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CATALYTIC OXIDATION OF BENZOTHIOPHENES WITH HYDROGEN PEROXIDE

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ชลดา โกมินทรชาติ : ออกซิเดชันแบบเร่งปฏิกิริยาของสารกลุ่มเบนโซไทโอฟีนด้วยไฮโดรเจนเปอร์ออกไซด์ (CATALYTIC OXIDATION OF BENZOTHIOPHENES WITH HYDROGEN PEROXIDE) อ.ที่ปรึกษา: รศ.ดร. วิมลรัตน์ ตระการพฤกษ์, 91 หน้า. ISBN 974-17-4892-2

ในงานวิจัยนี้ ได้ศึกษาออกซิเดชันของสารต้นแบบซัลเฟอร์เร่งปฏิกิริยาด้วยตัวเร่งปฏิกิริยาที่มีวานาเดียมและใช้ไฮโดรเจนเปอร์ออกไซด์เป็นสารออกซิไดซ์ สารประกอบซัลเฟอร์ที่ศึกษาได้แก่ เบนโซไทโอฟีน ไดเบนโซไทโอฟีน 4,6-ไดเมทิลไดเบนโซไทโอฟีนซึ่งกำจัดออกได้ยากจากน้ำมันดีเซล เตรียมตัวเร่งปฏิกิริยา $[W_6O_{19}]^{2-}$, $[V(VW_{11})O_{40}]^{4-}$, $[PVW_{11}O_{40}]^{4-}$, $[PVMo_{10}O_{40}]^{4-}$ และ $(VO)_2P_2O_7$ และตรวจสอบเอกลักษณ์ด้วยเทคนิค FTIR UV-Vis และ XRD ผลการทดลองแสดงให้เห็นว่าตัวเร่งปฏิกิริยาที่มีวานาเดียมเร่งปฏิกิริยาการเปลี่ยนรูปของสารประกอบซัลเฟอร์ไปเป็นซัลโฟน โดยลำดับของการเร่งปฏิกิริยาเป็น $[V(VW_{11})O_{40}]^{4-} > [W_6O_{19}]^{2-} > [PVW_{11}O_{40}]^{4-} \sim [PVMo_{10}O_{40}]^{4-} > (VO)_2P_2O_7$ ศึกษาพารามิเตอร์ที่มีผลต่อปฏิกิริยาได้แก่ ตัวทำละลาย ปริมาณของตัวเร่งปฏิกิริยา ปริมาณสารออกซิไดซ์ การเติมกรดอะซิติกและอุณหภูมิ เมื่อเพิ่มอัตราส่วนของกรดอะซิติกต่อไฮโดรเจนเปอร์ออกไซด์เป็น 1.5 ปฏิกิริยาการเปลี่ยนรูปของซัลเฟอร์เพิ่มขึ้น โดยมีค่าพลังงานก่อกัมมันต์ของไดเบนโซไทโอฟีน ไดเมทิลไดเบนโซไทโอฟีนและเบนโซไทโอฟีน เป็น 52.83, 57.35 และ 62.73 กิโลจูลต่อโมล ตามลำดับ โดยสัมพันธ์กับความว่องไวในการเกิดปฏิกิริยาที่ ไดเบนโซไทโอฟีน > ไดเมทิลไดเบนโซไทโอฟีน > เบนโซไทโอฟีน เพิ่มประสิทธิภาพในการกำจัดสารประกอบซัลเฟอร์หลังจากออกซิเดชันด้วยการสกัดด้วยตัวทำละลายและการดูดซับ พบว่าลดปริมาณซัลเฟอร์ในน้ำมันดีเซลจาก 0.575 เป็น 0.055 % โดยน้ำหนัก

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต Cholada Kominatarachat
ปีการศึกษา..................2548.............................ลายมือชื่ออาจารย์ที่ปรึกษา W. Trakarnpruk

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CHOLADA KOMINTARACHAT : CATALYTIC OXIDATION OF BENZOTHIOPHENES WITH HYDROGEN PEROXIDE. THESIS ADVISOR: ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph.D. 91 pp. ISBN 974-17-4892-2

In this work, the oxidation of sulfur model compounds catalyzed with vanadium containing catalysts were studied. The sulfur compounds studied are: benzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene that are typical refractory sulfur compounds in diesel fuels. The catalysts $[W_6O_{19}]^{2-}$, $[V(VW_{11})O_{40}]^{4-}$, $[PVW_{11}O_{40}]^{4-}$, $[PVMo_{10}O_{40}]^{4-}$ and $(VO)_2P_2O_7$ were prepared and characterized by FT-IR, UV-Vis and XRD. The experimental results show that vanadium containing catalysts catalyze the conversion of sulfur compounds to sulfone and the reactivity order of the catalyst is: $[V(VW_{11})O_{40}]^{4-} > [W_6O_{19}]^{2-} > [PVW_{11}O_{40}]^{4-} \sim [PVMo_{10}O_{40}]^{4-} > (VO)_2P_2O_7$. Parameters affecting the reaction were investigated: solvent, amount of catalyst, amount of oxidizing agent, addition of acetic acid and temperature. When the mole ratio of $[AcOH]/[H_2O_2]$ was increased up to 1.5, the oxidation activity was increased. Apparent activation energies of dibenzothiophene, 4,6 dimethyldibenzothiophene and benzothiophene oxidation were 52.83, 57.35 and 62.73 kJ/mol, respectively, which related to the reactivity of dibenzothiophene > 4,6-dimethyldibenzothiophene > benzothiophene. The removal of oxidized sulfur by combining extraction and adsorption became more effective. The results show that the catalysts can reduce the sulfur content of diesel fuels from 0.575 wt% to 0.055 wt%.

Field of study Petrochemistry and Polymer science Student's signature Cholada Komintaracha

Academic year..............2005..................... Advisor's signature W. Trakarnpruk

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LIST OF ABBREVIATIONS

M	metal
bp.	boiling point
^{o}C	degree Celsius
mmol	millimole
cm^{-1}	unit of wavenumber
ml	milliliter
g	gram(s)
M	molar
$CDCl_3$	deuterochloroform
^{1}H-NMR	proton nuclear magnetic resonance
h	hour(s)
IR	Infrared
TAML	tetraamidomacrocyclic ligand
TBHP	*tert*-butylhydroperoxide

CHAPTER I

INTRODUCTION

Environmental concerns are forcing dramatic changes in motor fuel specifications. It is clear today that motor fuel quality will continue to be modified to improve both combustion quality and post-combustion gas clean-up performance. Petroleum oils used as feedstocks for diesel oils are middle distillates in the 180-400 °C boiling range. They include straight run gas oil, largely paraffinic, ranging from light gas oil to heavy gas oil that usually contain from 1 to 3 wt% sulfur. Various processes are used to upgrade heavier petroleum fractions to highly aromatic. The sulfur compounds present in the various oils are mostly aliphatic sulfides, benzothiophenes and dibenzothiophenes.

The need for cleaner burning fuels has resulted in a continuing worldwide effort to reduce the sulfur levels in gasoline and diesel fuels. The reduction of gasoline and diesel sulfur has been considered to be an important means for improving air quality because of the negative impact fuel sulfur has on the performance of automotive engine exhaust inhibitors and may irreversibly poison noble metal catalysts in the converter. Emissions from an inefficient or poisoned converter contain levels of non-combusted, non-methane hydrocarbons and oxides of nitrogen and carbon monoxide. Such emissions are catalyzed by sunlight to form ground level ozone, more commonly referred to as smog. With the concern over the impact of automotive air pollution continuing, it is clear that further efforts to reduce the sulfur levels in automotive fuels will be required

Sulfur content in diesel fuel is an environmental concern because upon combustion, sulfur is converted to SO_x during combustion, which not only contributes to acid rain, but also poisons the catalytic converter for exhaust emission treatment. The main sources of $SO_{2(g)}$ emissions are the burning of fossil fuels (e.g., power plants and mobile sources) and the smelting of ores rich in sulfur. In the atmosphere, $SO_{2(g)}$ can react with various oxidants (e.g., O_2, O_3, H_2O, NO_X, OH radicals) to form sulfate aerosol, either as sulfuric acid droplets, or as neutralized particles such as ammonium sulfate, which play special role in atmospheric processes like acid rain and visibility degradation. Sulfur in petroleum products poisons catalytic converters, corrodes parts of internal combustion engines and refineries because of the formation of oxyacid of sulfur, and air pollution due to exhaust from diesel engines is a major concern to the public. The Ministry of Energy of Thailand has limited the sulfur level in diesel fuel to 350 ppm in 2004. Recently, legislation has been introduced to reduce the level of permitted sulfur in diesel fuel. Table 1 shows worldwide trend of sulfur limitation in diesel.

Table 1. Diesel sulfur specification (ppm)

Year	Japan	Europe	USA	Thai
1993	-	-	500	-
1996	-	-	-	500
1997	500	500	-	-
1999	-	-	-	-
2000	-	-	-	-
2004	50	350	-	350
2005	15	50	-	-
2006	-	-	15	-
2009	-	10	-	-

In the petroleum refining industry, hydrodesulfurzation (HDS) is currently used for reducing the sulfur content of the liquid products. However, this process is not cheap for several reasons. One of them is the hydrogen pressure needed for kinetic and catalyst stability purposes. Another reason is related to benzothiophene or dibenzothiophene compounds that constitute very refractory molecules in the process, resulting in significant difficulty in achieving the very low sulfur content presently required in the liquid fuel. The effectiveness of the HDS process depends on the type of sulfur compound. The complete removal of sulfur present in petroleum as sulfides, disulfide and mercaptans is relatively easy and an inexpensive process. However, benzothiophenes and dibenzothiophenes (DBTs) are difficult to remove by this process. Most of sulfur contamination in petroleum can be traced to the dibenzothiophene derivatives. In order to remove these compounds by HDS, it would require more hydrogen capacity and the maintenance of high temperature and pressure for longer time periods. This would increase operating costs and enhance the likelihood that saturation of olefins and aromatics will occur resulting in a lower-grade fuel and additional processing steps. Thus, it is likely that HDS processing has reached a stage where increasing temperature and pressure are just not enough to remove the residual sulfur without affecting the octane number. This process also produces increased volumes of hydrogen sulfide. Although HDS processes have dominated desulfurizaton of petroleum in the past, their cost and the requirements of strict fuel specifications combine to motivate the development of innovative process technology. All of these methods incur a cost penalty and this stimulated our interest in alternative form of desulfurization.

Oxidative desulfurization (ODS) is considered to be one of the promising new methods for deep desulfurization of fuel oil. Compare with the conventional catalytic hydrodesulfurization (HDS), ODS can be carried out under very mild condition: at room temperature and under atmospheric pressure. The divalent sulfur of dibenzothiophene (DBTs) can be oxidized by the electrophilic addition reaction of oxygen atom to the hexavalent sulfur of sulfones. The chemical and physical properties of sulfones are significantly different from those of hydrocarbon fuel oil. Therefor, they can easily removed by such separaion operations as distillation, solvent extraction, adsorption, and decomposition. Many different type of oxidants have been used, including HNO_3/AcOH, NO/NO_2, NO_2, HNO_3, H_2O_2/H_2SO_4, *t*-BuOOH and O_3. The objective of oxidation have been varied in that some have been aimed at desulfurization while other have aimed at cetane number enhancement. Use of nitrogen oxides as oxidizing agent can have the double effect of oxidizing the sulfur compounds present in the oil: nitroaromatics are thought to have high cetane number. However, reaction selective, safety and cost are the important concerns for the selection of oxidant, catalyst and operating conditions for ODS processing. The advantage of the ODS process that expensive hydrogen is not used. Another feature of ODS is that the refactory sulfur compounds in HDS are easily converted by oxidation.

