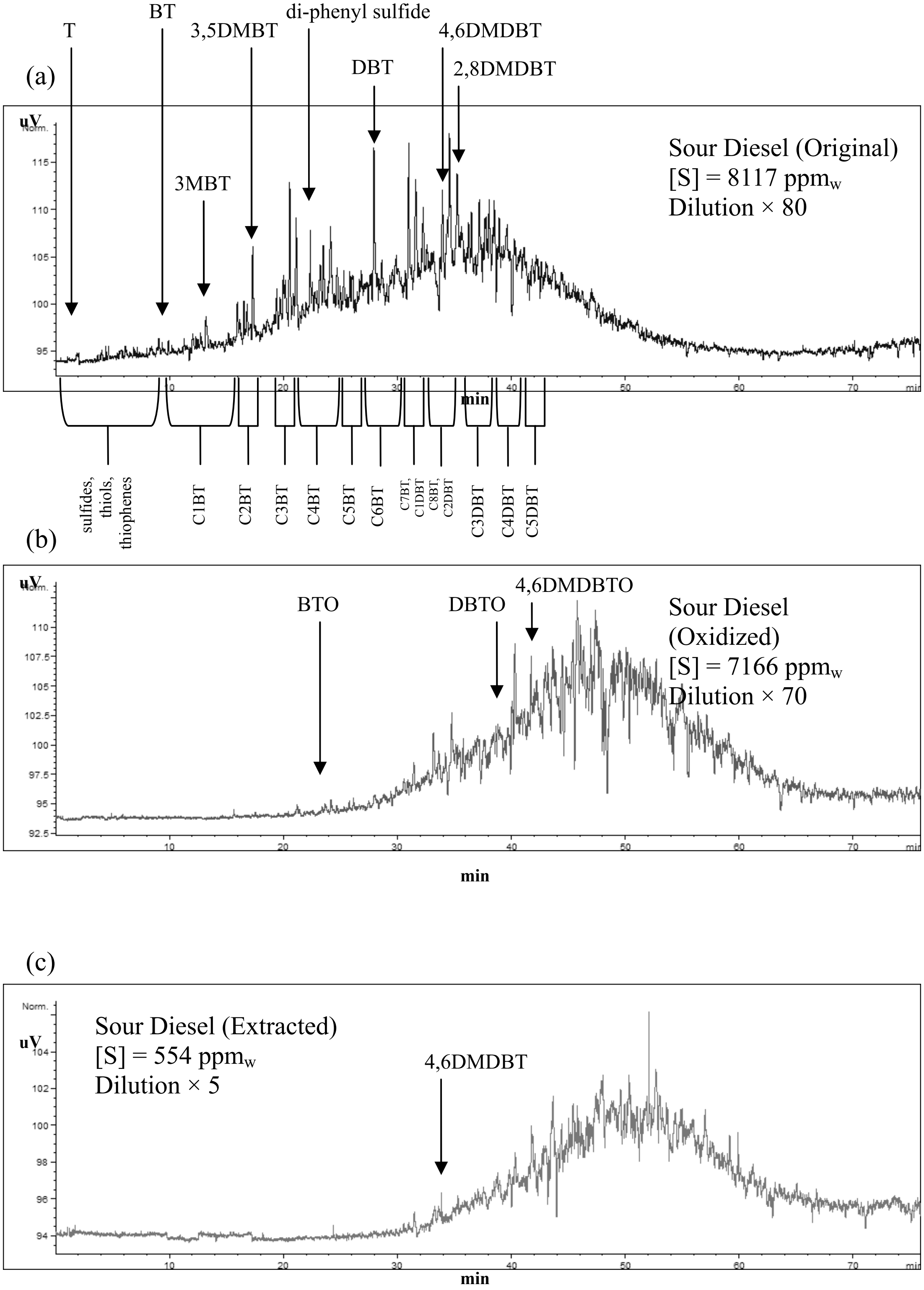


Figure 5.16 GC-SCD chromatogram of sour diesel at different stages of the process

Similar to MGO, sour diesel contains a variety of sulfur species as shown in Figure 5.16-a. Sour diesel contains mainly dibenzothiophene derivates (C1DBT to C5DBT), together with highly substituted benzothiophene derivates (C3BT to C8BT). Only trace amount of straight chain sulfides, thiols or thiophenes can be found in the sour diesel sample.

For the oxidized sour diesel, peaks of its chromatogram shifted to the right (Figure 5.16-b). It shows that OSCs are oxidized to the corresponding sulfones. The chromatogram peaks' intensities of sulfones in the oxidized sample are similar to those of the original sulfur compounds in the untreated sample. As listed in Table 5.3, only 7% of the sulfur content in the oxidized sour diesel can be removed by washing with DW. This is possibly due to the fact that the oxidant to sulfur ratio applied was too low and as a result further oxidation of sulfones yielded insignificant amount of sulfate.

The final sulfur content in the primary treated sour diesel was 554 ppm_w. As observed in the chromatogram (Figure 5.17-a), the remaining sulfur contents are presumably highly substituted DBT and other larger sulfur compounds. A secondary treatment with same the procedure (oxidation followed by extraction) was applied to the treated sour diesel to remove the remaining sulfur compounds. The chromatograms of sour diesel at different stages of the secondary treatment are illustrated in Figures 5.17-a to 5.17-c.

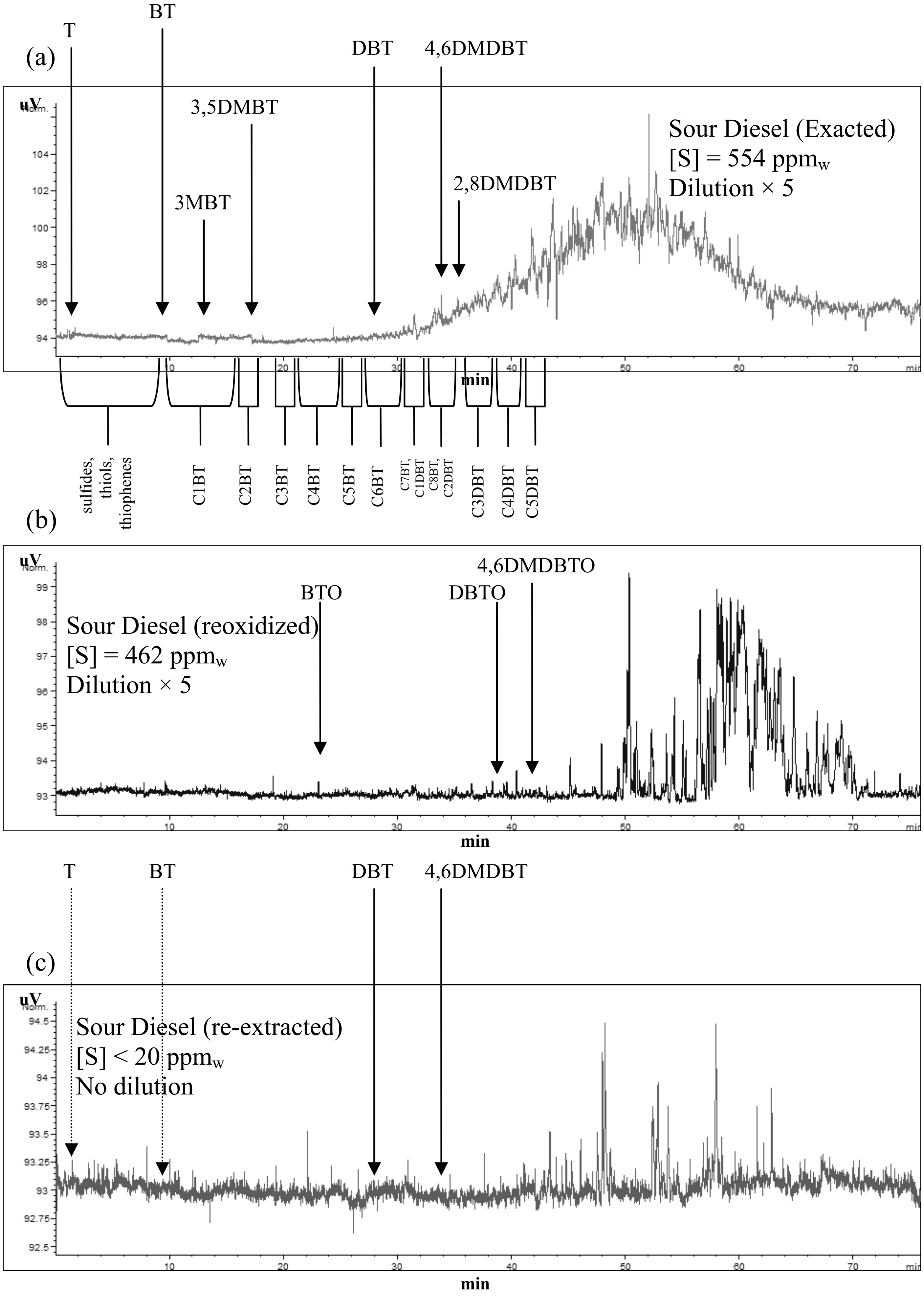


Figure 5.17 GC-SCD chromatogram of treated sour diesel at different stages of the process

As illustrated in Figures 5.17-a and 5.17-b, the chromatogram peaks shift to the right after the reoxidation process. It shows that the highly substituted DBTs remaining in the primary treated sour diesel can be oxidized to the corresponding sulfones in the secondary treatment process as shown in Figure 5.17-c. The sulfur content of the secondary treated sour diesel can be lowered to less than 20 ppm_w. Thus, two consecutive treatments of the oxidative desulfurization process with the application of KO_2 as oxidant can result end product which would be in compliance with ULSD.

From the chromatogram in Figure 5.17-c, it can be seen that there are several OSCs remaining the secondary treated sour diesel. These OSCs are possibly highly substituted DBTs (C2DBT or above). Further treatment may be required to produce “zero sulfur” diesel.

The chromatogram peaks’ intensities of sulfones in the oxidized sour diesel sample (Figure 5.16-b) are similar to those of the original sample (Figure 5.16-a). As listed in Table 5.3, only 6.8% of the sulfur content in the oxidized sour diesel can be removed by washing with DW. This is possibly because of low oxidant to sulfur ratio which caused further oxidation of sulfones to sulfate insignificant. Besides, further oxidation of highly substituted highly substituted OSCs may prove difficult due to their steric hindrance effect (Kimintarachat et al., 2006).

5.4.4 Characterization of Heavy-Distillates

Generally speaking, the major sulfur species in heavy-distillate are alkyl benzothiophene derivates, dibenzothiophene derivatives, benzonaphtho-thiophene derivatives and phenanthro-thiophene derivatives. Having GC-SCD chromatograms, some of the OSCs in the two heavy distillate samples, RO-6 and IFO, could be identified with reference to Table 5.1 and Table 5.2.