Polyoxometalates (POMs) are well known as oxidation and acid catalysts in which the redox and acid-base properties can be tuned by variation of the structure type, the central heteroatom or transition-metal. The catalytic function of the Keggin type, the kinds of metal substituted polyoxometalate structures has attracted much attention particularly because these compounds provide a good basis for the molecular design of mixed oxide catalysts and high capabilities in practical uses. The free acids are less stable than the salts but can be obtained in structurally better defined samples. There are several large-scale industrial processes that use heteropolyoxometalates as oxidation and acid catalysts both in the solid state and in solution. Heteropoly catalysts are promising green catalysts since most of them are environment friendly.

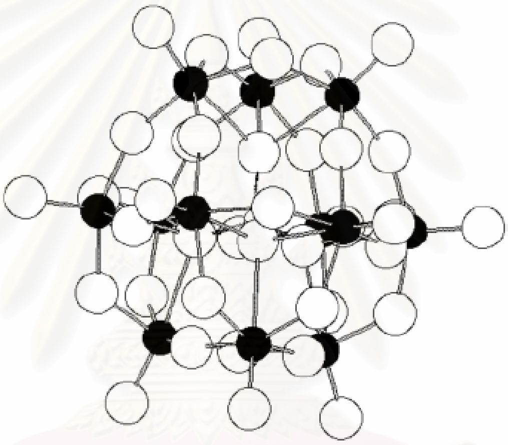


Fig. 1. Keggin structure of polyoxometalate. Black ball = Mo, W, V; white ball = O; P in center (not visible).

The liquid-liquid extraction bi-phase is system of the perspective ways of homogeneous catalysis in industry. This is a combination of phase transfer and metal complex catalysis. So, the substrate and reaction products are dissolved in organic phase and catalyst is presented in water phase. After the reaction proceeds to completion, the water phase can be easily removed and can be repeatedly used with the activity retention of catalyst. The liquid-liquid extraction procedure is based on the selective partitioning of a desired solute into a particular phase in order to recover it. The two liquids are immiscible on account of their large difference in hydrophobicity. The extraction occurs because of the relative affinity of the solute for the hydrophobicity or electric potential of the two phases and can be facilitated by the addition of salting or complexing agents or by chemical reaction.

This thesis involves oxidation of sulfur compounds in the presence of vanadium containing catalysts. Various reaction parameters, which influence the oxidation of sulfur model compounds are investigated. In addition, the selective tranformation of dibenzothiophenes contained in diesel fuels is also demonstrated.

1.2 The Objectives of Thesis

The objectives of thesis can be summarized as follows:

1. To synthesize and characterize vanadium containing catalysts
2. To optimize condition for the oxidation of sulfur model compounds (benzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene) using the prepared catalysts.
3. To utilize the resulting oxidation condition for diesel fuels.
4. To study kinetics of sulfur model compounds

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Sulfur compounds in crude oil

The chemical compositions of crude oil are uniform even though their physical characteristic vary widely. The elementary composition of crude oil usually falls within the following ranges in Table 2.1.

Table 2.1 Elementary composition of crude oil

Element	% wt
Carbon	84 – 87
Hydrogen	11 – 14
Sulfur	0 – 3
Nitrogen	0 – 0.6

Sulfur content and API gravity are two properties, which have had the greatest influence on the value of crude oil, although nitrogen and metal contents are increasing in importance. The sulfur content is expressed as percent sulfur by weight and varies from less than 0.1% to greater than 5%. Sulfur is the heteroatom frequently found in crude oil. Sulfur concentration can range from 0.1% to greater than 8% by weight; moreover, this content is correlated with the gravity of the crude oil and, therefore, its quality (light or heavy oil)

The sulfur compounds found in petroleum or synthetic oils are generally classified into two types: heterocycles and nonheterocycles. The latter comprises thiols, sulfides and disulfides. Heterocycles are mainly composed of thiophenes with one to several rings and their alkyl or aryl substituents. Examples of sulfur compounds are shown in Table 2.2.

Table 2.2 The common types of sulfur compounds in crude oil

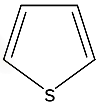
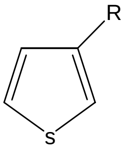
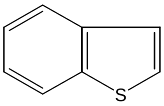
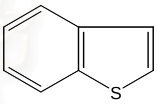
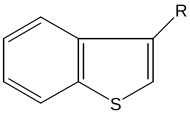
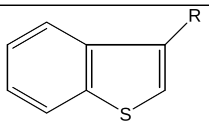
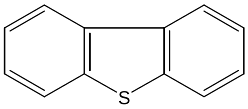
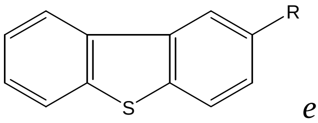
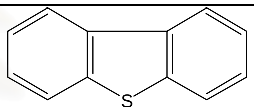
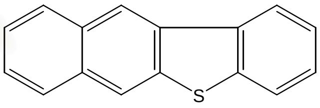
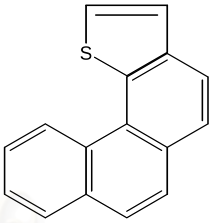
Common types	Compound class	Structure
Gasoline range: Naphtha, Fluid Catalytic Cracking (FCC)	mercaptanes	RSH
	sulfides	RSR′
	disulfides	RSSR′
	thiophene and its alkylated derivatives benzothiophene	  *etc.* 
Jet fuel range: heavy naphtha, middle distillate	benzothiophene (BT) and its alkylated derivatives	  *etc.*

Table 2.2 The common types of sulfur compounds in crude oil (Cont.)

Common types	Compound class	Structure
Diesel fuel range middle distillate, Light Cycle Oil (LCO)	alkylated benzothiophenes dibenzothiophene (DBT) and its alkylated derivatives	   *etc.*
Boiler fuels feeds: heavy oils, distillates	≥3-ring polycyclic sulfur compounds, including DBT, benzonaphtho-thiophene (BNT), phenanthro[4,5,b,c,d]thiophene (PT), and their alkylated derivatives	   *etc.*

International regulations on emission control will soon require reducing the sulfur content in fuels and distillates to less than 300 ppm. Under this incentive, intense research efforts are currently being directed to the development of more efficient or alternative routes to improve gasoline quality by reducing the content of sulfur without making significant changes in octane rating. Major source of aromatic sulfur compounds in gasoline are coking and cracking naphtha. In the latter, the content of sulfur may be as high as 1300 ppm with a 2:1 predominance of benzothiophene over thiophene.

2.1.2 Oxidizing agents [1]

Air, the cheapest oxidant, is used only rarely without irradiation and without catalysts. Examples of oxidations by air alone are the conversion of aldehydes into carboxylic acid (autoxidation). Usually, exposure to light, irradiation with ultraviolet light, or catalysts are needed.

Oxygen (O_2), exists in two states. Stable ground-state oxygen (triplet oxygen) has two odd electrons with parallel spins. It behaves like a diradical and is paramagnetic. In excited-state oxygen (singlet oxygen), the two odd electrons possess antiparallel spins. Such a molecule is unstable, with a half-life of 10^{-6} s, and is diamagnetic. Each form reacts differently with organic molecules.

Ozone (O_3), a blue gas or a dark blue liquid (bp. –106,-116 or –125^{o}C, depending on the source of data), is used in a mixture with oxygen. Ozonizations are carried out by passing ozone-containing oxygen through solution of organic compounds in solvent that do not react with ozone and liquid at low temperature. Cooling with dry ice-acetone bath (-78^{o}C) is frequently needed to prevent the decomposition of ozone, some of which are unstable at room temperature. The most common solvents are pentane, cyclohexane, dichloromethane, chloroform, methanol, acetic acid, and ethyl acetate.

Hydrogen peroxide (H_2O_2), an effective oxidant that could be used in many industrial processes. Because the only by-product of oxidation using hydrogen peroxide is water, it could become the ultimate green chemical for the manufacture of many oxygenated petrochemicals. However, the current method for producing is inefficient and too costly. It is commercially available in aqueous solutions of 30% or 90% concentration. The 30% hydrogen peroxide is a colorless liquid (*d* 1.110) and it is stabilized against decomposition, which occurs in the presence of traces of iron, copper, aluminum, platinum, and other transition metals. The 30% hydrogen peroxide does not mix with nonpolar organic compounds.

The 90% hydrogen peroxide is stable at 30°C (the decomposition rate is 1%/year), it decomposed slowly at high temperatures and rapidly with boiling at 140°C. The pure hydrogen peroxide solution is stable with weak decomposition. However, when it comes in contact with heavy metals or various organic compounds, or mixes with impurities, it produces oxygen gas and decomposition heat. When formic or acetic acid is used, the reacting species is the corresponding peroxy acid. Under such conditions, the products of oxidation by hydrogen peroxide resemble those obtained with peroxy acid.

***Tert*-butyl hydroperoxide ($(CH_3)_3COOH$),** a commercially available as a 70% or 90% solution containing water and *tert*-butyl alcohol. It must be handled with extreme care, because it may decompose violently in present of strong acid and some transition metals, especially manganese, iron, and cobalt. Oxidation with *tert*-butyl hydroperoxide consists of epoxidation of alkene in the presence of transition metals. In this way, α,β-unsaturated aldehyde and ketone are selectively oxidized to epoxide without the involvement of the carbonyl function. Other applications of *tert*-butyl hydroperoxide are the oxidation of lactam to imide, of tertiary amine to amine oxide, and of phosphite to phosphate. In the presence of a chiral compound, enantioselective epoxidation of alcohol is successfully accomplished with moredate to high enantiomeric excesses.

Peroxyformic acid (performic acid), HCO_3H, is always prepared *in situ* from hydrogen peroxide and formic acid. A much rare application of performic acid is the transformation of 2- or 4-dialkylaminoperhalopyridines into either amine oxides or N,N-dialkylhydroxylamines.

Peroxyacetic acid (peracetic acid), CH_3CO_3H, can be formed *in situ* from hydrogen peroxide with acetic acid. The most important applications of peroxyacetic acid are the epoxidation and anti hydroxylation of double bones, of tertiary amines to amine oxide, of sulfides to sulfoxides and sulfones, of iodo compounds to iodoso or iodoxy compounds, of alcohol to ketones, and of lactams to imides.

Peroxybenzoic acid (POB), RCO_3H, can be formed *in situ* by oxidation of benzaldehyde in the presence of ultraviolet light. It selectively oxidized dlbenzothiophene (DBT) to sulfoxide (DBTO) and sulfone ($DBTO_2$) under mild conditions.

Sodium hypochorite, NaOCl, is a potent oxidizing agent that has been shown to transfer oxygen atom. However, the insolubility of hypochlorite salts in hydrocarbons and organic solvents has prevented the use of this material as a reagent for the selective oxidation of organic substrates.

2.1.3 Homogeneous and heterogeneous catalysts

Homogeneous catalyst is in the same phase as the reactants, which provides a good contact with reactants so a more effective concentration can be achieved. Homogeneous catalyst has high selectivity. The disadvantage of this type of catalyst is separation which usually involves distillation. In some cases this makes catalyst recovery difficult because the high temperature can destroy the catalyst, and aggregation of catalyst to form dimer or multi-nuclear cluster, leading to the loss of catalytic activity [2].