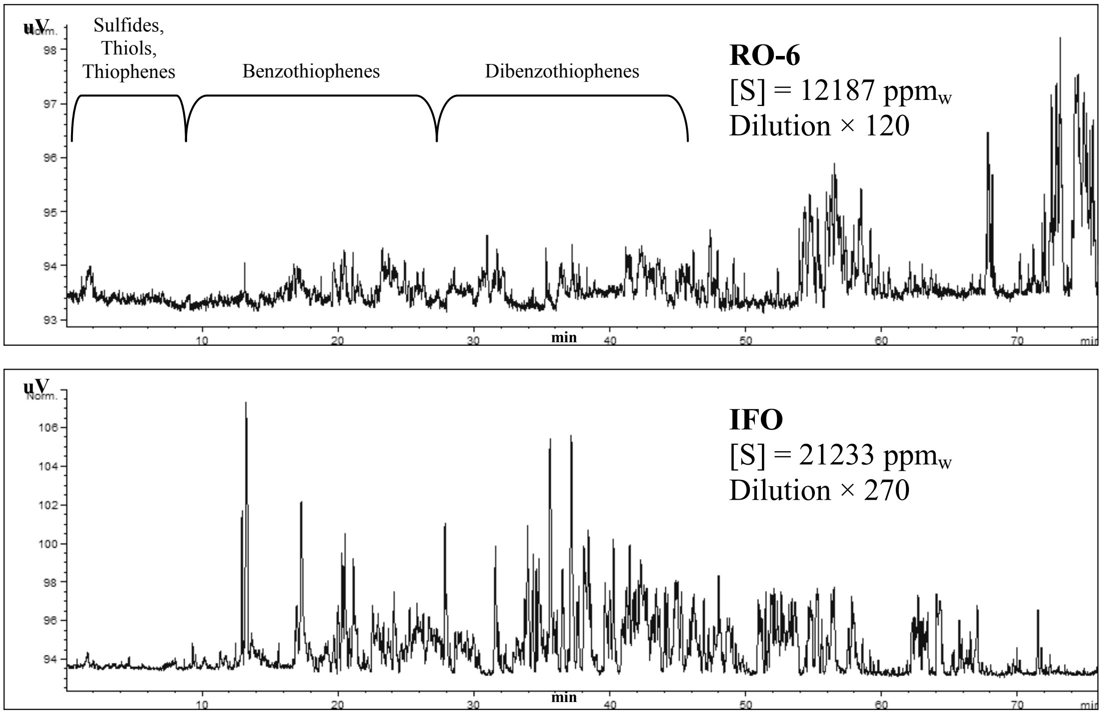


Figure 5.18 GC-SCD chromatograms of two untreated heavy distillates

According to the chromatograms of the untreated RO-6 and IFO illustrated in Figure 5.18, significant portion of the peaks having larger retention time than Ts, BTs and DBTs. Having longer retention time, these peaks are possibly highly substituted DBTs (C5DBT) or sulfur containing polycyclic aromatic hydrocarbons (PAHs) such as benzonaphtho-thiophene derivatives and phenanthro-thiophene derivatives as demonstrated in a microcoulometric sulfur detector (MCD) chromatogram shown in Figure 5.19.

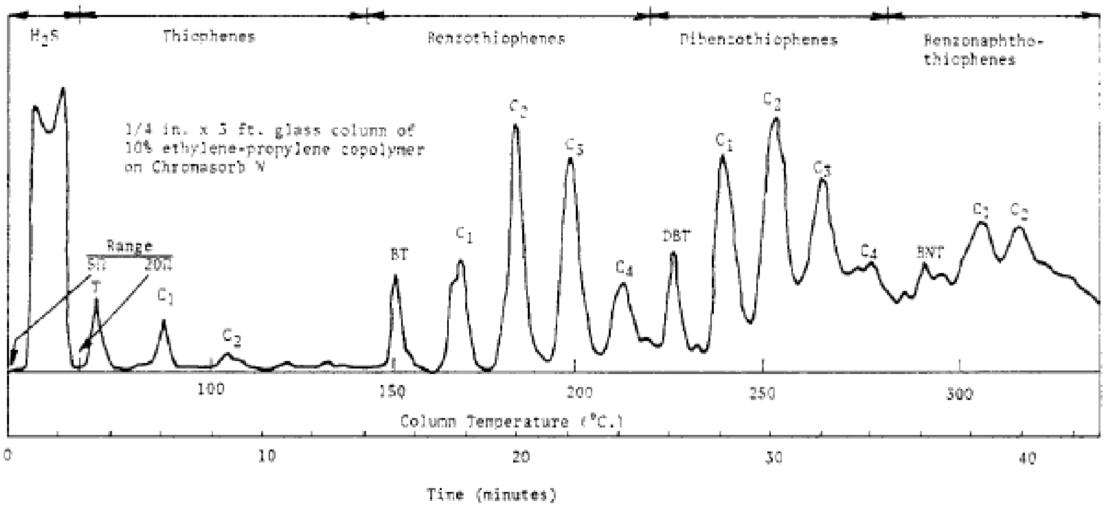


Figure 5.19 Typical GC-MCD chromatogram of vacuum gas oil (Drushel, 1969)

The oxidative desulfurization process with the application of KO_2 was applied to RO-6 and IFO with sulfur to oxidant ratios at 1:2.6. The GC-SCD chromatograms for RO-6 and IFO are illustrated in Figure 5.20 and Figure 5.21, respectively.

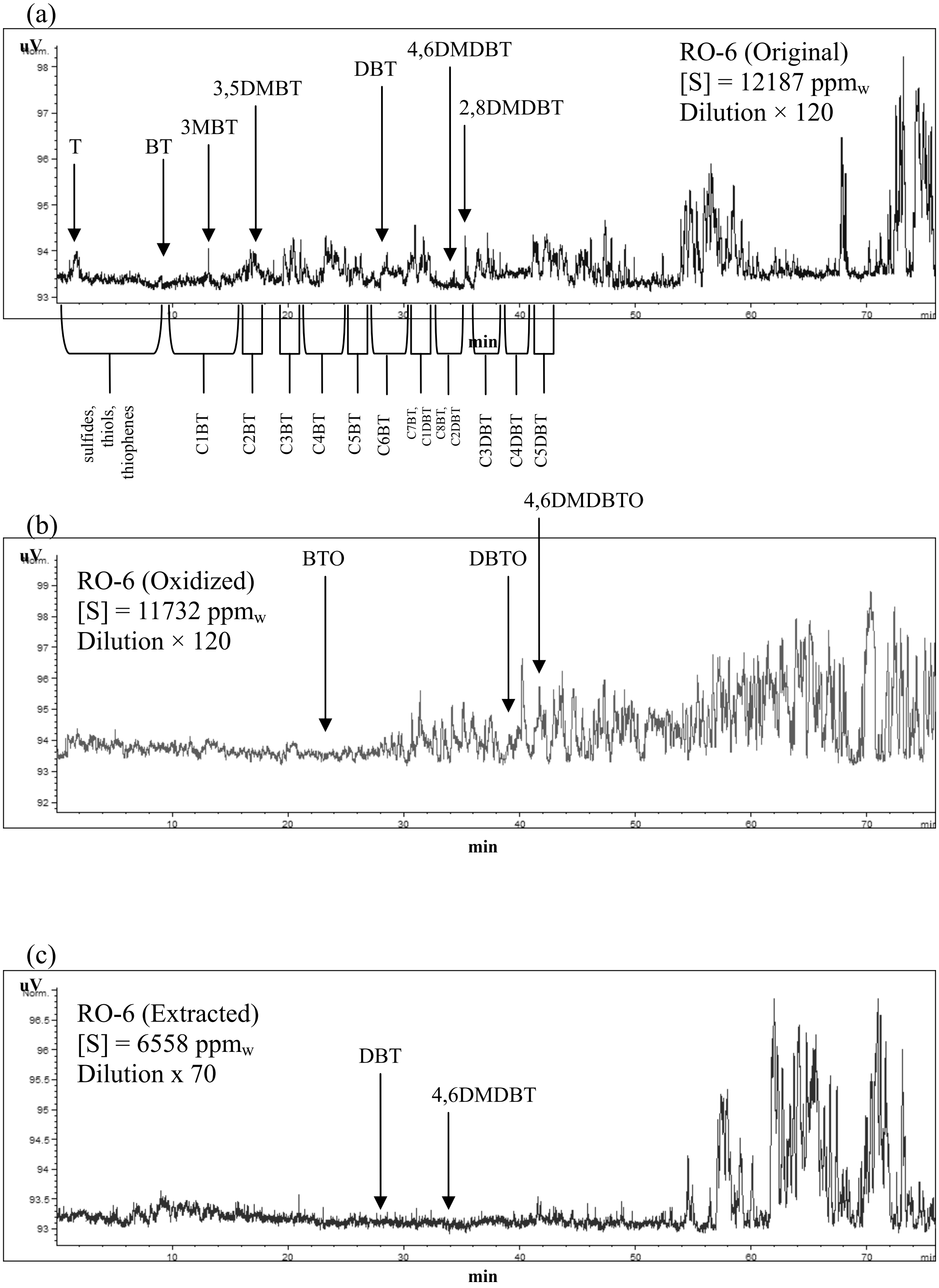


Figure 5.20 GC-SCD chromatogram of treated RO-6 at different stages of the process

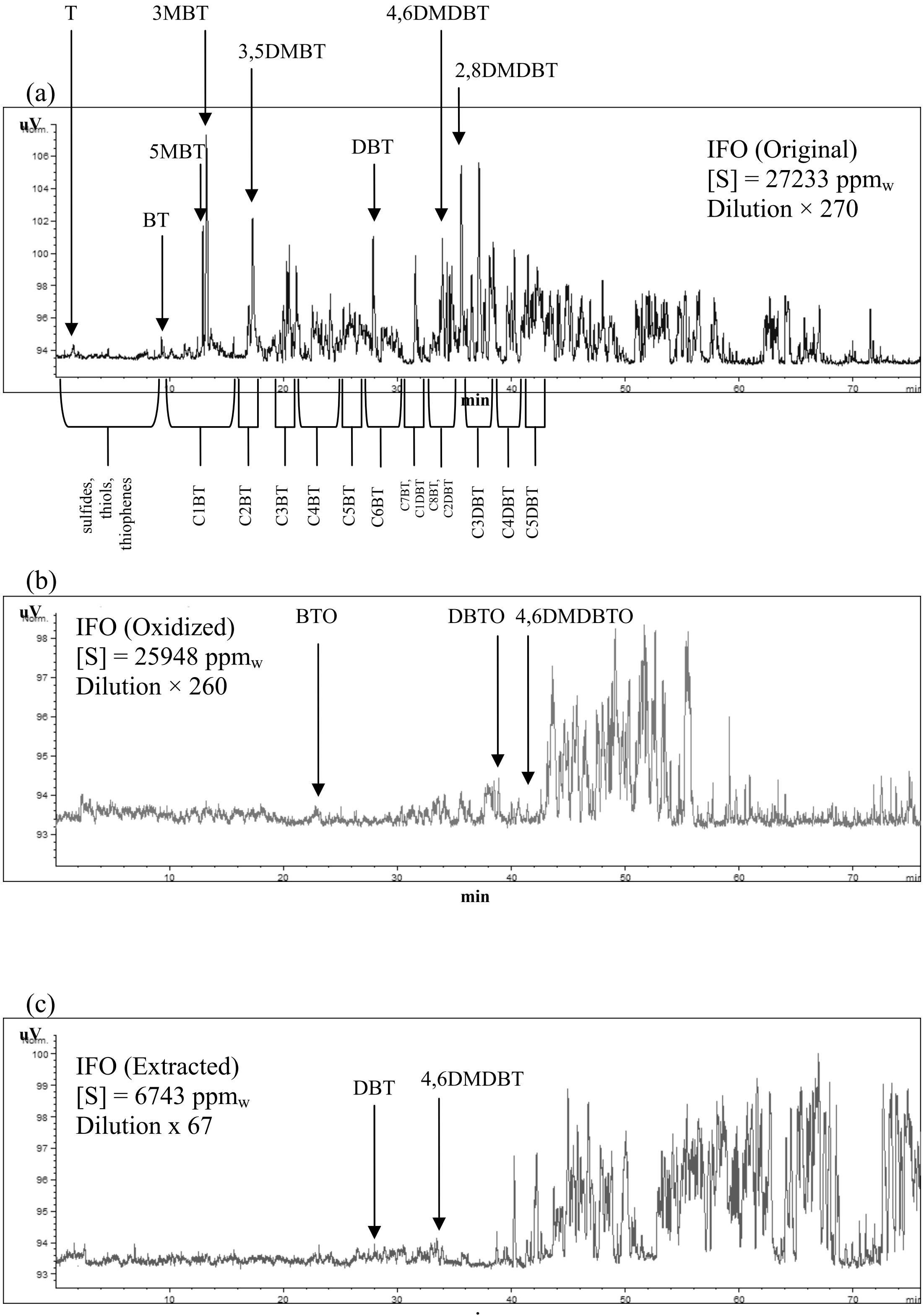


Figure 5.21 GC-SCD chromatogram of treated IFO at different stages of the process

As illustrated in Figure 5.20-a, the major OSCs in untreated RO-6 are highly substituted DBTs (C6DBT) or sulfur containing PAHs. It also contains smaller sulfur compounds including Ts, BTs, and DBTs. As can be seen, upon oxidation (Figure 5.20-b) and extraction (Figure 5.20-c), most of the peaks for the smaller OSCs are removed. However, majority of the larger OSCs remain in the sample as demonstrated in the chromatograms. Some of these compounds could be refractory which cannot be oxidized or extracted.

Compared with RO-6, IFO contains a larger portion of benzothiophenes and dibenzothiophenes derivatives. These OSCs are removed upon oxidation and extraction. However, the remaining portions are not susceptible to oxidation.

As can be seen in Figures 5.20 and 5.21, the sulfur contents in the treated samples are mainly larger OSCs such as C5DBT, benzonaphtho-thiophene derivatives and phenanthro-thiophene derivatives. RO-6 appears more difficult to desulfurize due to high content of these compounds. As discussed in Chapter 4, RO-6 can be desulfurized by approximately 50%, while IFO can be desulfurized up to 80%. Comparatively, sour diesel can be desulfurized by more than 95% with the same oxidant to sulfur ratio. Besides the difference in original sulfur species in the samples, other properties such as viscosity and presence of inhibitors in heavy distillates could also reduce the process efficiency.

Asphaltene content in heavy distillates could be one of the major factors affecting the desulfurization efficiency. Asphaltenes are considered as radical inhibitors by terminating free radical reactions through recombination and disproportionation (Bukowski et al., 1983). Asphaltenes can also suppress radical chain formation and the catalytic decomposition of organic sulfur compounds by peroxides and hydroperoxides (Herrington, 2004).

Upon oxidation, asphaltene could be converted to carboids (Yen, 1974). This could lead to asphaltene precipitation, flocculation and agglomeration (Margaril et al., 1971; Wattana et al, 2005). Thus, oil samples could show incompatibility towards refinery process involving oxidation (Speight, 2004).

5.5 Mechanism of Inorganic Sulfate Formation

As discussed in Chapter 4, third generation of UAOD process cannot treat heavy distillates due to heavy precipitation and agglomeration of asphaltenes during the treatment process. By utilizing superoxide in the modified UAOD process, asphaltenes precipitation can be greatly reduced. Formation of carboids is still observed (carboids are toluene insoluble portion). This could be another reason for the low desulfurization efficiency of heavy distillates.

Similar to the studies for the model compounds and the diesel samples, chromatogram peaks of benzothiophene derivatives and some of the dibenzothiophene derivatives are significantly reduced after oxidation. It is predicted that benzothiophene and dibenzothiophene derivatives could possibly be further oxidized or reacted forming other compounds.

One of the possible mechanisms for the disappearance of BT and DBT is further oxidation of the oxidized products. A few studies demonstrate that BT and DBT can be oxidized to the corresponding sulfones, and the sulfones can be oxidized to sulfonic acids, sulfites and sulfates through radical reactions initiated by hydroxyl radicals or photolysis (Andersson et al., 1992; Kim et al., 2003; Shiraishi et al., 2003). The oxidation mechanism for BTO and DBTO are illustrated in Figure 5.22 and Figure 5.23, respectively. By employing the superoxide radial in the modified UAOD process, decomposition of BT and DBT derivatives could follow a similar radical reaction as described above.

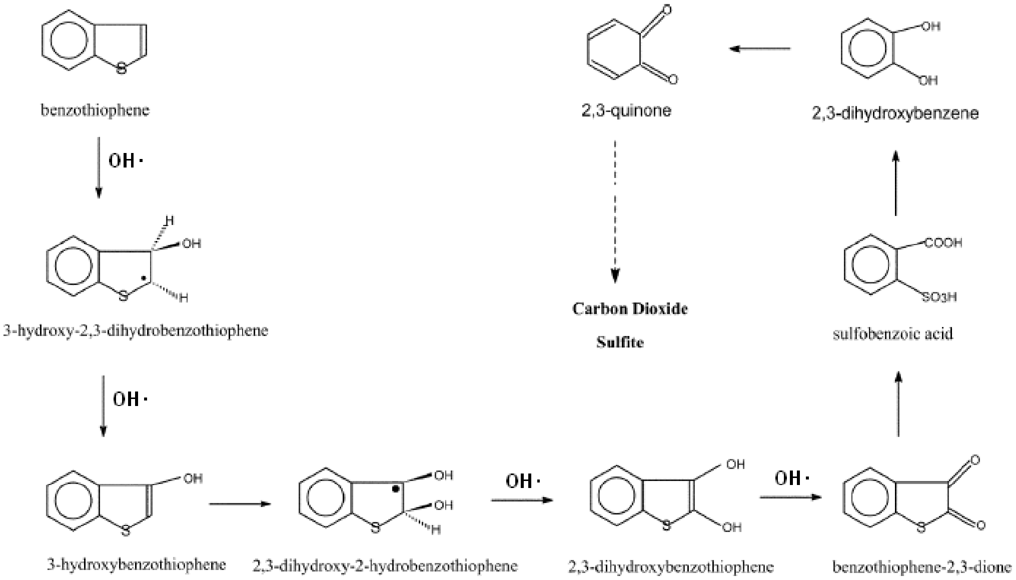


Figure 5.22 Possible BT destruction pathways by OH radicals (Kim et al., 2003)

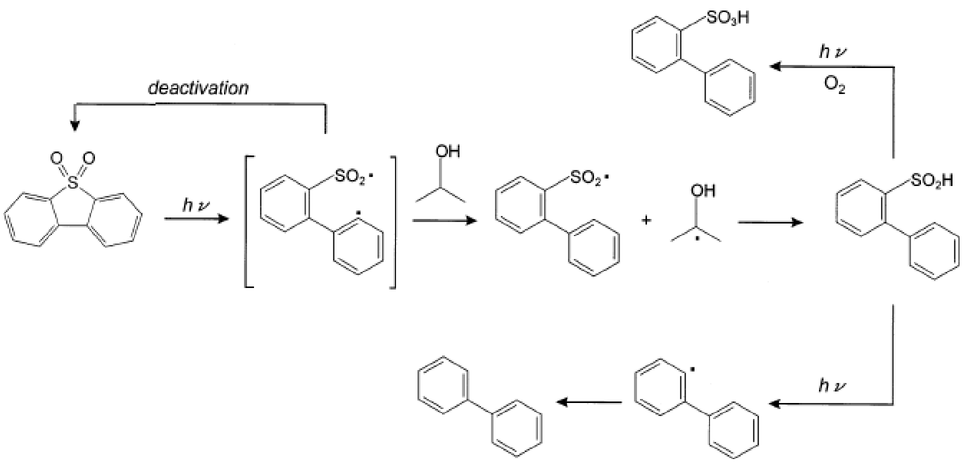


Figure 5.23 Photolysis of DBTO (Shiraishi et al., 2003)

5.6 Summary and Conclusion

With the aid of Gas Chromatography equipped with sulfur chemiluminescence detector, this study aimed as fingerprinting organic sulfur compounds in different fuel samples and also the oxidation products by the modified UAOD process with the application of superoxide. This information could provide a better understanding of the OSCs oxidation pathway, so as to predict the mechanism of the treatment process. Using GC-SCD to characterize sulfur species in oil sample is one of the standard test methods approved by ASTM.

In the model sulfur compounds studies, it was demonstrated that the modified UAOD process with superoxides can oxidize different organic sulfur compounds, including benzothiophene, dibenzothiophene and 4, 6 dimethyldibenzothiophene, to the corresponding sulfones. It was further demonstrated that the resulting water soluble inorganic sulfur compounds can be extracted and removed.

Two sulfone model compounds, benzothiophene sulfone and dibenzothiophene sulfone, were used to determine the oxidation by-product by the modified UAOD process with the application of superoxide. In the oxidation of benzothiophene sulfone, dibenzothiophene sulfone was recognized as a major by-product. The chromatogram shows several unidentifiable small peaks. Similarly, investigation of oxidation by-product was conducted on dibenzothiophene sulfone. It appears that dibenzothiophene sulfone was partially oxidized to form inorganic sulfate.

Three diesel samples, namely JP-8, MGO and sour diesel, were used in the diesel fuel studies. From the GC-SCD chromatograms, it was found out that JP-8 contains mainly benzothiophene derivatives, while MGO and sour diesel contain mainly dibenzothiophene derivatives. In all three cases, benzothiophene derivatives were mostly removed by the modified UAOD process with superoxide. Less than 28 ppm_w of dibenzothiophene derivatives were found in desulfurized JP-8 and desulfurized MGO. Depending upon the selection of ionic liquids and oxidant dosage, both JP-9 and MGO were desulfurized to ultralow sulfur diesel standard.

It was demonstrated that with the application of relatively low oxidant to sulfur ratio, sour diesel was desulfurized to 554 ppm_w. The remaining sulfur content was mostly dibenzothiophene derivatives. Further oxidation and extraction (secondary treatment) of the sour diesel lowered the sulfur content to less than 20 ppm_w. Only trace amounts of alkyl substituted dibenzothiophene derivatives remained in the sample.

RO-6 and IFO were used as the heavy-distillate samples in this study. Results indicated that the major components of heavy-distillates (RO-6 and IFO), mainly dibenzothiophene derivatives (C5DBT), benzonaphtho-thiophene derivatives and phenanthro-thiophene derivatives, were not removed in the treatment process. However, the process effectively removed benzothiophenes and lighter dibenzothiophenes (C1DBT to C4DBT).

Increasing superoxide dosage could be possible to increase desulfurization efficiencies of heavy distillates. However, high dosage of oxidant could affect the stability of asphaltene colloidal system causing heavy deposition. Further experiments are required to examine the optimal conditions to desulfurize heavy distillates. More sulfur markers are required to fingerprint the unidentified compounds.

It was demonstrated that sulfones of benzothiophenes and sulfones of dibenzothiophenes could be further oxidized to different compounds including sulfur-containing inorganic compounds such as sulfates and sulfites. Further studies using ion chromatography can quantitate sulfates and sulfites and other sulfur-containing ions.

In general, due to the formation of sulfonic acid, sulfites and sulfates, the sample's sulfur content can be removed by water extraction. This could reduce the use of chemical solvents such as acetonitrile or adsorbent such as alumina. Further studies should be conducted to identify the intermediate products to verify the hypothesis.

Due to the column temperature profile setting, some of the heavier fraction of OSCs including benzonaphtho-thiophene derivatives, phenanthro-thiophene derivatives and sulfur containing asphaltenes may not be shown in the GC-SCD chromatograms. Further studies are needed to resolve this problem.

CHAPTER 6: CONCEPTUAL MODEL FOR THE MODIFIED UAOD DESULFURIZATION PROCESS

6.1 Introduction

In the modified UAOD process with the application of superoxide, it is demonstrated that organic sulfur compounds can be oxidized with the aid of acid catalysis and phase transfer catalysis in a tri-phase system. Multiple oxidant species including superoxide radical, hydroxyl radical, hydrogen peroxide, singlet oxygen and peracid are produced by superoxide radicals with the application of acid catalysis. With both quaternary ammonium salt and ionic liquids as phase transfer catalysts, multi-ion pairing enhances the efficiency of active oxygen transfer to the organic phase, leading to the improvement of overall desulfurization efficiency. Unlike the previous generations of UAOD process, the modified UAOD process with the application of superoxide can oxidize certain OSCs to inorganic sulfur compounds.

In this chapter, the mechanism of the modified UAOD process using superoxide is developed based on the batch studies for various model sulfur compounds, mid-distillates and heavy distillates discussed in the previous chapters.

6.2 Model Overview

The modified UAOD process using superoxide employed the following components: solid oxidant, phase transfer catalyst, ionic liquid and acid catalyst. The process was carried out with continuous mixing of three phases: solid phase, polar phase and non-polar phase. The solid phase includes the solid oxidant – potassium superoxide. The polar phase includes acid catalysts and ionic liquid. The non-polar phase (or the organic phase) includes the organic liquid which contains organic sulfur compounds targeted to be removed. The conceptual model for the process was developed with twelve following steps (Figure 6.1).

Step 1: In the presence of potassium superoxide, KO_2, and quaternary ammonium salt, $[Q^+X^-]$, with lipophilic cation and hydrophilic anion, superoxide anion is released as $[Q^+O_2^{-}\cdot]$.

Step 2: Anions of acid catalysts, including acetic acid $[CH_3COOH]$ and trifluoroacetic acid $[CF_3COOH]$, are extracted by $[Q^+X^-]$ forming $[Q^+CH_3COO^-]$ and $[Q^+CF_3COO^-]$. The process is known as Stark's extraction mechanism as discussed in Chapter 2. Fluoride ion is selected as the counter ion $[X^-]$ in the quaternary ammonium salt due to its low lipophilicity and stability towards strong oxidants. The lipophilicities of the anions are in the following order: $MnO_4^- > ClO_4^- > SCN^- > I^- > ClO_3^- > NO_3^- > Br^- > CN^- > Cl^- > HSO_4^- > CH_3COO^- > F^- > SO_4^{2-} > CO_3^{2-} > PO_4^{3-}$ (Dehmlow et al., 1993).