Heterogeneous catalyst is in a different phase from the reactants. Reactants might be gas or liquid and the catalyst is a solid. Separating and recycling of the catalyst are facile. The solid catalysts are generally easier and safer to handle than liquid or gaseous ones. Good dispersion of active sites can lead to significant improvements in reactivity. However, the reaction rate is generally slow because reaction occurs only on the exposed active surface and often requires vigorous condition. Table 2.3 compares major differences between homogeneous and heterogeneous catalysis systems.

Table 2.3 Major differences between homogeneous and heterogeneous catalys

	Homogeneous	Heterogeneous
Active centers	all metal atoms	only surface atoms
Concentration used	low	high
Selectivity	high	low
Diffusion problems	practically absent	present
Reaction condition	mild (50-200^{o}C)	severe (> 250^{o}C)
Application	limited	wide
Activity loss	irreversible reaction with products (cluster formation) ; poisoning	sintering of the metal crystallites; poisoning
Catalyst properties		
Structure/stoichiometry	defined	undefined
Modification possibilities	high	low
Thermal stability	low	high
Catalyst separation	sometimes laborious (chemical decomposition, distillation, extraction)	fixed-bed: unnecessary suspension: filtration
Catalyst recycling	possible	unnecessary
Cost of catalyst losses	high	low

2.2 Literature reviews

2.2.1 Catalyst for oxidation of sulfur compounds

2.2.1.1 Acid as catalyst

In 1990, Tam *et al.* [3] investigated the oxidative-desulfurization (ODS) process to remove sulfur from diesel oils. This ODS process comprises two stages at ambient conditions: oxidation using nitrogen dioxide or nitric acid followed by liquid extraction with solvents having the capability to dissolve aromatics and olefinic compounds. γ-Butyrolactone is one of the best solvents. The extraction efficiency for atmospheric gas oil (AGO) was improved by proceeding the extraction with oxidation. For a given sulfur compound removal, the extraction results from oxidized oil showed higher extraction oil yield than the unoxidized oil. This oil yield enhancement was due to the oxidation which changed the sulfur compound such that they were more readily extracted by aromatic/ olefinic dissolving solvents. The distribution coefficients of extraction for several sulfur compounds identified in the AGO were increased by over 100% when the oil was oxidized.

In 1995, Zannikos *et al.* [4] reported the ability of several solvents to extract sulfur compounds selectivity from petroleum fractions. The sulfide was oxidized to the hexavalent (sulfone). The oxidation process itself leads to the removal of a substantial portion of the exitsting sulfur and makes the remaining sulfur compounds amenable to efficient removal by methanol which is not effective in extraction of the unoxidized sulfur compounds. Thus this combinations process is capable of removing up to 90% of the sulfur compounds in petroleum fractions at acceptable yields. The oxidation process has no deleterious effects on the distillation profile and other characteristics of the middle distillate fractions.

In 2000, Otsuki *et al.* [5] investigated the oxidation of model sulfur compounds (thiophene, benzothiophene and dibenzothiophene), straight run-light gas oil (SR-LGO, S: 1.35 wt%) and vacuum gas oil (VGO, S: 2.17 wt%). The reaction was conducted with a mixture of hydrogen peroxide and formic acid. The thiophene could not be oxidized at 50^{o}C while benzothiophene and dibenzothiophene with higher electron density can be oxidized. The sulfur compounds in SR-LGO and VGO appeared to be oxidized to a detectable levels (c.a., 0.01 wt% S) by GC-FPD analysis. The IR spectra of oxidized SR-LGO and VGO showed the formation of sulfones. The removal of sulfur compounds by extraction became more effective for the oxidized samples than for the original samples. The effective solvent was dimethylformamide (DMF), but the recovery of oil was low.

In 2002, Shiraishi *et al.* [6] investigated the desulfurization process for light oils based on the chemical oxidation of sulfur-containing compounds using hydrogen peroxide and acetic acid as oxidizing agent. The sulfur compounds dissolved in n-tetradecane were oxidized under moderate conditions and were removed successfully. By use of this process sulfur content failed to be reduced to the required deep desulfurization level (0.05 wt%). This is because the alkyl-substituted sulfones, produced during the oxidation of sulfur compounds, remain in the resulting light oils, owing to their high hydrophobicity. These, however, may be removed from the light oils by subsequent extraction, using an acetonitrile/water azeotropic mixture. The sulfur contents of the light oils were decreased to < 0.05 wt%, while maintaining a high oil recovery yield.

In 2002, Rappas *et al.* [7] investigated the process for desulfurizing hydrocarbons such as gasoline and similar petroleum products to reduce the sulfur content to a range from about 2 to 15 ppm sulfur without affecting the octane rating. The reaction was performed at slightly elevated temperatures with an oxidizing/extracting solution of formic acid and a small amount of hydrogen peroxide. The organic sulfones were removed by adsorption on alumina and eluted by hot methanol.

In 2004, Shiraishi *et al.* [8] investigated the oxidative desulfurization of vacuum gas oil (VGO) using H_2O_2 and acetic acid, followed by extraction of the oxidized compounds using an aqueous acetonitrile solution. The desulfurization behavior of VGO was compared with that of light oil feedstocks. By use of the desulfurization process, the sulfur content of the VGO was decreased to less than 11% of the corresponding feed values, and the desulfurization yield of the VGO was significantly higher than that of light oils. This is because polyaromatic thiophenes in the VGO that possess at least one naphthenic ring adjacent to the thiophenic ring have higher electron density on the sulfur atom than the sulfur compounds contained in light oils, and are oxidized more effectively.

2.2.1.2 Transition metal

In 1989, James *et al.* [9] studied the use of sodium hypochlorite (NaOCl) as a synthetically useful oxidizing agent for the oxidation of lipophilic organic sulfide substrates employing phase-transfer catalysis (PTC). The PTC results in nearly complete oxidation of the substrate in 20 min, with high selectivity to the sulfoxide, compared to 5 h in its absence. Kinetic studies show the reaction occurs via transfer of

$OC1^-$ into the organic phase. Under certain conditions the transfer is rate limiting. The addition of a transition metal catalyst (tetraphenylporphine manganese chloride, TPPMnCl) further increased the rate and led to the complete conversion of the sulfide to the sulfone.

In 1996, Brown and Espenson [10] investigated the oxidation of thiophene derivatives with hydrogen peroxide/methyltrioxorhenium (VII) (CH_3ReO_3). The 1:1 and 1:2 rhenium peroxides formed, transfers an oxygen atom to the sulfur atom of thiophene derivatives. Complete oxidation to the sulfone occurs readily by way of its sulfoxide intermediate. The rates for each oxidation step of dibenzothiophenes, benzothiophenes, and substituted thiophenes were determined. The rate constants for the oxidation of the thiophenes are 2-4 orders of magnitude smaller than those for the oxidation of aliphatic sulfides, whereas the rate constants are generally the same for the oxidation of the thiophene oxides and aliphatic sulfoxides. The rate constant for conversion of a sulfide to a sulfoxide increases when a more electron-donating substituent is introduced into the molecule, whereas the opposite trend was found for the reaction that converts a sulfoxide to a sulfone.

In 1997, Collins *et al.* [11] studied the oxidation of dibenzothiophene with hydrogen peroxide using phosphotungstic acid as catalyst and tetrabutyl-ammonium bromide as a phase transfer agent in a mixture of water and toluene. At a suitable condition, yields of dibenzothiophene sulfone approached 100%. Treament of gas oils with this catalyst system shows that all the sulfur compounds present are oxidized and highly substituted dibenzothiophenes are the most readily oxidized. Furthermore, oxidized sulfur compounds can be separated from the oil by adsorption on silica gel.

In 2001, Hulea *et* al. [12] investigated the sulfoxidation of aromatic sulfur compounds with hydrogen peroxide (H_2O_2) and Ti-containing molecular sieves as catalysts. It has been shown that the large pore catalytic materials, such as Ti-beta and mesoporous Ti-HMS (hexagonal mesoporous silica), are active for the selective oxidation of thiophenee derivatives to the corresponding sulfones, whereas the medium pore zeolites TS-1 (titanium silicalite) is totally inactive in the oxidation of polyaromatic sulfur compounds. For fuels, the best result was obtained using acetonitrile as solvent which is immiscible with the fuels. The polyaromatic sulfur compounds (benzo- and dibenzothiophene derivatives) are oxidized into their corresponding sulfoxides and sulfones which are then removed by simple liquid–liquid separation.

In 2001, Te *et al.* [13] studied the oxidation reactivities of dibenzothiophenes in toluene solution with a series of polyoxometalate/H_2O_2 system. The H_2O_2 solutions of phosphotungstic acid and its salt were very active catalyst systems for the model compound oxidation, while their molybdenum counterpart systems were much less active. The H_2O_2 solutions of silicotungstic and silicomolybdic compounds were the least active catalyst systems. Oxidation reactivities decreased in the order of dibenzothiophene > 4-methyldibenzothiophene > 4,6-dimethyldibenzothiophene. However, the oxidation of the dibenzothiophene was achieved under mild reaction conditions and it was easy to increase reaction temperature or reaction time to achieve high conversions. Interestingly, in a formic acid/H_2O_2 system, the oxidation reactivity of the dibenzothiophene showed the reverse trend, suggesting that steric hindrance might play a role when bulky polyoxoperoxo species, which likely forms in a hydrogen peroxide solution, acts as catalyst.

In 2001, Sato *et al.* [14] reported the oxidation of aromatic and aliphatic sulfides in chlorohydrocarbon solvent to sulfones via the sulfoxides intermediates with various tungsten (W) catalysts such as H_2WO_4, $Na_2WO_4.2H_2O$ and 30wt% H_2O_2 and a quaternary ammonium salt as a phase-transfer catalyst. Both systems with phosphonic acid ($C_6H_5PO_3H_2$) as promoter gave product as diphenyl sulfone in 72%. The reaction proceeds more rapidly at higher temperatures with lower catalyst loading. Under the aqueous/organic biphase conditions sulfone was obtained in 96% yield. The oxidation can also be performed with hexane, toluene, or ethyl acetate as co-solvent.

In 2002, Hangun *et* al. [15] developed a series of iron(III) complexes called TAML$^{@}$ (for Tetra Amino Macrocyclic Ligand) activators that enhance the oxidizing ability of hydrogen peroxide at low catalyst concentration and mild reaction conditions. The general structure of TAML$^{@}$ activators is shown in Figure 1. The R and X groups are used to control activator reactivity, selectivity and lifetime. They are non-toxic and are most effective at very low concentration (1-5 μM). Micromolar concentration of FeF_2B and H_2O_2 converted > 99% of dibenzothiophene derivatives to the corresponding sulfones under mild conditions.

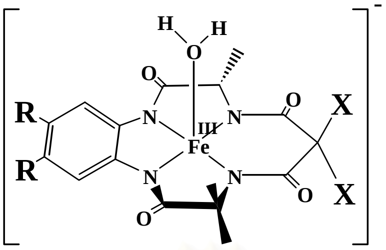


Figure 2.1. Structure of TAML activators.