Step 3: In the mixture of [$Q^+O_2^{-}\cdot$] and acid, hydrogen peroxide and other active oxygen species are generated.

Step 4: Hydrogen peroxide can react with [$Q^+CH_3COO^-$] and [$Q^+CF_3COO^-$] generating peroxyacetate: [$Q^+CH_3COOO^-$] and trifluoroperacetate: [$Q^+CF_3COOO^-$].

Step 5: With tetraoctylammonium ion as the lipophilic cation, the active nucleophile anions are transferred to the non-polar phase in the form of [$Q^+O_2^{-}\cdot$], [$Q^+CH_3COOO^-$] and [$Q^+CF_3COOO^-$] without losing their activities.

Step 6: The active nucleophile anions, [CH_3COOO^-] and [CF_3COOO^-] in the organic phase oxidize the organic sulfur compounds to the corresponding sulfones.

Step 7: Superoxide radicals in the organic phase can oxidize some of the organic sulfur compounds into a radical form of the corresponding sulfone anion, which can be further oxidized to inorganic sulfur compounds.

Step 8: After oxidation, the reduced form of the ion pairs, [$Q^+CH_3COO^-$] and [$Q^+CF_3COO^-$], return to the polar phase.

Step 9: Ionic liquid provides another mean of active anion extraction, resulting enhancement of phase transfer catalysis. With appropriate alkyl sulfate ion [RSO_4^-] as the counter ion, alkyl persulfate anion [$RSO_6^{-}\cdot$] can be produced by reacting with superoxide radical.

Step 10: Similar to quaternary ammonium cation, alkyl methylimidazolium [RMIM$^+$] type of ionic liquid can serve as a phase transfer catalyst which can transfer [RSO$_6^-$•] to the organic phase in the form of [RMIM$^+$RSO$_6^-$•].

Step 11: [RMIM$^+$RSO$_6^-$•] can oxidize organic sulfur compounds to the corresponding sulfones or inorganic sulfate as described in Step 6 and 7.

Step 12: The reduced form of [RMIM$^+$RSO$_4^-$] returns to the polar phase for reactivation in the catalysis cycle.

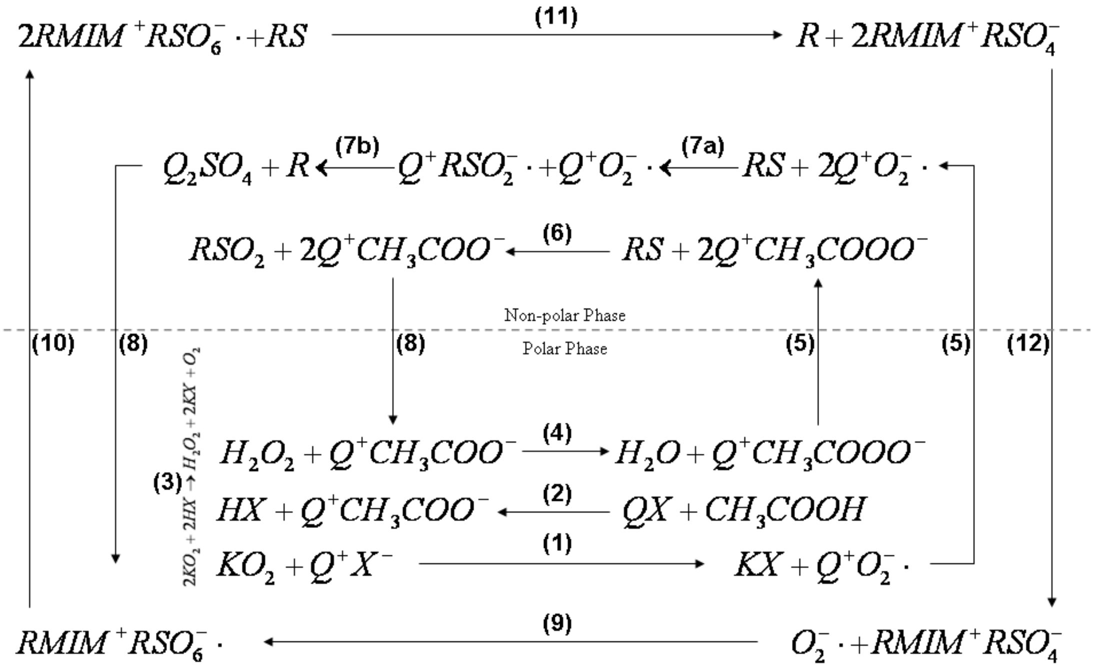


Figure 6.1 Conceptual model of 4th generation UAOD process

6.3 Summary

In this chapter, a conceptual model of the modified UAOD process with the application of superoxide is developed consisting of twelve steps. They include: (1) extraction of superoxide radical by phase transfer catalyst; (2) extraction of anion from acid catalysts; (3) generation of active oxygen species from superoxide; (4) generation of peroxyacetic acid; (5) transfer of active nucleophiles to organic phase; (6) oxidation of organic sulfur compounds by peroxyacetic acid; (7) oxidation of organic sulfur compounds by superoxide radical; (8) regeneration of catalysts in the polar phase; (9) oxidation of ionic liquid anion to form alkyl persulfate anion; (10) transfer of alkyl persulfate anion to organic phase; (11) oxidation of organic sulfur by alkyl persulfate anion; and (12) regeneration of ionic liquid's ion pair.

CHAPTER 7: CONCLUSION AND RECOMMENDATIONS

7.1 Summary and Conclusion

With the tightened environmental regulations on sulfur content of fuels including diesel and residual fuel oil, an advance desulfurization method is required to produce ultralow sulfur diesel fuel with sulfur content less than 15 ppm_w and low sulfur residual fuel oil with sulfur content less than 5000 ppm_w. The 3rd generation UAOD process is capable of producing ultralow sulfur diesel at low temperature and ambient pressure. However, the requirement for high dosage of oxidant and high energy consumption diminish its economical viability. Additionally, previous generations of UAOD could cause heavy precipitation of asphaltene, thus are considered not applicable to desulfurize residual fuel oil. Therefore, this research developed a 4th generation UAOD, called the modified UAOD process with the application of superoxide, summarized in the ensuing paragraphs.

It was demonstrated that oxidation of more than 97% of various model compounds including thiophene derivatives, benzothiophene derivatives, and dibenzothiophene derivatives can be achieved by the 4th generation UAOD process at low oxidant to sulfur ratio. Together with a post treatment to remove sulfones by either liquid-liquid extraction or solid adsorption, the process can be used to produce ultralow sulfur diesel. This process can also be used to achieve up to 80% desulfurization on residual fuel oil.

The 4th generation UAOD is designed with the following essential components: oxidation; phase transfer catalysis; acid catalysis; and ultrasonication. Quaternary ammonium salt and ionic liquid are used as phase transfer catalysts to extract active oxidant (superoxide) to the organic phase. Specific type of solid oxidant, such as metallic superoxide, KO_2, is used to oxidize organic sulfur compounds. Acetic acid and trifluoroacetic acid are used together with mixing and/or ultrasonication to enhance the oxidation process. The major concepts and important points from the experiments are discussed below.

1. Oxidant selection is one of the major issues in the development of the 4th generation UAOD. In the previous generations of UAOD, diluted (0.3% to 30% wt) hydrogen peroxide was used as oxidant to oxidize organic sulfur compounds. However, high dosage (greater than 1:100 of sulfur to oxidant ratio) of oxidant was required to achieve 95% desulfurization. In order to reduce the dosage of oxidant, a stable oxidant with high purity is required. Therefore, solid oxidants including potassium permanganate, sodium superoxide, and potassium superoxide were investigated. However, in the 4th generation of UAOD process using potassium superoxide, only 1:30 of sulfur to oxidant ratio is required to achieve 95% desulfurization of various OSCs. At low sulfur to oxidant ratio of 1:4, potassium superoxide can still achieve 90% oxidization of organic sulfur compounds.

Superoxide can also achieve a faster desulfurization as compared with hydrogen peroxide. For instance, 80% to 90% desulfurization for various model sulfur compounds including T, 2MT, BT, 2MBT, DBT and 4,6DMDBT can be achieved using potassium superoxide within reaction period of 60 minutes,, while it requires 100 minutes to achieve the same desulfurization efficiencies by hydrogen peroxide (Cheng et al., 2009). It is because free radical oxidation by superoxide anion is stronger than chemical oxidation by hydrogen peroxide.

2. Phase transfer catalysts applied includes both quaternary ammonium salt and ionic liquid. Quaternary ammonium salt can extract superoxide anion from solid phase to liquid phases. Quaternary ammonium salt reduced the surface tension between phases, and facilitates oxidant into the organic phase. Selection of counter ion in quaternary ammonium salt is important because it can affect active nucleophile anions extraction efficiency. Highly lipophobic ion such as fluoride ion, can effectively suppress the degree of hydration around active nucleophile anions to achieve better phase transfer. Due to its stability against strong oxidants, no halogenated by-products would be formed during the process. Therefore, quaternary ammonium fluoride is selected as one of the phase transfer agents in the 4th generation UAOD.

3. Ionic liquid is the second phase transfer catalyst applied in the process. Similar to quaternary ammonium salt, ionic liquid can extract active nucleophile anions into organic phase so as to oxidize organic sulfur compounds. Due to the thermostability,

chemostability, and low vapor pressure, ionic liquids are considered as new generation of green solvents and catalysts. However, certain types of ionic liquids are susceptible to decomposition with the use of strong oxidant and ultrasonication. For example, one of the most common types of ionic liquid, hexafluorophosphate [PF_6] anion based ionic liquids could be oxidized by strong oxidant such as hydrogen peroxide, or decomposed under ultrasonication. Corrosive fume of hydrogen fluoride is reported as one of the major product from [PF_6] degradation.

Ionic liquids with alkylsulfate as anion are considerably more stable and relatively low in toxicity, and therefore as a substitute to [PF_6] based ionic liquid, the following four compounds were selected in this study: 1-ethyl-3-methylimidazolium ethylsulfate [EMIM][$EtSO_4$], 1,2,3-trimethylimidazolium methylsulfate [TMIM][$MeSO_4$], and tributylmethyl-phosphonium methylsulfate [TMBP][$MeSO_4$]. Among these ionic liquids, [EMIM][$EtSO_4$] demonstrated ease of application, excellent catalytic performance and achieved greater than 98% desulfurization efficiency in the model sulfur compound study.

4. Acetic acid and trifluoroacetic acid applied in the 4th generation of UAOD can be oxidized to peracetic acid and trifluoroperacetic acid, respectively. With the aid of phase transfer catalysts, the peracids generated were able to oxidize organic sulfur compounds in the oil phase.

5. Ultrasonication used in these desulfurization studies provided local high temperature and pressure, causing decomposition of OSCs. Desulfurization efficiency of 95% was achieved after 2 hours of reaction time. Furthermore, 98% efficiency was reached by increasing the reaction time by 10 minutes.

6. It was demonstrated in the model sulfur compounds studies that the 4th generation UAOD can oxidize various organic sulfur compounds including thiophene (T), 2-methyl thiophene (2MT), benzothiophene (BT), 2-methyl benzothiophene (2BT), dibenzothiophene (DBT), and 4, 6-dimethyl dibenzo-thiophene (4,6DMDBT). From the results of kinetic studies, it was demonstrated that the oxidation efficiencies of the tested model sulfur compounds decrease in the following order: BT > 2MBT > DBT > 4, 6DMDBT > T > 2MT.

7. It was concluded that high energy consumption by ultrasonication could limit the applications of the 4th generation UAOD. Preliminary studies were conducted using ultraviolet assisted desulfurization process as an alternative enhancement process to ultrasonication. The results demonstrated this process can reduce energy consumption by 85%. Ultraviolet irradiation could be a possible alternative to ultrasonication.

8. To demonstrate the applicability of the 4th generation UAOD process to real fuels, various fuels including JP-8, MGO, sour diesel, RO-6 and IFO were tested. It was demonstrated that ultralow sulfur diesel can be produced from these fuels. The process

can achieve 95% desulfurization on mid-distillates even at sulfur to oxidant ratio of 1:2.8. For heavy distillates, a maximum of 80% desulfurization can be achieved.

9. From the results of gas chromatography with sulfur chemiluminescence detector (GC-SCD), it was shown that condensed ring structured sulfur compounds including alkyl-substituted DBTs, benzonaphtho-thiophene derivatives and phenanthro-thiophene derivatives are the major sulfur constituents in the desulfurized fuel samples.

10. From the GC-SCD chromatograms, it was determined that the 4th generation UAOD can oxidize some of the organic sulfur compounds to compounds other than sulfones. The most likely products are inorganic sulfur compounds. A possible mechanistic explanation would be that radical reactions initiated by superoxide anion can convert organic sulfur compounds such as BT and DBT to inorganic sulfur compounds.

11. A conceptual model for the 4th generation UAOD process was developed with the following twelve steps: (1) extraction of superoxide radical by phase transfer catalyst; (2) extraction of anion from acid catalysts; (3) generation of active oxygen species from superoxide; (4) generation of peroxyacetic acid; (5) transfer of active nucleophiles to organic phase; (6) oxidation of organic sulfur compounds by peroxyacetic acid; (7) oxidation of organic sulfur compounds by superoxide radical; (8) regeneration of catalysts in the polar phase; (9) oxidation of ionic liquid anion to form alkyl persulfate anion; (10) transfer of alkyl persulfate anion to organic phase; (11) oxidation of organic sulfur by alkyl persulfate anion; and (12) regeneration of ionic liquid's ion pair.

12. Based on bench scale studies, a simplified cost evaluation for different generations of UAOD processes is illustrated in Table 7.1. It is demonstrated that the total chemical cost for the 4th generation UAOD is considerably less than others.

		1st Generation UAOD		**2nd Generation UAOD**		**3rd Generation UAOD**		**4th Generation UAOD**	
	Price ($/kg)	Dosage (g)	Cost ($)	Dosage (g)	Cost ($)	Dosage (g)	Cost ($)	Dosage (g)	Cost ($)
H_2O_2 (30%)	452	10	4.52	10	4.52	5	2.26		
KO_2	718							0.7	0.5
TMC	884	0.1	0.09	0.1	0.09				
HAc	30.92					1.4	0.04	1.9	0.06
TFA	216					0.6	0.13	0.1	0.02
QBr	2875	0.1	0.29						
QF	3528			0.1	0.35	0.6	2.12	0.1	0.35
IL	245					10	2.45	5	1.23
Total		10.2	**4.90**	10.2	**4.96**	17.6	**7.00**	7.8	**2.16**

Table 7.1 Chemical cost comparison of different UAOD generations to desulfurize 10 grams sample with 1000ppm_w DBT in bench scale study

13. A schematic diagram of the 4th generation UAOD process is illustrated in Figure 7.1. A premixer was used to mix phase transfer catalysts including ionic liquid and quaternary ammonium salt with potassium superoxide in order to release superoxide anion in the liquid phase. Fuel oil was subsequently mixed with acid catalysts, superoxide and phase

transfer catalysts in the main reactor to achieve OSCs oxidation at 70°C and ambient pressure. A phase separation vessel was used to separate fuel oil from the polar phase which contained mainly the spent catalysts. Solvent acetonitrile was then used for sulfone extraction. Desulfurized fuel oil was separated from spent solvent. Spent solvent was regenerated via distillation. Regenerated solvent was reused for sulfone extraction.

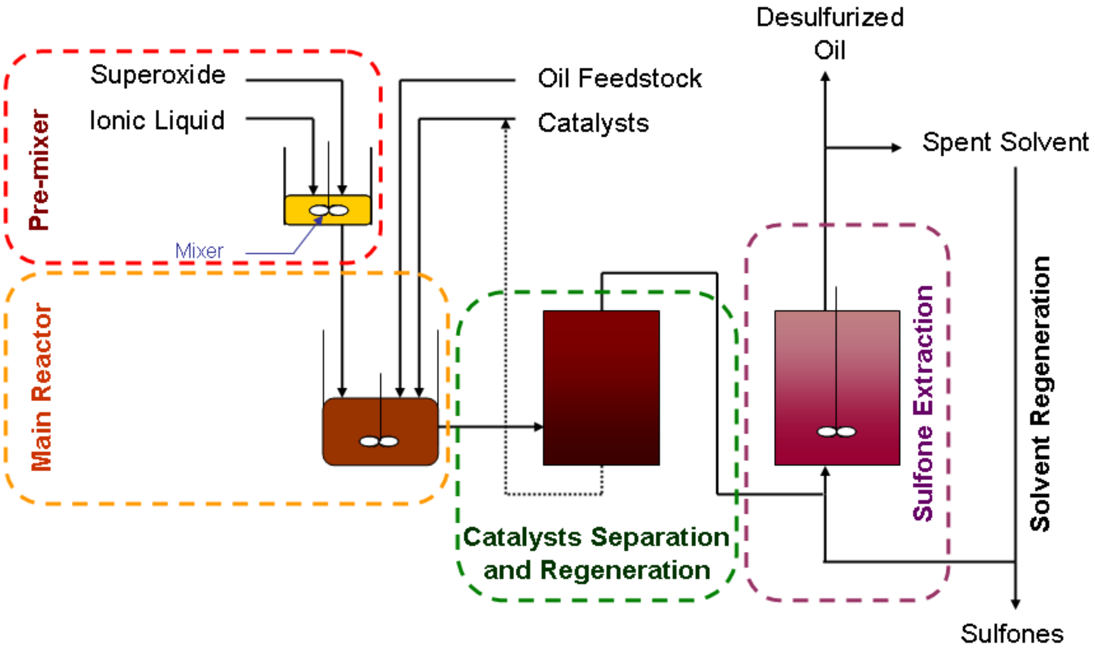


Figure 7.1 Schematic diagram of the 4th generation UAOD process

7.2 Recommendations for Future Work

Conduct bench-scale completely mixed flow reactor (CMFR) studies to further refine the 4th generation UAOD process. Some of the most significant issues are discussed below.

1. Enhanced treatment of heavy distillates. It was shown that the 4th generation UAOD process can achieve greater than 95% desulfurization for various mid-distillates. However, only a maximum of 80% desulfurization can be achieved for heavy-distillates. Therefore, it is important to improve desulfurization efficiency for heavy-distillates. A pre-treatment step to remove asphaltenes from heavy distillates could be one possible method. To reach this goal, it is necessary to identify and quantify the remaining sulfur compounds in heavy-distillates in order to implement the required treatment steps.

2. It was proposed that the 4th generation UAOD process can oxidize some organic sulfur compounds such as benzothiophenes and dibenzothiophenes to multiple products including sulfones and inorganic sulfur compounds. To design an effective post-treatment step, it is important to qualitatively and quantitatively determine the organic and inorganic sulfur compounds as well as other by-products at each step of treatment. This can be accomplished by: i) gas chromatography equipped with sulfur chemiluminescence detector can be used to detect organic sulfur compounds, ii) ion chromatograph equipped with pulsed electrochemical detector can be used to detect inorganic sulfate or sulfite

ions, and iii) gas chromatography equipped with mass spectrometer can be used to identify organic products.

3. Investigate the applicability of ultraviolet irradiation for desulfurization of OSCs. It was demonstrated in the preliminary studies that ultrasonication process could cost 15 times more than that of UV irradiation. Accordingly, UV assisted oxidative desulfurization process could potentially be one of the next generations of desulfurization treatment technologies.

Addition of solid catalyst such as titanium (IV) oxide which can increase free radical generation under UV irradiation should also be considered in the future development.

4. Solar power would be another alternative for desulfurization of OSCs. Demonstrated in a recent publication (Shiraishi et al., 2003), dibenzothiophene sulfuroxide can be photolysed to biphenyls and inorganic sulfur compounds with the application of xenon lamp ($\lambda > 300$ nm). Therefore, photo-irradiation could be used as a possible post treatment step for the 4th generation UAOD process.

5. With the addition of potassium superoxide, various potassium salts could be generated. It is important to investigate the fate of potassium in the process. Recovery of potassium should also be considered in the future investigations.

6. Greener chemicals, including oxidants, solvents and catalysts should be investigated in the future development.

7. Conduct pilot-scale studies to optimize the process efficiency and assess its economical viability.

REFERENCES

Afanas'ev, I. *Superoxide Ion: Chemistry and Biological Implications.* Florida: CRC Press, 1989

Al-Ekabi, H., Edwards, G., Holden, W., Safarzadeh-Amiri, A. and Story, J. *Chemical Oxidation.* Pennsylvania: Technomic Publishing Company Inc., 1992

Andari, M., Behbehani, H. and Qabazard, H. "Database for Organic Sulfur Compounds Using GC-SCD Method. Determination of Sulfur Containing Compounds in Straight Run Gas Oils (SRGO)." *Fuel Science & Technology Int'l.*, **14**(7): 897 – 908, 1996

Andersson, J. and Bobinger, S. "Polycyclic Aromatic Sulfur Heterocycles. II. Photochemcial Oxidation of Benzo[b]thiophene in Aqueous Solution." *Chemosphere*, **24**(4): 383 – 389, 1992

Arce, A., Earle, M., Katdare, S., Rodriguez, H. and Seddon, K. "Application of Mutually Immiscible Ionic Liquids to the Separation of Aromatic and Aliphatic Hydrocarbons by Liquid Extraction: a Preliminary Approach." *Phys. Chem. Chem. Phys.*, **10**: 2538 – 2543, 2008

Armstrong, S., Sankey, B. and Voordouw. G. "Conversion of Dibenzothiophene to Biphenyl by Sulfate-Reducing Bacteria Isolated from Oil Field Production Facilities." *Biotechnology Letters*, **17**(10): 1133-1136, 1995

Baba, Y. "the Photo-Desulfurization of Crude Naphtha by UV Irradiation." *Bulletin of the Chemical Society of Japan*, **47**(1): 204 – 209, 1974

Bäckvall, J. *Modern Oxidation Methods.* Weinheim: Wiley, 2004

Baker, K., Robertson, V. and Duck, F. "a Review of Therapeutic Ultrasound: Biophysical Effects." *Phys. Ther.*, **81**(7): 1351 – 1358, 2001

Barrer, R. “the Viscosity of Pure Liquids II: Polymerised Ionic Melts.” *Trans. Faraday Soc.* **39**: 59 – 67, 1943

Becker, G. and Colmsjo, A. “Gas Chromatography-Atomic Emission Detection for Quantification of Polycyclic Aromatic Sulfur Heterocycles.” *Analytica Chimica Acta*, **376**: 265 – 272, 1998

Beckett, M. and Hua, I. “Impact of Ultrasonic Frequency on Aqueous Sonoluminescence and Sonochemistry.” *J. Phys. Chem. A*, **105**(15): 3796 – 3802, 2001

Benner, R. and Stedman, D. “Universal Sulfur Detection by Chemiluminescence.” *Anal. Chem.*, **61**(11): 1268 – 1271, 1989

Berlan, J. and Mason, T. “Dosimetry for Power Ultrasound and Sonochemsitry.” *Advances in Sonochemistry*, **4**: 1 –73, 1996

Beychok, M. *Fundamentals of Stack Gas Dispersion.* California: M.R. Beychok, 2005

Bianchini, C., Casares, J., Osman, R., Pattison, D., Peruzzini, M., Perutz, R. and Zanobini, F. “C-H Bond Cleavage in Thiophenes by [$P(CH_2CH_2PPh_2)_3Ru$]. UV Flash Kinetic Spectroscopy Discloses the Ruthenium-Thiophene Adduct Which Precedes C-H Insertion.” *Organometallics*, **16**(21): 4611 – 4619, 1997

Bochet, C., Draper, T., Bocquet, B., Pope, M. and Williams, A. “^{182}Tungsten Mossbauer Spectroscopy of Heteropolytungstates.” *Dalton Trans.*, 5127 – 5131, 2009

Bockris, J. and Reddy, A. *Modern Electrochemistry 1: Ionics.* New York: Springer, 1998

Boikov, E., Vakhrushin, P. and Vishnetskaya, M. “Oxidative Desulfurization of Hydrocarbon Feedstock.” *Chemistry and Technology of Fuels and Oils*, **44**(4): 271 – 274, 2008

Borrás-Almenar, J., Coronado, E. Müller, A. and Pope, M. *Polyoxometalate Molecular Science (NATO Science Series II: Mathematics, Physics and Chemistry).* The Netherlands: Kluwer Academic Publishers, 2003