In 2003, Yazu *et al.* [16] reported that the dibenzothiophenes are oxidized effectively with hydrogen peroxide in the presence of 12-tungstophosphoric acid (TPA) in tetradecane/acetonitrile (MeCN) and tetradecane/acetic acid (AcOH) biphasic system to sulfones. The oxidation proceeds in the aqueous phase and sulfones do not migrate into the oil phase. 4,6-Dimethyldibenzothiophene, one of the most unreactive sulfur compounds during hydrodesulfurization, was also oxidized and removed effectively from the oil phase. The rates of removal of dibenzothiophene sulfones in the tetradecane/AcOH system were larger than those in the tetradecane/MeCN.

In 2003, Anisimov *et al.* [17] investigated the oxidation of sulfur organic compounds and diesel fuel desulfurization catalyzed by vanadium peroxo complexes/hydrogen peroxide in biphase system. All vanadium complexes show high activity in oxidation of diphenylsulfide and phenylbenzyl sulfide to the corresponding sulfoxides. The oxidation of diesel fuel (S: 0.86 wt.%) with this catalyst system reduces the amount of sulfur in the fuel to 0.2 wt%.

In 2003, Shiraishi *et al.* [18] investigated the oxidative desulfurization process for light oil using a vanadosilicate molecular sieve as the catalyst and H_2O_2 as the oxidizing agent. The catalytic activities for three kinds of vanadosilicates, having different structures and pore-size distributions, were compared with those for the corresponding titanosilicates. The oxidation of dibenzothiophene and benzothiophene in acetonitrile was catalyzed more effectively by vanadosilicates than titanosilicates, where the mesoporous vanadosilicate showed the highest activity. The vanadosilicate also accelerated the desulfurization of the actual light oil in an oil/acetonitrile two-phase system: the sulfur content of the oil was decreased successfully from 425 ppm to less than 50 ppm. The vanadosilicate, recovered following the reaction, could not be reused for further treatment of light oil. This is owing to the dissolution of vanadium species in the silica framework into the acetonitrile solution.

In 2003, Wang *et al.* [19] investigated the oxidation of sulfur compounds in kerosene, conducted with *t*-BuOOH in the presence of various catalysts. The oxidation activities of dibenzothiophene (DBT) in kerosene for a series of Mo catalysts supported on Al_2O_3 were estimated. The results show that the oxidation activity of DBT increased with increasing Mo content up to about 16wt% and decreased when Mo content was beyond this value. The oxidation of benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) dissolved in decalin was also carried out on 16wt% Mo/Al_2O_3 catalyst with *t*-BuOOH. The results showed the order of oxidation reactivities of these sulfur compounds: DBT > 4-MDBT > 4,6-DMDBT >> BT. The oxidation of sulfur compound is a first-order reaction.

In 2004, Murata *et al.* [20] investigated the oxidative desulfurization of diesel fuels with molecular oxygen using cobalt salts and aldehydes. A mixture of benzene, dibenzothiophene, n-octanal, and cobalt acetate or chloride was stirred at 40 °C under atmospheric pressure of oxygen to afford dibenzothiophene sulfone in almost quantitative yield within 15 min. Dibenzothiophene sulfone produced could be easily removed from the model oils by silica or alumina adsorption. Several organic sulfides including thioanisole, diphenyl sulfide, benzothiophene, and 4,6-dimethyldibenzothiophene also converted to the corresponding sulfones in almost quantitative yields. Sulfur-containing compounds in the diesel fuel were oxidized, removed by alumina adsorption and/or solvent extraction. The resulting oil contained less than 5 ppm of sulfur (more than 97% sulfur removal). The mechanism is shown in Scheme 2.1

$$\mathrm{RCHO} + \mathrm{DBT} + 3/2\mathrm{O_2} \longrightarrow \mathrm{RCO_2H} + \mathrm{DBTO_2}$$

$$\mathrm{RCHO} + \mathrm{O_2} \longrightarrow \mathrm{RCO_3H}$$

$$2\mathrm{RCO_3H} + \mathrm{DBT} \longrightarrow 2\mathrm{RCO_2H} + \mathrm{DBTO_2}$$

Scheme 2.1 Oxidation by molecular oxygen-cobalt catalyst-aldehyde system

In 2004, Ramírez-Verduzco *et al.* [21] investigated the desulfurization of diesel by oxidation and extraction. A diesel with 320 ppm of total sulfur was employed to evaluate the elimination of sulfur compounds. The oxidation reaction was carried out with 30wt% hydrogen peroxide in a heterogeneous WO_x/ZrO_2 catalyst (15 wt% W). The experiments were done in a batch reactor at 60°C and atmospheric pressure. The sulfur content in the diesel after treatment was 90 ppm. The solubility of dibenzothiophene sulfone in the extraction solvent decreases with following sequence: 2-ethoxyethanol > acetonitrile > butyrolactone > dimethylformamide.

In 2004, Villaseñor *et al.* [22] studied the oxidation of dibenzothiophene and diesel fuel in hexane and ethanol biphasic system. The reaction was performed using 10 mM of DBT in the molar ratio $[H_2O_2]/[DBT] = 2$ and phosphotungstic acid as catalyst. The result showed a rate constant -6.1×10^{2} min^{-1} in this system. A sample of diesel fuel containing 342 ppm of sulfur was oxidized by an excess of hydrogen peroxide and phosphotungstic acid in ethanol at 60 °C 3 hours and atmospheric pressure. No sulfur could be detected in these samples after an additional extraction with an equal volume of ethanol.

In 2005, Ishihara *et al.* [23] investigated the oxidation of sulfur compounds present in light gas oil (LGO; sulfur content: 39 ppm) with tert-butyl hydroperoxide as the oxidant using 16 wt.% MoO_3/Al_2O_3 catalyst. The oxidation activity of the sulfur compounds increased when the oxidant/sulfur molar ratio increased up to 15. The reactivity decreased in the order: DBT >> 4,6- DMDBT > C_3-DBT irrespective of the temperature, the activation energy were 32 ± 2 kJ/mol. The treated light gas oil was further removed sulfur by adsorption over a silica gel at ambient temperature. The total sulfur content could be decreased after oxidation/adsorption to less than 5 ppm.

In 2005, Despande *et al.* [24] reported on the oxidation of refractory sulfur compound 4,6-dimethyldibenzothiophene (4,6-DMDBT) in a biphasic diesel and acetonitrile system using hydrogen peroxide and sodium carbonate in the presence of ultrasonics. This technique removed > 90% of 4,6-DMDBT from diesel phase. The application of an ultrasonic pulse used for good contact between phases. The use of mild condition and the absence of hydrogen at high pressure makes it an attractive process. The reaction rate is low at low concentration of 4,6-DMDBT and the activation energy of pseudo first order reaction was determined to be 57 kJ/mol.

CHAPTER III

EXPERIMENTAL

In the present study of oxidation of benzothiophene and dibenzothiophenes with vanadium containing catalysts, the experiment was divided into four steps.

1. Preparation and characterization of vanadium containing catalysts.
2. Study of the optimum conditions for oxidation using vanadium containing catalysts.
3. Oxidation of sulfur compounds contained in diesel fuels with the prepared catalysts.
4. Study on kinetics of sulfur compounds oxidation.

The detail of the experiments was explained in the following.

3.2 Reagents and Solvents

The reagents and solvents in this experiment were analytical grade.

Table 3.1 Chemical reagents and suppliers

Reagents and Solvents	Supplier
benzothiophene	Fluka Chemie A.G., Switzerland
dibenzothiophene	Fluka Chemie A.G., Switzerland
4,6-dimethyldibenzothiophene	Aldrich Chemical Co., Inc., USA
hexane	Lab Scans Co., Ltd., Ireland
toluene	Lab Scans Co., Ltd., Ireland
dichloromethane	Lab Scans Co., Ltd., Ireland
acetonitrile	Merck, Germany

Table 3.1 Chemicals reagents and suppliers (continued)

Reagents and Solvents	Supplier
N,*N*-dimethylformamide	Lab Scans Co., Ltd., Ireland
dimethylsulfoxide	Lab Scans Co., Ltd., Ireland
ethanol	Merck, Germany
methanol	Merck, Germany
30% hydrogen peroxide	Merck, Germany
tretabutyl ammonium bromide	Fluka Chemie A.G., Switzerland
tert-butyl hydroperoxide (80%)	Merck, Germany
sodium sulfate anhydrous	Merck, Germany
Celite	Fluka Chemie A.G., Switzerland
alumina 90	Fluka Chemie A.G., Switzerland
ammonium *meta* vanadate	Fluka Chemie A.G., Switzerland
sodium dihydrogen orthophosphate	APS Chemicals, Ltd., Australia
sodium hydroxide	Lab Scans Co., Ltd., Ireland
sodium tungstate dihydrate	Aldrich Chemical Co., Inc., USA
vanadium pentaoxide	Fluka Chemie A.G., Switzerland
isobutyl alcohol	Merck, Germany
benzyl alcohol	Fluka Chemie A.G., Switzerland
acetic acid	Merck, Germany
hydrochloric acid (37%)	Lab Scans Co., Ltd., Ireland
nitric acid (85%)	Lab Scans Co., Ltd., Ireland
n-decane	Fluka Chemie A.G., Switzerland
2-bromoethylbenzene	Aldrich Chemical Co., Inc., USA
ultra high purity nitrogen gas (99.99%)	Thai Industry Gas Co., Ltd., Thailand

3.2 Analytical Measurements

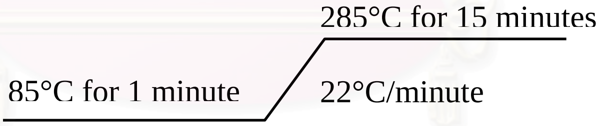
3.2.1 Gas chromatography (GC) for substrates

Gas chromatography analyses were performed on a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25μm film thickness) capillary column. The condition used for the determination of %conversion of substrate and %yield of products was set as follows:

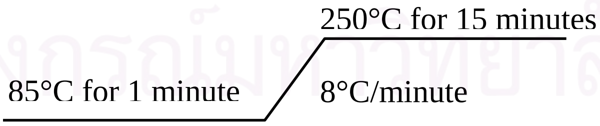
Table 3.2 The GC condition for substrates

Entry	Substrate	Carrier gas	Carrier gas pressure (kPa)	Detector temperature (°C)	Injection Temperature (°C)
1	BT	Nitrogen	70	270	240
2	DBT	Nitrogen	80	300	250
3	DMDBT	Nitrogen	80	300	250

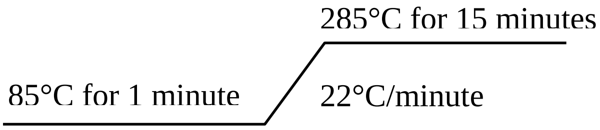
Programmed temperature for DBT :



Programmed temperature for BT :



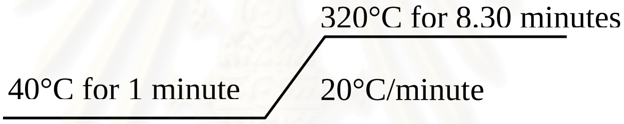
Programmed temperature for DMDBT



3.2.2 Gas chromatography (GC) for diesel fuels

Gas chromatography analyses were performed on a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25µm film thickness) CP-5 capillary column. The condition used for the determination of diesel was set as follows:

Injector	: 298°C.
Detector	: 320°C.
Carrier gas	: Helium.
Flow rate	: 1.5 ml/min.
Split ratio	: 1:2
Programmed temperature	:



3.2.3 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer. The liquid samples were coated on NaCl cells. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 cm^{-1} to 4,000 cm^{-1} in transmittance mode.