Bregeault, J. "Transition-metal complexes for liquid-phase catalytic oxidation: some aspects of industrial reactions and of emerging technologies." *Dalton Trans.*, 3289 – 3302, 2003

Bukowski, A. and Milczarska, T. "Asphalts as Inhibitors of Radical Rolymerization." *Journal of Applied Polymer Science*, **28**: 1001 – 1009, 1983

California Air Resource Board. *California Low Sulfur Diesel Fuel.* 2003

Callahan, L., She, Z. and Nosek, T. "Superoxide, Hydroxyl Radical, and Hydrogen Peroxide Effects on Single-Diaphragm Fiber Contractile Apparatus." *J. Appl. Physiol.*, **90**: 45 – 54, 2001

Campos-Martin, J., Capel-Sanchez, M. and Fierro, J. "Highly Efficient Deep Desulfurization of Fuels by Chemical Oxidation." *Green Chem.*, **6**: 557 – 562, 2004

Chan, N., Lin, T. and Yen, T. "Superoxides: Alternative Oxidants for the Oxidative Desulfurization Process." *Energy & Fuels*, **22**: 3326 – 3328, 2008

Chan, N., Fan, W., and Yen, T., "the Desulfurization Process of Heavy Fuel Oil." *Am. Chem. Soc., Div. Fuel Chem. (Prepr.)*, **54**(1): 70 – 71, 2009

Chang, H., Yon, G., and Kim, Y. "Facile Synthesis of 2-Substituted Aminobenzoxazole One Pot Cyclodesulfurization of N-(2-Hydroxylphenyl)-N'-Phenylthioureas with Superoxide Radical Anion." *Chem. Letters*, 1291 – 1294, 1986

Chen, L., Guo, S., and Zhao, D. "Oxidative Desulfurization of Simulated Gasoline over Metal Oxide-Loaded Molecular Sieve." *Chi. J. Chem. Eng.*, **15**(4): 520 – 523, 2007

Cheng, S. *Ultra Clean Fuels via Modified UAOD Process with Room Temperature Ionic Liquid (RTIL) & Solid Catalyst Polishing.* California: University of Southern California. Libraries, 2008

Cheng, S. and Yen, T. "Use of Ionic Liquids as Phase-Transfer Catalysis for Deep Oxygenative Desulfurization." *Energy & Fuels*, **22**: 1400 – 1401, 2008

Cheng, S. and Yen, T. “Ultra Clean Fuel via Modified Ultrasound Assisted Oxidative Desulfurization Process.” *Prepr. A.C.S. Div. Pert. Chem.*, **54**(1): 15 – 17, 2009

Collins, C. “Implementing Phytoremediation of Petroleum Hydrocarbons.” *Methods in Biotechnology*, **23**: 99 – 108, 2007

Coyle, J. *Introduction to Organic Photochemistry.* Chichester: John Wiley & Sons Ltd., 1991

Crum, L., Mason, T., Reisse, J. and Suslick, K. *Sonochemistry and Sonoluminescence.* The Netherlands: Kluwer Academic Publishers, 1998

Crum, L. and Roy, R. “Sonoluminescence.” *Science*, **266**: 233 – 234, 1994

Dehkordi, A., Kiaei, Z. and Sobati, M. “Oxidative Desulfurization of Simulated Light Fuel Oil and Untreated Kerosene.” *Fuel Processing Technology*, **90**(3): 435 – 445, 2009

Dehmlow, E. and Dehmlow, S. *Phase Transfer Catalysis (3rd).* Weinheim: VCH, 1993

Dermeikand, S. and Sasson, Y. “Synthesis of Quaternary Ammonium Fluoride Salts by a Solid-Liquid Halogen Exchange Process in Protic Solvents.” *J. Org. Chem.*, **54**: 4827 – 4829, 1989

Dhir, S., Uppaluri, R. and Purkait, M. “Oxidative Desulfurization: Kinetic Modelling.” *Journal of Hazardous Materials*, **161**: 1360 – 1368, 2009

Didenko, Y. and Suslick, K. “the Energy Efficiency of Formation of Photons, Radicals and Ions during Single-Bubble Cavitation.” *Nature*, **418**: 394 – 397, 2002

Domanska, U. Pobudkowska, A. and Krolikowski, M. “Separation of Aromatic Hydrocarbons from Alkanes Using Ammonium Ionic Liquid C_2NTf_2 at T = 298.15K.” *Fluid Phase Equilibria*, **259**: 173 – 179, 2007

Drushel, H. “Sulfur Compound Type Distributions in Petroleum Using an In-Line Reactor or Pyrolysis Combined with Gas Chromatography and a Microcoulometric Sulfur Detector.” *Anal. Chem.*, **41**(4): 569 – 576, 1969

Earle, M. and Seddon, K. “Ionic Liquids: Green Solvents for the Future.” *Pure Appl. Chem.*, **72**(7): 1391 – 1398, 2000

Ellzy, M. and Janes, L. *Sulfur Chemiluminescence Detection Compared to Sulfur Flam Photometric Detection.* Maryland: Edgewoood, 1998

Endo, K., Miyasaka, T., Mochizuki, S., Aoyagi, S., Himi, N., Asahara, H., Tsujioka, K. and Sakai, K. “Development of a Superoxide Sensor by Immobilization of Superoxide Dismutase.” *Sensors and Actuators*, **B83**: 30 – 34, 2002

Energy Information Administration (EIA). *The Transition to Ultra-Low-Sulfur Diesel Fuel: Effects on Prices and Supply.* U.S. Department of Energy, SR/OIAF/2001-01, 2001

Environment and Conservation. *New Source Performance Standards.* Department of State (TN) Division of Publications, 1200-03-16, 2009

Etemadi, O. and Yen, T. “Aspect of Selective Adsorption among Oxidized Sulfur Compounds in Fossil Fuels.” *Energy and Fuels*, **21**: 1622 – 1627, 2007

Etemadi, O. and Yen, T. “Selective Adsorption in Ultrasound-Assisted Oxidative Desulfurization Process for Fuel Cell Reformer Application.” *Energy and Fuels*, **21**: 2250 – 2257, 2007

Etemadi, O. and Yen, T. “Surface Characterization of Adsorbents in Ultrasound-Assisted Oxidative Desulfurization Process of Fossil Fuels.” *J. of Colloid and Interface Science*, **313**: 18 – 25, 2007

Fang, X., Mark, G. and Sonntag, C. “OH Radical Formation by Ultrasound in Aqueous Solutions Part I: the Chemistry Underlying the Terephthalate Dosimeter.” *Ultrasonics Sonochemistry*, **3**: 57 – 63, 1996

Filippis, P. and Scarsella, M. "Oxidative Desulfurization: Oxidation Reactivity of Sulfur Compounds in Different Organic Matrixes." *Energy Fuels*, **17**(6): 1452 – 1455, 2003

Foote, C. *Active Oxygen in Chemistry (Structure, Energetics and Reactivity in Chemistry).* London: Chapman & Hall, 1995

Fox, D., Gilman, H., Morgan, A., Shield, J., Maupin, P., Lyon, R., De Long, H. and Trulove, P. "Flammability and Thermal Analysis Characterization of Imidazolium-Based Ionic Liquids." *Ind. Eng. Chem. Res.*, **47**(16): 6327 – 6332, 2008

Frank, S. and Bard, A. "Heterogeneous Photocatalytic Oxidation of Cyanide Ion in Aqueous Solutions at Titanium Dioxide Powder." *J. Am. Chem. Soc.*, **99**(1): 303 – 304, 1977

Freemantle, M. "Designer Solvents: Ionic Liquids may Boost Clean Technology Development." *Chemical & engineering news*, **76**: 32 – 37, 1998

Fukuto, J., Stefano, E., Burstyn, J., Valentine, J. and Cho, A. "Mechanism of Oxidation of N-Hydroxyphentermine by Superoxide." *Biochemistry*, **24**: 4161 – 4167, 1985

Galvanic Applied Sciences (GAS) Inc. *Sulfur Chemiluminescence Analyzers.* 2004

Gaitan, F., Crum, L., Church, C. and Roy, R. "Sonoluminescence and Bubble Dynamics for a Single, Stable, Cavitation Bubble." *J. Acoust. Soc. Am.*, **91**: 3166 – 3183, 1992

Garcia, C., Becchi, M., Loustalot, M., Paisse, O. and Szymanski, R. "Analysis of Aromatic Sulfur Compounds in Gas Oils Using GC with Sulfur Chemiluminescence Detection and High-Resolution MS." *Anal. Chem.*, **74**: 3849 – 3857, 2002

Gatan, R., Barger P. and Gembicki, V. "Oxidative Desulfurization: a New Technology for ULSD." *Fuel Chemistry (Preprint)*, **49**(2): 577- 579, 2004

Fibilisco, S. *Alternative Energy Demystified.* New York: McGraw-Hill, 2006

Girgis, M. and Gates, B. “Reactivities, Reaction Networks and Kinetics in High-pressure Catalytic Hydroprocessing.” *Ind. Eng. Chem.*, **30**: 2021-2058, 1991

Gokel, G., Cram, D., Liotta, C., Harris, H. and Cook, F. “18-Crown-6.” *Org. Synth.*, **57**: 30, 1988

Gold, V., Loening, K., McNaught, A. and Shemi, P. *Compendium of Chemical Terminology.* International Union of Pure and Applied Chemistry, 1987

Greenspan, F. “Oxidation Reactions with Aliphatic Peracids.” *Ind. Eng. Chem.*, **39**(7): 847 – 848, 1947

Greenspan, H. and Nadim, A. “Sonoluminescence of an Oscillating Gas Bubble.” *Physics of Fluid A: Fluid Dynamics*, **5**(4): 1065 – 1067, 1993

Guida, W. and Mathre, D. “Phase-Transfer Alkylation of Heterocycles in the Presence of 18-Crown-6 and Potassium Tert-Butoxide.” *J. Org. Chem.*, **45**(16): 3172 – 3176, 1980

Herrington, P. “Effect of Concentration on the Rate of Reaction of Asphaltenes with Oxygen.” *Energy & Fuels*, **18**: 1573 – 1577, 2004

Hough, W., Smiglak, M., Rodriguez, H., Swatloski, R., Spear, S., Daly, D., Pernak, J., Grisel, J., Carliss, R., Soutullo, M., Davis, J. and Rogers, R. “the Third Evolution of Ionic Liquids: Active Pharmaceutical Ingredients.” *New Journal of Chemistry*, **31**: 1429 – 1436, 2007

Huang, C., Chen, B., Zhang, J., Liu, Z. and Li, Y. “Desulfurization of Gasoline by Extraction with New Ionic Liquids.” *Energy and Fuels*, **18**: 1862 – 1864, 2004

Huang, D., Lu, Y., Wang, Y. And Luo, G. “Catalytic Kinetics of Dibenzothiophene Oxidation with the Combined Catalyst Quaternary Ammonium Bromide and Phosphotungstic Acid.” *Ind. Eng. Chem. Res.*, **46**: 6221 – 6227, 2007

Huddleston, J., Willauer, H., Swatloski, R., Visser, A. and Rogers, R. “Room Temperature Ionic Liquids as Novel Media for Clean Liquid-Liquid Extraction.” *Chem. Commun.*, 1765 – 1766, 1998

Jess, A. and Eber, J. "Deep Desulfurization of Oil Refinery Streams by Extraction with Ionic Liquids." *Electrochemical Society Proceedings*, **24**: 572-582, 2004

Johnson, K. "What's an Ionic Liquid." *Interface*, **16**(1): 38 – 41, 2007

Jones, R. *Quaternary Ammonium Salts: Their Use in Phase-Transfer Catalysis.* California: Academic Press, 2001

Juaristi, M., Aizpurua, J., Lecea, B. and Palomo, C. "Reagents and Synthetic Method 41: Oxidations with Chromium Trioxide under the Influence of Crown Ethers." *Can. J. Chem.*, **62**: 2941 – 2944, 1984

Kaneko, M. and Okura, I. *Photocatalysis Science and Technology.* New York: Springer, 2002

Kim, I. and Jung, O. "Sonochemical Reaction Mechanism of a Polycyclic Aromatic Sulfur Hydrocarbon in Aqueous Phase." *Bull. Korean Chem. Soc.*, **23**(7): 990 – 994, 2002