3.2.4 Nuclear magnetic resonance (NMR)

^{1}H-NMR spectrum were obtained on Bruker ACF 200 MHz. The NMR spectra were measured in chloroform-d and deuterium oxide (D_2O) at room temperature. The center peak of chloroform-d and deuterium oxide were used as the internal reference (at 7.2 ppm and 4.6 ppm, respectively).

3.2.5 UV-visible spectrophotometry (UV-vis)

UV-Visible spectra were recorded on Milton Roy Spectronic 3000 Array.

3.2.6 X-ray diffraction (XRD)

The XRD patterns of catalysts were obtained on Rigaku, DMAX 2002 Ultima Plus X-ray powder diffractometer equipped with a monochromator and a Cu-target X-ray tube (40 kV, 30 mA) and angles of 2θ ranged from 5-50 degree.

3.2.7 X-ray fluorescence spectrometry (XRF)

Sulfur content in diesel fuels was determined using a SISONS X-ray fluorescence spectrometer ARL 8410 (ASTM D4294 method).

3.3 Preparation of catalysts

3.3.1 Polyoxotungstate complex, $[W_6O_{19}]^{2-}$ [25]

Sodium tungstate dehydrate ($Na_2WO_4.2H_2O$ 3.3 g) was dissolved in water (100 ml) followed by the addition of acetonitrile (100 ml). After stirring, added hydrochloric acid (10M HCl 1.5 ml) tetrabutyl ammonium bromide ($n\text{-}Bu_4NBr$ 3 g) were added to precipitate a white salt, which was filtered, washed with water and ethanol. The crude salt was further purified by recrystallization from 40 ml of a 3:1 (v/v) acetonitrile:ethanol solution.

3.3.2 11-Tungstovanadate, $[V(VW_{11})O_{40}]^{4-}$ [26]

The solution of sodium tungstate dehydrate ($Na_2WO_4.2H_2O$ 8.3 g) and ammonium *meta* vanadate (NH_4VO_3 2.9 g) of warm water (225 ml) was added acetonitrile (250 ml). To clear solution was added dropwise 9.2 M of perchloric acid ($HClO_4$ 27 ml) with vigorous stirring. The resultant orange solution was heated at 70 °C for 24 hours. During the time, an excess of vanadium(V) was precipitated as a reddish brown oxide. After cooling to room temperature the precipitates were filtered off. To the filtrate was added tetrabutyl ammonium bromide (n-Bu_4NBr 5 g) to precipitate an orange salt. The salt was collected by filtration and washed with water, ethanol and air dried. The salt was purified by recrystallization from a 5:2 (v/v) acetonitrile : ethanol solution.

3.3.3 11-Tungsto-1-vanadophosphate, $[PVW_{11}O_{40}]^{4-}$ [27]

Sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$ 0.39 g) was the solution of sodium tungstate dihydrate ($Na_2WO_4.2H_2O$ 8.25 g) in water (100 ml) followed by the addition of hydrochloric acid (conc. HCl 21.7 ml). After stirring, 5 ml of vanadium stock solution (NH_4VO_3 2.9 g and NaOH 2.0 g in 100 ml of water) was added to a mixed solution. The addition of water made it was volume 150 ml. After heating at 80 °C for 3 days added tetrabutyl ammonium bromide (n-Bu_4NBr 8.0 g), the yellow precipitates were filtered off, washed with water and ethanol and dried at room temperature. The compound was recrystallized from acetonitrile.

3.3.5 Molybdo vanadophosphate, $[PV_2Mo_{10}O_{40}]^{4-}$ [28]

A solution of ammonium *meta* vanadate (NH_4VO_3 0.585 g in 1 M NaOH) was added slowly to a solution of sodium dithionite ($NaMo_2O_4.2H_2O$ 6.05 g) and sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$ 0.39 g) in hydrochloric acid (1.6 M HCl 40 ml). The resultant brown solution was heated to boiling for 2 h. After cooling the solution to room temperature, tetrabutyl ammonium bromide (n-Bu_4NBr 3.5 g) was added to precipitate an orange salt. The salt was isolated by filtration and washed with water, ethanol and air dried. To purify the salt further, the salt (2.5 g) was dissolved in acetonitrile (90 ml) and was reprecipitated by the addition of ethanol (90 ml).

3.3.4 Vanadyl pyrophosphate, $(VO)_2P_2O_7$ [29]

Vanadium phosphorus oxide (V_2O_5 10.0 g) was refluxing in a mixture of 2-butanol (30 ml) and benzyl alcohol (15 ml) for 14 hours followed by addition of the phosphoric acid (85%H_3PO_4 0.0549 mmol) and refluxing for further 6 hours to form a light green precipitate. The precipitate was filtered off and dried at 110 °C overnight and then calcined in air at 400 °C for 4 hours.

3.4 Oxidation and extraction procedure for dibenzothiophenes

In a round bottom flask, connected with a condenser, dibenzothiophene, solvent and the catalyst were mixed. Then the oxidant was added into the reaction mixture and stirred for the desired time and temperature. After the reaction finished, the extraction solvent was added to the mixture and stirred for 10 minutes. The biphasic mixture was separated by decantation. After being dried over anhydrous sodium sulfate (Na_2SO_4), 1 ml of aqueous phase was passed through a capillary column containing celite to remove the catalyst. Then the remaining dibenzothiophene and product were quantified by GC. % Conversion and % yield were calculated from peak areas of dibenzothiophene and product.

The intermediate sulfoxide which occured in some batches (when using $(VO)_2P_2O_7$ catalyst) was detected by TLC and then isolated by passing through a silica gel column and eluted with a mixture of hexane-ethyl acetate (1:1). The quantity of sulfoxides was quantified by GC.

3.5 Study on the optimum conditions for the oxidation of sulfur model compounds

Various parameters affecting the oxidation of dibenzothiophenes were investigated.

- reaction solvent
- extraction solvent
- temperature
- amounts of oxidant and catalyst
- catalyst type

3.6 Study on the oxidation of sulfur compounds in diesel fuels

The mixture of diesel (50 ml), catalyst, hydrogen peroxide and acetic acid was stirred at 70 °C for 5 h. After 5 h of the reaction times, the oil obtained demonstrated a dark yellow color, compared with the initial pale yellow color of diesel. The resulting oil was extracted with acetonitrile (50 ml) three times and passed through the glass column (1 x 25 cm) containing alumina (Al_2O_3 10 g) to remove oxidized sulfur. The oxidized oil was washed with water and dried over anhydrous sodium sulfate (Na_2SO_4). Concentration of the remaining sulfur compounds was determined by the XRF method (ASTM D4294).

3.7 Kinetics study on modeling of oxidation reaction

The reaction of the oxidation of benzothiophene (DBT) was studied by using $[V(VW_{11})O_{40}]^{4-}$ as catalyst. DBT (0.5 mmol) was dissolved in hexane (50 ml), hydrogen peroxide (50 mmol) were added to the flask. The flask immersed in the heating bath was stirred (50-70 °C). The catalyst (0.0065 mmol) and acetic acid (50 mmol) were added to initiate the reaction. Reaction samples were withdrawn at 1, 2, 3, 4 and 5 hours and quatified by GC.

The conversions of dibenzothiophenes were calculated using their initial concentrations at 0 min (C_o) and after t min reaction (C_t). Conversion x is expressed as

$$\boldsymbol{x} = \frac{Co - Ct}{Co} \tag{3.1}$$

Assuming that the volume and mass of the reaction mixtures were constant, since only small amounts of liquid samples (1 ml each) were withdrawn during the reaction.

If benzothiophene oxidation follows pseudo first order reaction kinetics, then the rate constant k and reaction time t can be described using the following equation:

$$\ln \frac{(Ct)}{(Co)} = -kt \qquad (3.2)$$

$$k = Ae^{-Ea/RT} \qquad (3.3)$$

The rate constant *k* is affected by the temperature, it can be obtained from the slope of a plot of ln (C*t*/C*o*) versus reaction time *t*.

A is the pre-exponential factor, *E*a the apparent activation energy, *R* and *T* are gas constant and the reaction temperature (K), respectively. From Arrhenius equation 3.3, transforming it with ln, equation 3.4 was obtained.

$$-\ln k = \frac{Ea}{RT} - \ln A \qquad (3.4)$$

A plot between –ln *k* versus 1/*T* was done, and the slope is -*E*a/*R* of which the apparent activation energies (*E*a) was calculated.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation and characterization of catalysts

All catalysts synthesized: $[W_6O_{19}]^{2-}$, $[V(VW_{11})O_{40}]^{4-}$, $[PVW_{11}O_{40}]^{4-}$, $[PV_2Mo_{10}O_{40}]^{4-}$ and $(VO)_2P_2O_7$ were characterized by fourier transform infrared techniques, UV-visible spectrophotometry, X-ray diffraction and melting temperature.

4.1.1 Polyoxotungstate, $[W_6O_{19}]^{2-}$ [25]

Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) was dissolved in deionized water followed by the addition of acetonitrile. After stirring, 10 M hydrochloric acid (HCl) and tetrabutyl ammoniumbromide (n-Bu_4NBr) were added to precipitate a white salt, which was filtered, washed with deionized water and ethanol. The crude salt was further purified by recrystallization from a mixture of acetonitrile:ethanol solution.

XRD (2θ): 8.9°, 9.5°, 10.8°,14.0°, 25.9°.
FT-IR (KBr): ν (cm^{-1}) 979, 889, 813, 586, 444 cm^{-1}.
ref. [25]: 976, 890, 812, 588, 442 cm^{-1}.
UV-Visible spectrum: λ_{max} = 275 nm.
ref. [30]: 275 nm.
Melting temp. 168-170°C (dec).

4.1.2 11-Tungstovanadate, $[V(VW_{11})O_{40}]^{4-}$ [26]

Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$), ammonium *meta* vanadate (NH_4VO_3) were dissolved in warm water and added acetonitrile, then added perchloric acid ($HClO_4$) with vigorous stirring. The resultant orange solution was heated, after cooling to room temperature the precipitates were filtered off. To the filtrate was added tetrabutyl ammonium bromide to precipitate an orange salt, washed with deionized water, ethanol and air dried. It was recrystallized from a mixture of acetonitrile: ethanol solution.

XRD (2θ): 6.6°, 7.0°, 8.0°, 8.5°, 29.9°.
FT-IR (KBr): ν (cm^{-1}) 967, 894, 777, 518 cm^{-1}.
ref. [26]: 967, 897, 775, 520 cm^{-1}.
UV-Visible spectrum: λ_{max} = 265 nm.
ref.[26]: 265 nm.
Melting temp. 332-335°C (dec).

4.1.3 11-Tungsto-1-vanadophosphate, $[PVW_{11}O_{40}]^{4-}$ [27]

Sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$) was dissolved in the solution of sodium tungstate dihydrate ($Na_2WO_4.2H_2O$), followed by the addition of conc. hydrochloric acid (conc. HCl). After stirring, add vanadium stock solution to a mixed solution, then heating and added tetrabutyl ammonium bromide, the yellow precipitates were filtered off, washed with deionized water and ethanol and dried, recrystallized from acetonitrile.

XRD (2θ): 6.6°, 7.6°, 12.1°, 23.5°, 29.9°.
FT-IR (KBr): ν (cm^{-1}) 1095, 1071, 963, 810, 890 cm^{-1}.
ref. [27]: 1096, 1070, 963, 810, 889 cm^{-1}.
UV-Visible spectrum: λ_{max} = 261 nm.
ref. [27]: 261 nm.
Melting temp. 235-238°C (dec).

4.1.4 Molybdophosphate complex, $[PV_2Mo_{10}O_{40}]^{4-}$ [28]

Ammonium *meta* vanadate (NH_4VO_3) was dissolved in 1 M sodium hydroxide (NaOH) followed by the addition of a solution of sodium molybdate ($NaMo_2O_4.2H_2O$) and sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$) in 1.6 M hydrochloric acid (HCl) The resultant brown solution was heated to boiling. After cooling to room temperature, tetrabutyl ammonium bromide was added to precipitate an orange salt. The salt was isolated, washed with water, ethanol and air dried. It was recrystallized from acetonitrile:ethanol.

XRD (2θ): 6.7°, 7.7°, 12.1°, 23.5°, 30.0°.

FT-IR (KBr): ν (cm^{-1}) 1075, 1057, 941, 873, 800 cm^{-1}.

ref. [28]: 1075, 1055, 942, 873, 801 cm^{-1}.

UV-Visible spectrum: λ_{max} = 308 nm.

ref. [28]: 308 nm.

Melting temp. 178-182°C (dec).

4.1.5 Vanadyl pyrophosphate, $(VO)_2P_2O_7$ [29]

Vanadium phosphorus oxide (V_2O_5) was refluxed in a mixture of 2-butanol and benzyl alcohol followed by addition of the 85% phosphoric acid (H_3PO_4) to form a light green precipitate, which was filtered off and dried then calcined in air.

XRD (2θ): 23.0°, 28.4°, 29.9°.

ref. [29]: 23.1°, 28.4°, 29.9°.

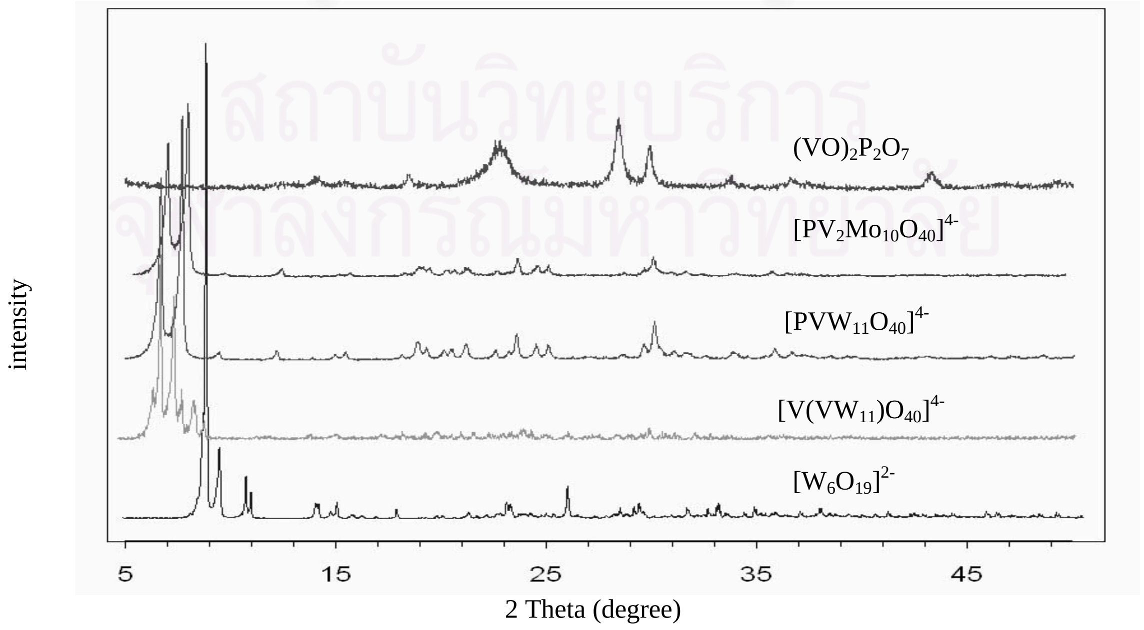
FT-IR (KBr): ν (cm^{-1}) 1246, 1135, 1081, 962, 639 cm^{-1}.

ref. [31]: 1244, 1080, 960 cm^{-1}.

UV-Visible spectrum: λ_{max} = 267 nm.

Melting temp. 332-335°C (dec).

The XRD technique was used to characterize structure of catalysts. The different structures obtained were listed in Table 4.1 and the XRD patterns were shown in Figure 4.1.



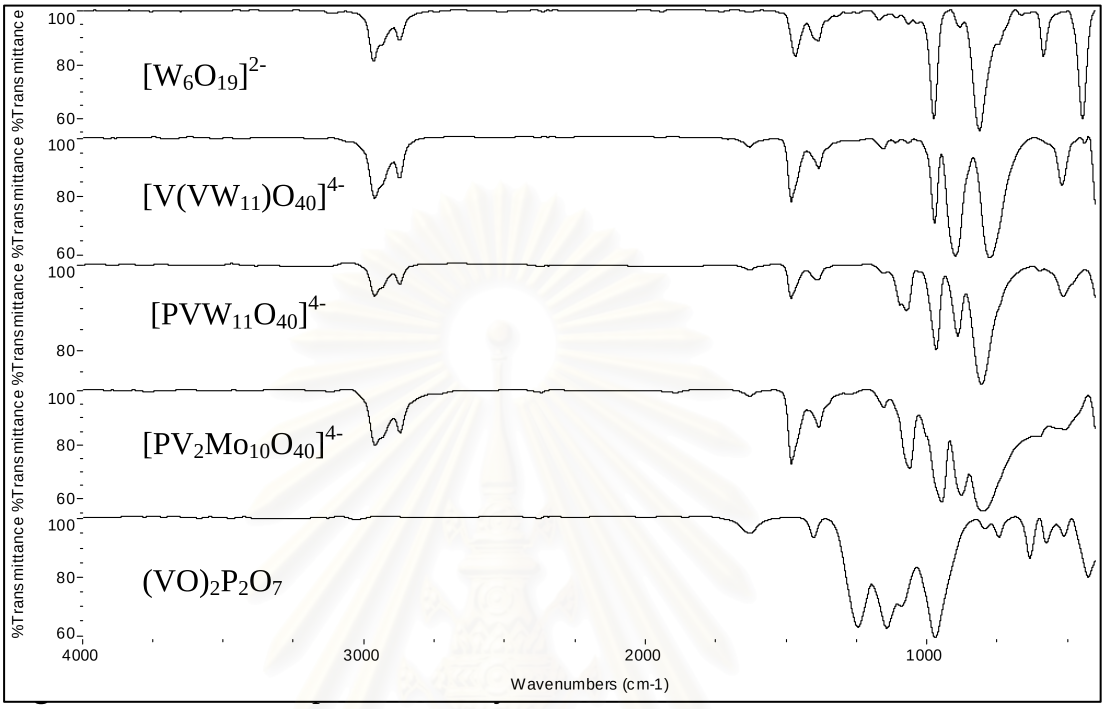
Figures 4.1 The XRD patterns of catalysts.

From XRD data of all catalysts, they show the existence of the structures. The structure of $[W_6O_{19}]^{2-}$ was orthorhombic with *a* = 1.052 nm, *b* = 1.634 nm, *c* = 1.990 nm. The $[V(VW_{11})O_{40}]^{4-}$ was tetragonal structure with *a* = 2.086 nm, *c* = 5.044 nm. The $[PVW_{11}O_{40}]^{4-}$ was monoclinic structure with *a* = 1.475, *b* = 1.880, *c* =3.797 nm. The $[PV_2Mo_{10}O_{40}]^{4-}$ was orthorhombic with *a* = 1.103 nm, *b* = 2.095 nm, *c* = 2.638 nm. The $(VO)_2P_2O_7$ was monoclinic with *a* = 0.778 nm, *b* = 1.653 nm, *c* = 0.963 nm.

Table 4.1 Unit cell lengths of the catalysts

Entry	**Catalyst**	**Crystal system**	**2*θ* (°)**	**h**	**k**	**l**	**Unit cell length (nm)**		
							a	**b**	**c**
1	$[W_6O_{19}]^{2-}$	orthorhombic	8.9 9.5 10.8 14.0 25.9	0 1 0 1 3	0 0 2 2 0	2 1 0 1 0	1.052	1.634	1.990
2	$[V(VW_{11})O_{40}]^{4-}$	tetragonal	6.7 7.6 8.0 8.5 29.9	1 0 2 2 6	0 0 0 0 0	3 4 0 0 1	2.086	-	5.044
3	$[PVW_{11}O_{40}]^{4-}$	monoclinic	6.6 7.6 12.1 23.5 29.9	0 2 1 4 6	0 0 1 0 0	2 0 1 1 1	1.475	1.880	3.797
4	$[PV_2Mo_{10}O_{40}]^{4-}$	orthorhombic	6.7 7.7 12.1 23.5 30.0	0 0 0 4 6	0 2 2 0 0	2 0 0 1 1	1.103	2.095	2.638
5	$(VO)_2P_2O_7$	monoclinic	23.0 28.4 29.9	2 0 0	0 4 2	0 2 3	0.778	1.653	0.963

The FT-IR technique was used to characterize functional group of catalysts. The FT-IR spectra of catalyst presented the characteristic peaks. The FT-IR spectra and data were shown in Figure 4.2 and Table 4.2 respectively.



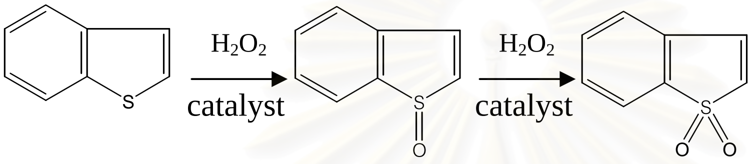
Figures 4.2 The FTIR spectra of catalysts.

Table 4.2 The IR stretching frequencies of complexes

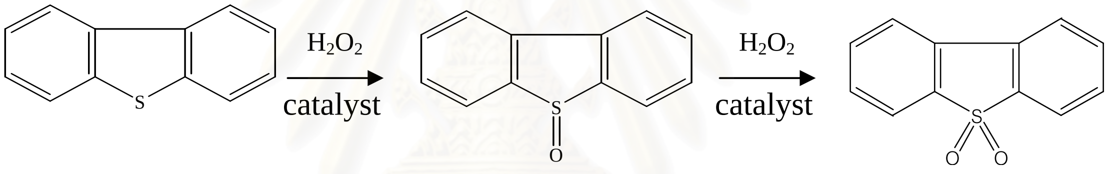
Catalyst	Wave number (cm^{-1})			
	P-O st.	P-O-M st.	M-O st.	M-O-M st.
$[W_6O_{19}]^{2-}$	-	-	976	889 813
$[V(VW_{11})O_{40}]^{4-}$	-	-	967	894 777
$[PVW_{11}O_{40}]^{4-}$	1097	1070	963	888 810
$[PV_2Mo_{10}O_{40}]^{4-}$	1057	1075	941	873 810
$(VO)_2P_2O_7$	1081	-	962	-

4.2 Study on the optimum conditions for the oxidation of model sulfur compounds

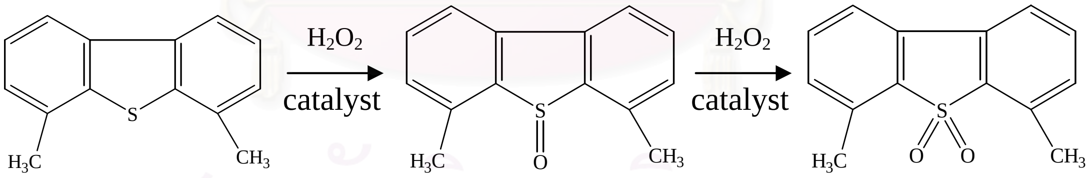
Benzothiophene (BT), dibenzothiophene (DBT) and dimethyldibenzothiophene (DMDBT) were selected as representatives of sulfur compounds present in diesel. A series of model reactions was carried out to optimize the reaction condition. Sulfone and sulfoxide were the possible products from the oxidation reaction, as shown in equations (4.1)-(4.3).