Kim, I., Yoa, S., Lee, J. and Huang, C. "Reaction Pathways and Kinetic Modeling for Sonochemical Decomposition of Benzothiophene." *Korean J. Chem. Eng.*, **20**(6): 1045 – 1053, 2003

Kim, Y., Lim, S. and Chang, H. "Activation of Superoxide; Efficient Desulfurization of Thioamides to the Corresponding Amides using a Peroxyphosphorus Intermediate Generated from Phenylphosphonic Dicholoride and Superoxide." *Chem. Commun.*, 36 – 37, 1990

Kirimura, K., Furuya, T., Sato, R., Ishii, Y., Kino, K. and Usami, S. "Biodesulfurization of Naphthothiophene and Benzothiophene through Selective Cleavage of Carbon-Sulfur Bonds by Rhodococcus sp. Strain WU-K2R." *Applied and Environmental Microbiology*, **68**(8): 3867-3872, 2002

Kong, S., Liochev, S. and Fridovich, I. "Aluminum(III) Facilitates the Oxidation of NADH by the Superoxide Anion." *Free Radical Biology & Medicine*, **13**: 79 – 81, 1992

Kozhevnikov, I. *Catalysts for Fine Chemical Synthesis, Catalysis by Polyoxo-metalates.* West Sussex: Wiley, 2002

Kropp, K., Goncalves, J., Andersson, J. and Fedorak, P. "Microbially Mediated Formation of Benzonaphthothiophenes from Benzo[b]thiophenes." *Applied and Environmental Microbiology*, **60**(10): 3624 – 3631, 1994

Kwon, J., Moon, J., Lee, D., Bae, Y., Sohn, H. and Lee, C. "Adsorptive Desulfurization and Denitrogenation of Refinery Fuels using Mesoporous Silica Adsorbents." *ChemSusChem*, **1**(4): 307-309, 2008

Lanju, C., Shaohui, G., Dishun, Z., Jialin, W. and Tong, M. "Oxidation of Thiophenes over Silica Gel Using Hydrogen Peroxide and Formic Acid." *Energy Sources*, **30**(4): 370 – 376, 2008

Lee, B., Chi, Y., Lee, J., Choi, I., Song, C., Namgoong, S. and Lee, S. "Imidazolium Ion-Terminated Self-Assembled Monolayers on Au: Effects of Counteranions on Surgace Wettability." *J. Am. Chem. Soc.*, **126**: 480 – 481, 2004

Lee, S. "Comparison of the Atomic Emission Detector to Other Element-Selective Detectors for the Gas Chromatographic Analysis of Pesticide Residues." *J. Agric. Food Chem.*, **39**: 2192 – 2199, 1991

Lee, S., Speight, J. and Loyalka, S. *Handbook of Alternative Fuel Technologies.* Florida: CRC Press, 2007

Levshin, V. and Rzhevkin, S. "Mechanism of Luminescence in Liquids under Ultrasonic Treatment." *Doklady Akademii Nauk SSSR*, **16**: 399 – 404, 1973

Li, F., Zhang, Z., Feng, J., Cai, X. and Xu, P. "Biodesulfurization of DBT in Tetradecane and Crude Oil by a Facultative Thermophilic Bacterium Mycobacterium Goodie." *Journal of Biotechnology*, **127**: 222–228, 2007

Li, F., Zhao, D., Li, H. and Liu, R. "Photochemical Oxidation of Thiophene by O_2 in an Oil/Acetonitrile Two-Phase Extraction System." *Ann. N. Y. Acad. Sci.*, **1140**: 383 – 388, 2008

Li, H., Zhu, W., Wang, Y., Zhang, J., Lu, J. and Yan, Y. "Deep Oxidative Desulfurization of Fuels in Redox Ionic Liquids Based on Iron Chloride." *Green Chem.*, **11**: 810 – 815, 2009

Li, X., Zhao, J., Li, Q., Wang, L. and Tsang, S. "Ultrasonic Chemical Oxidative Degradation of 1,3-Dialkylimidazolium Ionic Liquid and Their Mechanistic Elucidations." *Dalton Trans.*, 1875 – 1880, 2007

Lin, J and Yen, T. "an Upgrading Process through Cavitation and Surfactant." *Energy and Fuels*, **7**: 111 – 118, 1993

Liu, B., Xu, D., Chu, J. and Au, C. "Deep Desulfurization by the Adsorption Process of Fluidized Catalytic Cracking (FCC) Diesel over Mesoporous Al-MCM-41 Materials." *Energy & Fuel*, **21**: 250-255, 2007

Liu, J., Jiang, G., Chi, Y., Cai, Y., Zhou, Q. and Hu, J. "Use of Ionic Liquids for Liquid-Phase Microextraction of Polycyclic Aromatic Hydrocarbons." *Anal. Chem.*, **75**(21): 5870 – 5876, 2003

Lo, W., Yang, H. and Wei, G. "One-Pot Desulfurization of Light Oils by Chemical Oxidation and Solvent Extraction with Room Temperature Ionic Liquids." *Green Chem.*, **5**: 639 – 642, 2003

Lohse, D. "Sonoluminescence: Inside a Micro-Reactor." *Nature*, **418**: 381 – 383, 2002

Ma, X., Sakanishi, K. and Mochida, I. "Hydrodesulfurization reactivity of Various Sulfur Compounds in Vacuum Gas Oil." *Ind. Eng. Chem. Res.*, **35**: 2487-2494, 1994

Ma, X., Sun, L. and Song, C. "Deep Desulfurization of Diesel Fuels by a Novel Integrated Approach." *U.S. AAD Document Control Center*, M/S 921-107, 2001

Ma, X., Sun, L., Yin, Z. and Song, C. "New Approaches to Deep Desulfurization of Diesel Fuel, Jet Fuel, and Gasoline by Adsorption for Ultra-Clean Fuels and for Fuel Cell Applications." *Am. Chem. Soc., Div. Fuel Chem. (Prepr.)*, **46**: 648 – 649, 2001

Magaril, R. and Aksenova, E. “Investigation of the Mechanism of Coke Formation During Thermal Decomposition of Asphaltenes.” *Khimiyai Tekhnologiya Toplivi Masel*, **7**: 22 -24, 1970

Margulis, M. *Sonochemistry and Cavitation.* Amsterdam: Gordon and Breach Publishers, 1995

Marsh, K., Deev, A., Wu, A., Tran, E. and Klamt, A. “Room Temperature Ionic Liquids as Replacement for Conventional Solvents – A Review.” *Korean J. Chem. Eng.*, **19**(3): 357 – 362, 2002

Mason, T. *Sonochemistry.* Oxford: OUP Inc., 1999

Mason, T. and Lorimer, J. *Applied Sonochemistry: Uses of Power Ultrasound in Chemistry and Processing.* Weinheim: Wiley-VCH, 2002

Matsumoto, M., Mochiduki, K., Fukunishi, K. and Kondo, K. “Extraction of Organic Acids Using Imidazolium-Based Ionic Liquids and Their Toxicity to Lactobacillus Rhamnosus.” *Separation and Purification Technology*, **40**(1): 97 – 101, 2004

Mei, H., Mei, B. and Yen, T. “a New Method for Obtaining Ultra-Low Sulfur Diesel Fuel via Ultrasound Assisted Oxidative Desulfurization.” *Fuel*, **82**: 405 – 414, 2003

Meindersma, G., Podt, A., Klaren, M. and Haan, A. “Separation of Aromatic and Aliphatic hydrocarbons with Ionic Liquids.” *Chem. Eng. Comm.*, **193**(11): 1384 - 1396, 2006

McFarland, B. “Biodesulfurization.” *Current Opinion in Microbiology*, **2**: 257-264, 1999

Milazzo, G., Caroli, S. and Sharma, V. *Tables of Standard Electrode Potentials.* New York: Wiley, 1978

Moschopedis, S. and Speight, J. “Water-Soluble Derivatives of Athabasca Asphaltenes.” *Fuel*, **50**(1): 34 – 40, 1971

Mukherjee, R. *Fundamentals of Photochemistry.* New Delhi: New Age International, 1978

Munson, C., Boudreau, L., Driver, M. and Schinski, W. "Separation of Olefins from Paraffins Using Ionic Liquid Solutions." *U.S. Patent Application Publication*, US2002/0063240 A1, 2002

Murata, S., Murata, K., Kidena, K. and Nomura, M. "a Novel Oxidative Desulfurization System for Diesel Fuels with Molecular Oxygen in the Presence of Cobalt Catalysts and Aldehydes." *Energy Fuels*, **18**(1): 116 – 121, 2004

Murov, S., Carmichael, I. and Hug, G. *Handbook of Photochemistry.* New York: Marcel Dekker, 1993

Noltingk, B. and Neppiras, E. "Cavitation Produced by Ultrasonics." *Proceedings of Physical Society, London*, **63B**: 674 – 685, 1950

Oae, S., Takata, T. and Kim, Y. "Reaction of Organic Sulfur Compounds with Superoxide Anion – III Oxidation of Organic Sulfur Compounds to Sulfinic and Sulfonic Acids." *Tetrahedron*, **32**: 37 – 44, 1981

Ohl, C. "Luminescence from Acoustic-Driven Laser Induced Cavitation Bubbles." *Phys. Rev. E*, **61**: 1497 – 1500, 2000

Otsuki, S., Nonaka, T., Takashima, N., Qian, W., Ishihara, A., Imai, T. and Kabe, T. "Oxidative Desulfurization of Middle Distillate Using Ozone." *J. of Jap. Pet. Ins.*, **42**(5): 315 – 320, 1999

Otsuki, S., Nonaka, T., Takashima, N., Qian, W., Ishihara, A., Imai, T. and Kabe, T. "Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction." *Energy Fuels*, **14**(6): 1232–1239, 2000

Oxley, J., Prozorov, T. and Suslick, K. "Sonochemistry and Sonoluminescence of Room-Temperature Ionic Liquids." *J.A.C.S.*, **125**: 11138 – 11139, 2003

MEPC. *Annex 13: Amendments to the Annex of the Protocol of 1997 to Amend the International Convention for the Prevention of Pollution from Ships, 1973, as Modified by the Protocol of 1978 Relating Thereto.* IMO, 2008

MEPC. *The Protocol of 1997: Annex VI - Regulations for the Prevention of Air Pollution from Ships.* IMO, 1997

Paniv, P., Pysh'ev, S., Gaivanovich, V. and Lazorko, O. "Noncatalytic Oxidation Desulfurization of the Kerosene Cut." *Chem. and Tech. of Fuels and Oils*, **42**(3): 159 - 168, 2006

Park, B., Lee, J., Lee, Y., Hong, J. and Jung, O. "Anion Effects on the Formation of Cross-Linked Argentophilic Interaction. Synthesis and Structural Properties of AgX Bearing Bis(S-pyridyl)dimethylsilane ($X^- = CF_3SO_3^-$, PF_6^-, and NO_3^-)." *Bull. Chem. Soc. Jpn.*, **78**, 1624 – 1628, 2005

Parvulescu, V. and Hardacre, C. "Catalysis in Ionic Liquids." *Chem. Rev.*, **107**(6): 2615 – 2665, 2007

Poole, C. "Chromatographic and Spectroscopic Methods for the Determination of Solvent Properties of Room Temperature Ionic Liquids." *J. of Chromatography A*, **1037**: 49 – 82, 2004

Preston, W. and Dong, Y. "Physical and Chemical Characterization of Residual Oil-Fired Power Plant Emissions." *Energy and Fuels*, **23**: 2544 – 2551, 2009

Priyanto, S., Mansoori, G. and Suwono, A. "Measurement of Property Relationships of Nano-Structure Micelles and Coacervates of Asphaltene in a Pure Solvent." *Chem. Eng. Science*, **56**: 6933-6939, 2001

Rantwijk, F., Lau, R. and Sheldon, R. "Biocatalytic Transformations in Ionic Liquids." *TRENDS in Biotechnology*, **21**(3): 131 – 138, 2003

Ranu, B. and Jana, R. “Ionic Liquids as Catalyst and Reaction Medium – a Simple, Efficient and Green Procedure for Knoevenagel Condensation of Aliphatic and Aromatic Carbonyl Compounds Using a Task-Specific Basic Ionic Liquid.” *Eur. J. Org. Chem.*, **16**: 3767 – 3770, 2006