BT (4.1)



DBT (4.2)



DMDBT (4.3)

4.2.1 Oxidation of dibenzothiophene (DBT)

4.2.1.1 Various condition for DBT oxidation using $[W_6O_{19}]^{2-}$

Various parameters were evaluated to find optimum conditions for the DBT oxidation. The parameters studied in this reaction are solvent types, amount of oxidant, amount of catalyst and temperature.

Table 4.3 The effect of solvent for oxidation of DBT using $[W_6O_{19}]^{2-}$

Entry	S/C	O/S	Reaction solv.	Conversion (%)
1	100	5	toluene	45
2	100	5	decane	48
3	100	5	hexane	43

Condition: DBT 0.1 mmol, $[W_6O_{19}]^{2-}$ 0.001 mmol, solvent 5 ml, 60 °C 3 h.
S = substrate
O = oxidant
C = catalyst

The reactions carried out using different solvents show that %conversions are comparable. As hexane has lower boiling point (69 °C) than toluene (110 °C) and decane (174 °C), it was chosen for further experiments. Low temperature solvent is preferred for this oxidation reaction as the hydrogen peroxide oxidant is decomposed at high temperature [1].

The effect of amount of catalyst and oxidant on the oxidation of DBT were investigated. The results were collected in Table 4.4.

Table 4.4 The effect of catalyst and oxidant amount for oxidation of DBT using $[W_6O_{19}]^{2-}$

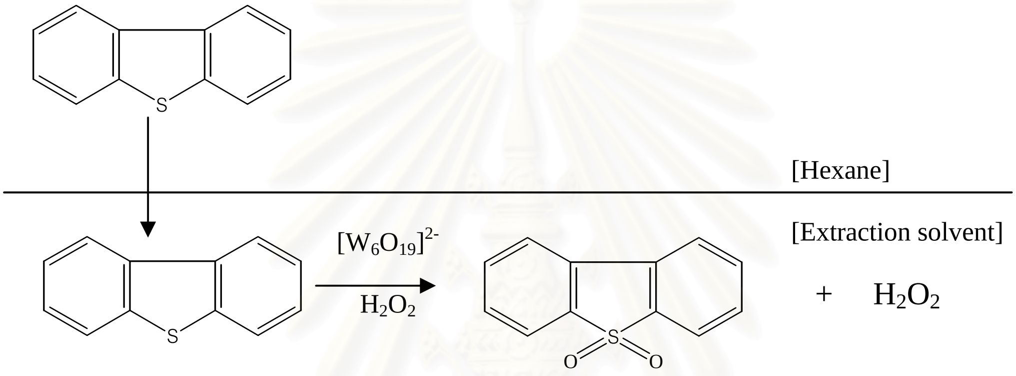
Entry	S/C	O/S	Conversion (%)	DBT content in ext. solv. (%)
1	100	5	58	20
2	50	5	78	18
3	25	5	83	9
4	100	10	80	11
5	100	20	86	7

Condition: DBT 0.1 mmol, hexane 5 ml, dimethylsulfoxide (DMSO) 5 ml, 60 °C 3 h.

From the experiment data, %conversion is a function of substrate/catalyst (S/C) mole ratio. When the amount of the catalyst was increased, %conversion was increased (entries 1-3). Also, %conversion was increased with amount of oxidant (entries 1, 4 and 5). This result was consistent with that reported [19]. From this result it can be seen that the amount of oxidant is more important than the amount of catalyst.

The product from the oxidation of DBT was confirmed by gas chromatography to be sulfone. It was more polar than the substrate DBT. Therefore polar solvent should be able to dissolve it. In order to remove the oxidized product, sulfone from the reaction, one method is solvent extraction.

In some previous reported results [32], it was shown that DMSO is a good solvent for sulfone extraction. However, some DBT was also in this phase. Therefore, in this work, some solvents were tested for the extraction. The result was collected in Table 4.5.



Scheme 4.1 DBT oxidation in the biphasic system.

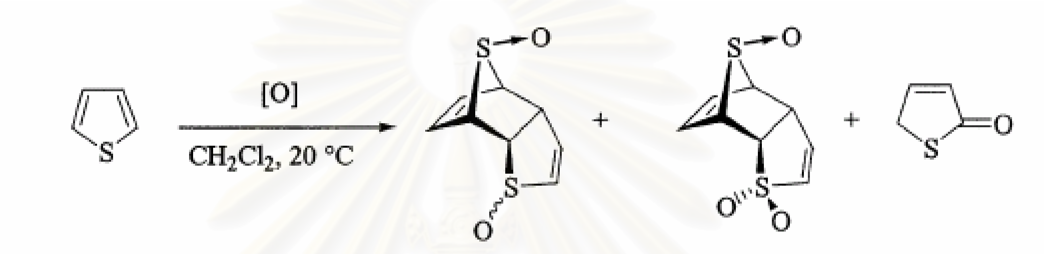
Table 4.5 The effect of extraction solvent for oxidation of DBT using $[W_6O_{19}]^{2-}$

Entry	Extraction solv.	Conversion (%)	DBT content in ext. solv. (%)
1	$EtOH/H_2O$	50	22
2	CH_3CN	56	25
3	DMSO	58	20
4	DMF	61	-

Condition: DBT 0.1 mmol, $[W_6O_{19}]^{2-}$ 0.001 mmol, S/C = 100, O/S = 5, hexane 5 ml, extraction solvent 5 ml, 60 °C 3 h.

Comparing extraction solvents tested, it was found that dimethylsulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile (CH_3CN) yield higher oxidation conversion than $EtOH/H_2O_2$. This agrees well with that reported [6, 33]. The ability to extract sulfone corresponds to the polarity of solvent which decreased in order: DMSO > CH_3CN > DMF > EtOH [6]. In this work, DMF (entry 4) was chosen as extraction solvent because no DBT was detected in this solvent phase. Therefore it is suitable for the complete separation between substrate and sulfone.

It was commonly known that adding acid to the reaction can increase the reaction rate [34]. In the previous report, the reaction of peracetic acid mixed with H_2O_2 is much faster than H_2O_2 [35]. In the presence of an excess of acid, it leads to the formation of thiophene sulfoxide and sulfone [36] as shown in Scheme 4.2. Therefore, in this work, acetic acid addition was tested and the result was shown in Table 4.6.



Scheme 4.2 Product distribution of thiophene oxidation in the presence of peracid.

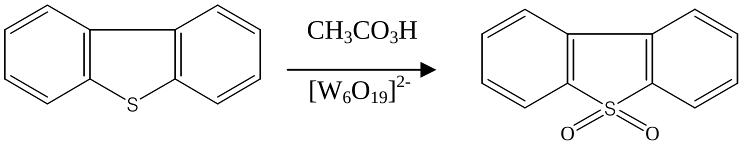
Table 4.6 The effect of acetic acid for DBT oxidation using $[W_6O_{19}]^{2-}$

Entry	$[AcOH]/[H_2O_2]$	Conversion (%)
1	0	61
2	1	70

Condition: DBT 0.1 mmol, $[W_6O_{19}]^{2-}$ 0.001 mmol, S/C = 100, O/S = 5, $[AcOH]/[H_2O_2] = 1$, hexane 5 ml, DMF 5 ml and 60 °C 3 h.

In the presence of acetic acid, the percent conversion was slightly increased compared to only hydrogen peroxide treatment. The addition of acetic acid accelerated the reaction. Reaction proceeds *via* oxidation by peracetic acid, which was prepared *in situ* from a mixture of hydrogen peroxide and acetic acid according to the equation (4.4).

$$CH_3COOH + H_2O_2 \longrightarrow CH_3CO_3H + H_2O \qquad (4.4)$$



$+ H_2O$ (4.5)

Table 4.7 The effect of AcOH for DBT oxidation using $[W_6O_{19}]^{2-}$

Entry	$[AcOH]/[H_2O_2]$	Conversion (%)
1	0.5	57
2	1.0	70
3	1.5	76
4	1.7	46
5	2.0	15

Condition: DBT 0.1 mmol, $[W_6O_{19}]^{2-}$ 0.001 mmol, S/C = 100, O/S = 5, hexane 5 ml, DMF 5 ml, 60 °C 3 h.

When the mole ratio of $[AcOH]/[H_2O_2]$ was up to 1.5 the oxidation activities was increased and then decreased beyond this value.

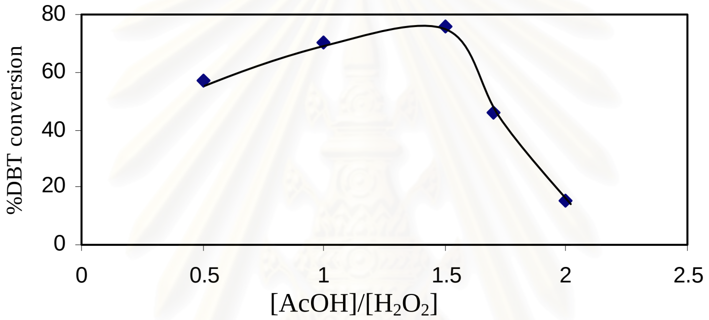


Figure 4.3 %DBT conversion at different $[AcOH]/[H_2O_2]$.

The next parameters studied was the effect of temperature. The result was shown in Table 4.8.

Table 4.8 The effect of temperature for oxidation of DBT using $[W_6O_{19}]^{2-}$

Entry	T (°C)	Conversion (%)
1	50	69
2	60	90
3	70	89
4	80	58
5	100	47

Condition: DBT 0.1 mmol, $[W_6O_{19}]^{2-}$ 0.001 mmol, S/C = 100, O/S = 40, $[AcOH]/[H_2O_2]$ = 1, hexane 5 ml, DMF 5 ml and time 3 h.

The oxidation activity was increased with the increasing temperature. Above 60 °C, the oxidation activities decreased; this may be attributed to decrease in the concentration of oxidant due to its low thermostability at high temperature.

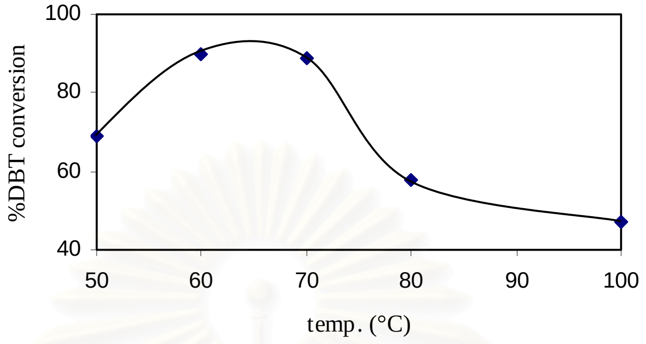


Figure 4.4 %DBT conversion at various temperature.

After determining the optimum condition for oxidation, different types of catalyst was tested and compared, V_2O_5 was also compared as reference. The result was shown in Table 4.9.