Rashidi, L., Mohebali, G., Darian, J. and Rasekh, B. “Biodesulfurization of Dibenzothiophene and its Alkylated Derivatives through the Sulfur-Specific Pathway by the Bacterium RIPI-S81.” *African Journal of Biotechnology*, **5**(4): 351-356, 2006

Robert, D. and Maloto, S. “Solar Photocatalysis: a Clean Process for Water Detoxification.” *the Science of the Total Environment*, **291**(1-3): 85 – 97, 2002

Rogers, R., Seddon, K. and Volkov, S. *Green Industrial Applications of Ionic Liquids*. The Netherlands: *Kluwer Academic Publishers*, 2003

Rosa, M., Lamberti, M., Pellecchia, C., Scettri, A., Villano, R. and Soriente, A. “an Efficient solvent free catalytic oxidation of sulfides to sulfoxides with hydrogen peroxide catalyzed by a binaphthyl-bridged Schiff base titanium complex.” *Tetrahedron Letters*, **47**(40): 7233 – 7235, 2006

Rose, A., Moffett, J. and Waite, T. “Determination of Superoxide in Seawater Using 2-Methyl-6-(4-methoxyphenyl)-3,7-dihydroimidazo[1, 2-a]pyrazin-3(7H)-one Chem-iluminescence.” *Anal. Chem.*, **80**: 1215 – 1227, 2008

Ryerson, T., Barkley, R. and Sievers, R. “Selective Chemiluminescence Detection of Sulfur-Containing Compounds Coupled with Nitrogen-Phosphorus Detection for Gas Chromatography.” *Journal of Chromatorgraphy A*, **670**: 117 – 126, 1994

Safarik, D. and Eldridge, R. “Olefin/Paraffin Separations by Reactive Absorption: a Review.” *Ind. Eng. Chem. Res.*, **37**: 2571 – 2581, 1998

Saiyasitpanich, P., Lu, M., Keener, T., Liang, F. and Khang, S. “The Effect of Diesel Fuel Sulfur Content on Particulate Matter Emissions for a Nonroad Diesel Generator.” *J. Air & Waste Manage. Assoc.*, **55**: 993-998, 2005

Schulz, H. “Walter Böhringer, Peter Waller and Farid Ousmanov, Gas oil deep hydrodesulfurization: refractory compounds and retarded kinetics.” *Catalysis Today*, **49**: 87-97, 1999

Sdeghi, K., Lin, J. and Yen, T. “Sonochemical Treatment of Fossil Fuels.” *Energy Sources*, **16**(3): 439 – 449, 1994

Shiraishi, Y., Tachibana, K., Hirai, T. and Komasawa, I. “Photochemical Production of Biphenyls from Oxidized Sulfur Compounds Obtained by Oxidative Desulfurization of Light Oils.” *Energy & Fuels*, **17**: 95 – 100, 2003

Simanzhenkov, V. and Idem, R. *Crude Oil Chemistry.* New York: Marcel Dekker Inc., 2003

Smith, D. *Photochemistry Vol. 1*, London: RSC Publishing, 1970

Song, C. and Roh, E. “Practical Method to Recycle a Chiral (salen)Mn Epoxidation Catalyst by Using an Ionic Liquid.” *Chem. Commun.*, **10**: 837 – 838, 2000

Speight, J. *The Chemistry and Technology of Coal.* New York: Marcel Dekker Inc., 1994

Speight, J. *The Chemistry and Technology of Petroleum.* New York: Marcel Dekker Inc., 1999

Speight, J. *The Desulfurization of Heavy Oils and Residua.* New York: Marcel Dekker Inc., 1999

Speight, J. “Petroleum Asphaltenes Part 2: The Effect of Asphaltenes and Resin Constituents on Recovery and Refining Processes.” *Oil and Gas Science and Technology*, **59**(5): 479 – 488, 2004

Suarez, P., Dullius, J., Einloft, S., Souza, R. and Dupont, J. “the Use of New Ionic Liquids in Two-Phase Catalytic Hydrogenation Reaction by Rhodium Complexes.” *Polyhedron*, **15**(7): 1217 – 1219, 1996

Starks, C. “Phase-Transfer Catalysis I: Heterogeneous Reactions Involving Anion Transfer by Quaternary Ammonium and Phosphonium Salts.” *J. Am. Chem. Soc.*, **93**(1): 195 – 199, 1971

Starks, C. and Halper, M. *Phase-Transfer Catalysis: Fundamentals, Applications, and Industrial Perspectives*. New York: Chapman & Hall, 1994

Steynberg, A. and Dry, M. *Fischer-Tropsch Technology*, The Netherlands: Elsevier, 2004

Storey, B. and Szeri, A. “A Reduced Model of Cavitation Physics for Use in Sonochemistry.” *Proc. R. Soc. Lond.*, **457**: 1685 – 1700, 2001

Suslick, K., Didenko, Y., Fang, M., Hyeon, T., Kolbeck, K., McNamara, W., Mdleleni, M. and Wong, M. “Acoustic Cavitation and Its Chemical Consequences.” *Phil. Trans. R. Soc. Lond. A*, **357**: 335-353, 1999

Suzuki, H. and Kakinuma, K. “Formation of a TBA Reaction Product from Crown Ether in the Presence of KO_2.” *J. Biochem.*, **85**: 1547 – 1549, 1979

Thompson, L. and Doraiswamy, L. “Sonochemistry: Science and Engineering.” *Ind. Eng. Chem. Res.*, **38**(4): 1215 – 1249, 1999

Takahama, U. “Oxidation Products of Kaempferol by Superoxide Anion Radical.” *Plany Cell Physiol.*, **28**(5): 953 – 957, 1989

Takahashi, A., Yang, F. and Yang, R. “New Sorbents for Desulfurization by *ð*-Complexation: Thiophene/Benzene Adsorption.” *Ind. Eng. Chem. Res.***,** **41**: 2487-2496, 2002

Takishima, T. *Basic and Clinical Aspects of Pulmonary Fibrosis.* Florida: CRC Press, 1994

Tam, P., Kittrell, J. and Eldridge, J. “Desulfurization of Fuel Oil by Oxidation and Extraction. 1. Enhancement of Extraction Oil Yield.” *Ind. Eng. Chem Res*., **29**: 321-324, 1990

Tam, P., Kittrell, J. and Eldridge, J. "Desulfurization of Fuel Oil by Oxidation and Extraction. 2. Kinetic Modeling of Oxidation Reaction." *Ind. Eng. Chem Res.*, **29**: 324-329, 1990

Tang, H., Li, W., Liu, Q., Guan, L., Song, J., Xing J. and Liu, H. "Adsorptive Desulfurization of Diesel with Mesoporous Aluminosilicates." *Science in China Series B: Chemistry*, **52**(3): 276-281, 2009

Te, M., Fairbridge, C. and Ring, Z. "Oxidation Reactivities of Dibenzothiophenes in Polyoxometalate/H_2O_2 and Formic Acid/H_2O_2 Systems." *Applied Catalysis A*, **219**: 267 – 280, 2001

Tetsuo, A. and Yamamoto, D. "Oxidative Desulfurization of Liquid Fuels." *ACS Div. of Fuel Chem.*, **39**(2): 623 – 626, 1994

U.S. EPA. *Control of Emissions of Air Pollution from Nonroad Diesel Engines and Fuel; Final Rule.* Federal Register, **69**(124), 2004

Vanýsek, P. *Handbook of Chemistry and Physics.* Florida: CRC Press, 2006

Venkatachalapathy, C., Rajarajan, M., Banu, H. and Pitchumani, K. "Clay-Supported Tetrabutylammonium Periodate as a Versatile Oxidant for Alcohols and Sulfides." *Tetrahedron*, **55**: 4071 – 4076, 1999

Venkatadri, R. and Peters, R. "Chemical Oxidation Technologies: Ultraviolet Light/Hydrogen Peroxide, Fenton's Reagent, and Titanium Dioxide-Assisted Photocatalysis." *Hazardous Waste & Hazardous Materials*, **10**(2): 107 – 149, 1993

Voronkov, M. and Deryagina, E. "Thermal Transformations of Organic Compounds of Divalent Sulfur." *Russian Chemical Reviews*, **69**(1): 81 – 94, 2000

Wan, M. and Yen, T. "Enhance Efficiency of Tetraoctylammonium Fluoride Applied to Ultrasound-Assisted Oxidative Desulfurization (UAOD) Process." *Applied Catalysis A: General*, **319**: 237 – 245, 2007

Wan, M. and Yen, T. "Portable Continuous Ultrasound-Assisted Oxidative Desulfurization Unit for Marine Gas Oil." *Energy and Fuels*, **22**: 1130 – 1135, 2008

Wang, D., Qian, E., Amano, H., Okata, K., Ishihara, A. and Kabe, T. "Oxidative Desulfurization of Fuel Oil Part I: Oxidation of Dibenzothiophenes Using Tert-Butyl Hydroperoxide." *Applied Catalysis A: General*, **253**: 91 – 99, 2003

Wang, M. and Rajendran, V. "Kinetics for Dichlorocyclopropanation of 1,7-Octadiene under the Influence of Ultrasound Assisted Phase-Transfer Catalysis Conditions." *J. of Molecular Catalysis A: Chemical*, **273**(1-2): 5 – 13, 2007

Wasserscheid, P. and Keim, W. "Ionic Liquids – New "Solutions" for Transition Metal Catalysis." *Angewandte Chemie*, **39**(21): 3772 – 3789, 2000

Wasserscheid, P. and Welton, T. *Ionic Liquids in Synthesis.* Weinheim: Wiley, 2002

Wattana, P. and Fogler, H. "Characterization of Polarity-Based Asphaltene Subfractions." *Energy & Fuels*, **19**: 101 – 110, 2005

Willis, P. *Watching the Directives: Scientific Advice on the EU Physical Agents (Electromagnetic Fields) Directive.* London: the Science and Technology Committee, 2007

Wypych, G. *Handbook of Solvents*, New York: ChemTec Publishing, 2001

Yan, X., Lei, J., Liu, D., Guo, L. And Wu, Y. "Oxidation Reactivities of Organic Sulfur Compounds in Fuel Oil Using Immobilized Heteropoly Acid as Catalyst." *Journal of Wuhan University of Technology-Mater. Sci.*, **22**(2): 320 – 324, 2007

Yasui, K. "Light Emission Mechanism of Sonoluminesence." *Bussei Kenkyu*, **72**(3): 337 –344, 1999

Yazici, E., Deveci, H., Alp, I. and Uslu, T. "Generation of Hydrogen Peroxide and Removal of Cyanide from Solutions Using Ultrasonic Waves." *Desalination*, **216**: 209 – 221, 2007

Yazu, K., Makino, M. and Ukegawa, K. “Oxidative Desulfurization of Diesel Oil with Hydrogen Peroxide in the Presence of Acid Catalyst in Diesel Oil/Acetic Acid Biphasic System.” *Chemistry Letters*, **33**(10): 1306 – 1307, 2004

Yen, T. “Correlation between Heavy Crude Sources and Types and Their Refining and Upgrading Methods.” *Petroleum Industry Press*, **2**: 2137 – 2144, 1998

Yen, T. “Structure of Petroleum Asphaltene and Its Significance.” *Energy Sources A*, **1**(4): 447 – 463, 1974

Yen, T, Mei, H. and Lu, S. “Oxidative Desulfurization of Fossil Fuels with Ultrasound.” *U. S. Patent Application*, 2000

Young, F. *Sonoluminescence.* Florida: CRC Press, 2005

Yu, B., Xu, P., Shi, Q. and Ma, C. “Deep Desulfurization of Diesel Oil and Crude Oils by a Newly Isolated Rhodococcus erythropolis Strain.” *Appl. Environ. Microbiol.*, **72**(1): 54-58, 2006

Zhang, S., Zhang, Q. and Zhang, Z. “Extractive Desulfurization and Denitrogenation of Fuels Using Ionic Liquids.” *Ind. Eng. Chem. Res.*, **43**: 614 – 622, 2004

Zhao, D., Liao, Y. and Zhang, Z. “Toxicity of Ionic Liquids.” *Clean – Soil, Air, Water,* **35**(1): 42 – 48, 2007

Zapata, B., Pedraza, F. and Valenzuela, M. “Catalyst Screen for Oxidative Desulfurization using Hydrogen Peroxide.” *Catalysis Today*, **106**: 219 – 221, 2005

Zhou, L. *Adsorption: Progress in Fundamental and Application Research.* New Jersey: World Scientific Publishing Co., 2007