Table 4.9 The effect of catalyst type for oxidation of DBT without acid

Entry	Catalyst	Conversion (%)
1	$[W_6O_{19}]^{2-}$	61
2	$[V(VW_{11})O_{40}]^{4-}$	65
3	$[PVW_{11}O_{40}]^{4-}$	56
4	$[PV_2Mo_{10}O_{40}]^{4-}$	53
5	$(VO)_2P_2O_7$	18
6	V_2O_5	16

Condition: DBT 0.1 mmol, hexane 5 ml, DMF 5 ml, S/C = 100, O/S = 5, 60 °C 3 h.

The oxidation reactivity order of the catalyst is: $[V(VW_{11})O_{40}]^{4-} > [W_6O_{19}]^{2-} > [PVW_{11}O_{40}]^{4-} \sim [PV_2Mo_{10}O_{40}]^{4-} > (VO)_2P_2O_7 \sim V_2O_5$. As is found out that acetic acid addition can enhance the rate, and also for comparison between without and with acid addition, therefore experiments were performed in the presence of acid, together with higher amount of oxidant and catalyst in order to increase %conversion. The results are in Table 4.10.

Table 4.10 The effect of catalyst type for oxidation of DBT with AcOH

Entry	Catalyst	S/C	O/S	Conversion (%)
1	$[W_6O_{19}]^{2-}$	100	5	70
2	$[W_6O_{19}]^{2-}$	25	20	91
3	$[V(VW_{11})O_{40}]^{4-}$	100	5	74
4	$[V(VW_{11})O_{40}]^{4-}$	25	20	94
5	$[PVW_{11}O_{40}]^{4-}$	100	5	62
6	$[PVW_{11}O_{40}]^{4-}$	25	20	90
7	$[PV_2Mo_{10}O_{40}]^{4-}$	100	5	64
8	$[PV_2Mo_{10}O_{40}]^{4-}$	25	20	85
9	$(VO)_2P_2O_7$	100	5	28
10	$(VO)_2P_2O_7$	25	20	40

Condition: DBT 0.1 mmol, hexane and DMF 10 ml, $[AcOH]/[H_2O_2] = 1$, 60 °C 3 h.

The oxidation reactivity order of the catalyst in the presence of acetic acid is: $[V(VW_{11})O_{40}]^{4-} > [W_6O_{19}]^{2-} > [PVW_{11}O_{40}]^{4-} \sim [PV_2Mo_{10}O_{40}]^{4-} > (VO)_2P_2O_7$. Figure 4.5 shows the conversion of dibenzothiophene when added acetic acid. A much higher %conversion was obtained when increasing amount of oxidant and catalyst.

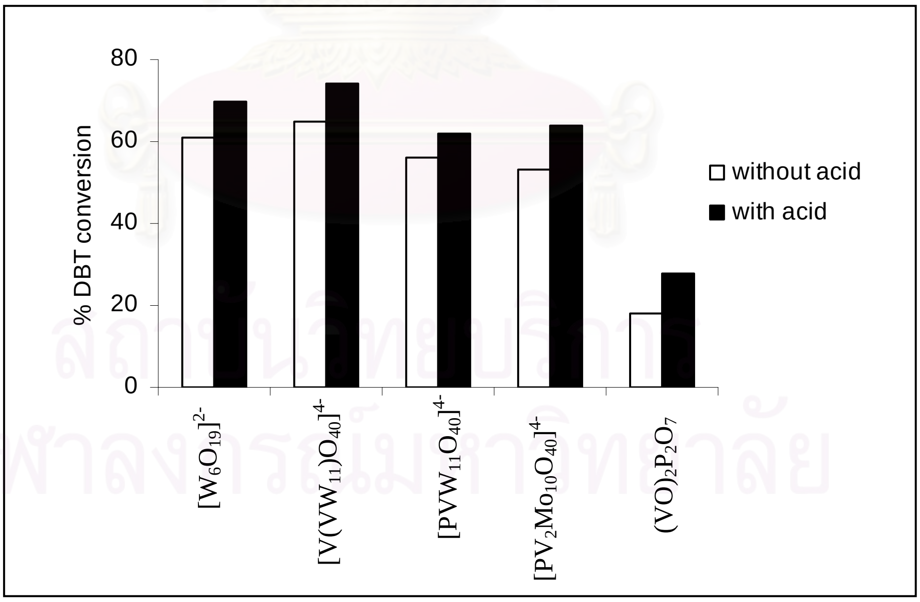


Figure 4.5 %DBT conversion when acetic acid was added.

Among the various catalysts tested in this work, the experimental results show that the catalyst containing vanadium and tungsten, $[V(VW_{11})O_{40}]^{4-}$ is the most active.

Vanadium pentaoxide (V_2O_5) and vanadyl pyrophosphate ($(VO)_2P_2O_7$) are the least active, in addition, both gave rise to trace of sulfoxide (that was confirmed by FT-IR technique). Figures 4.6-4.9 show structures of all catalysts.

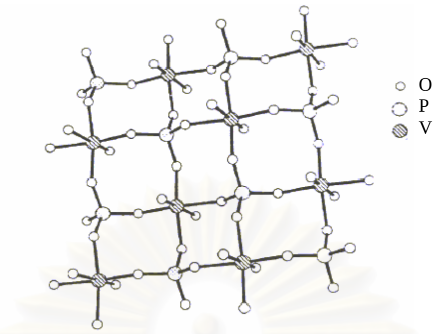


Figure 4.6 The layered structure of $(VO)_2P_2O_7$ [37].

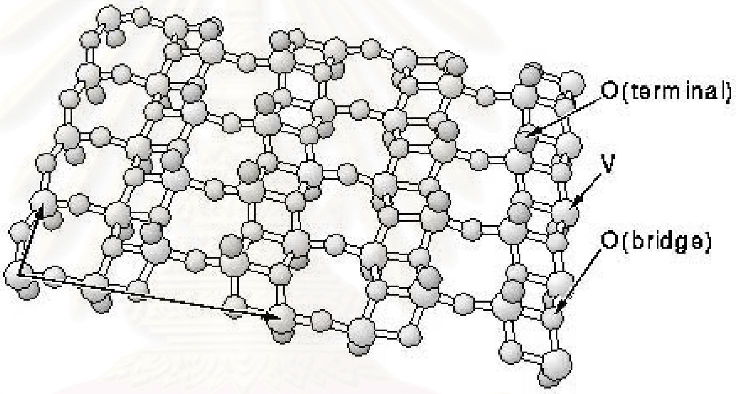


Figure 4.7 The layered structure of V_2O_5.

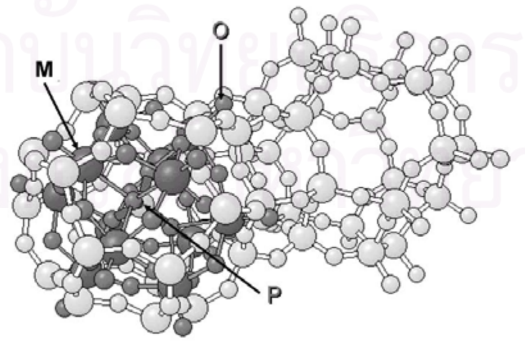


Figure 4.8 The structure of $[PV_xM_{12-x}O_{40}]^{(3+x)-}$ (M = V, W, Mo; x = 1-2)

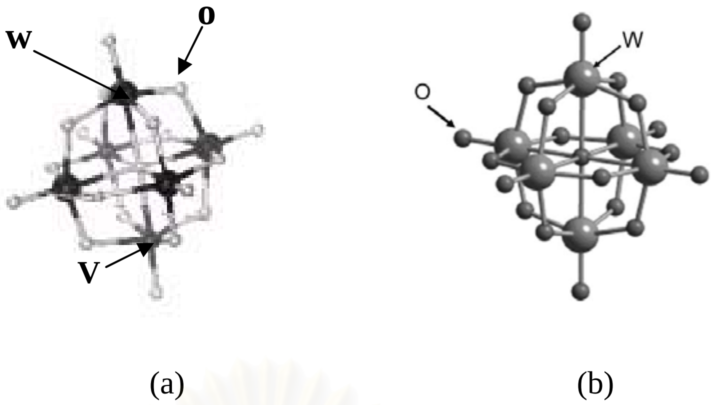


Figure 4.9 The structures of (a) $[V(VW_{11})O_{40}]^{4-}$ and (b) $[W_6O_{19}]^{2-}$.

For the polyoxometalates, they consist of metal oxygen cluster. It is well known that polyoxometalate was converted to polyoxoperoxo species in the presence of hydrogen peroxide [13]. In $[V(VW_{11})O_{40}]^{4-}$ catalyst, it is believed that vanadium center is an active site for the oxidation. By substitution W with V, it makes the catalyst more oxophilic, so that reaction with oxygen from hydrogen peroxide is easier. As a result, the oxidation activity of $[V(VW_{11})O_{40}]^{4-}$ is higher than that of $[W_6O_{19}]^{2-}$.

For catalysts containing phosphorus: $[PVW_{11}O_{40}]^{4-}$ and $[PV_2Mo_{10}O_{40}]^{4-}$ the oxidation activity is lower than $[V(VW_{11})O_{40}]^{4-}$. This is due to the basic phosphorus atom which decreases the acidity of the catalyst. It was reported that when phosphomolybdic acid is partly substituted by vanadium atoms, the acid strength diminishes [38]. The acidity of the catalyst is also important in the oxidation as was studied that oxovanadium complex catalyzed oxygenation of disulfides is facilitated by Lewis acids.

For $(VO)_2P_2O_7$, it has layered structure as V_2O_5, the lowest activity of both might be due to their unsuitable structure and acidity.

About the catalysts, adsorption of sulfur compound on the catalyst surfaces helps increasing the collision probability of sulfur compound and the active oxygen of hydrogen peroxide. Furthermore, hydroxyl radicals produced from hydrogen peroxide can be resonance-stabilized on the catalyst surface, which could also enhance the oxidation conversion of sulfur compound.

In the catalytic oxidation of sulfur compound with hydrogen peroxide in the presence of acetic acid, it is believed that the acetic acid has two roles. Its acid nature is favorable to the oxidation of sulfur compound on the catalyst; secondly, it interacts with hydrogen peroxide to form peracetic acid which can oxidize DBT.

In order to investigate the difference of reactivity between different sulfur compounds, the oxidation of more refractory sulfur compounds was carried out. In the experiments performed, reaction temperature and reaction time were increased to achieve high oxidation conversions.

4.2.2 Oxidation of benzothiophene (BT) and dibenzothiophenes (DBTs)

The oxidation of benzothiophene and dibenzothiophenes was at 70 °C in 5 hours. The results are collected in Table 4.11 and displayed in Figure 4.10.

Table 4.11 Oxidation of different sulfur compounds.

Entry	catalyst	% conversion		
		DBT	4,6-DMDBT	BT
1	$[W_6O_{19}]^{2-}$	87	74	50
2	$[V(VW_{11})O_{40}]^{4-}$	99	80	55
3	$[PVW_{11}O_{40}]^{4-}$	88	70	40
4	$[PV_2Mo_{10}O_{40}]^{4-}$	86	70	42
5	$(VO)_2P_2O_7$	50	39	20

Condition: substrates 0.1 mmol, hexane and DMF 5 ml, S/C = 100, O/S = 30, $[AcOH]/[H_2O_2] = 1$, 70 °C 5 h.

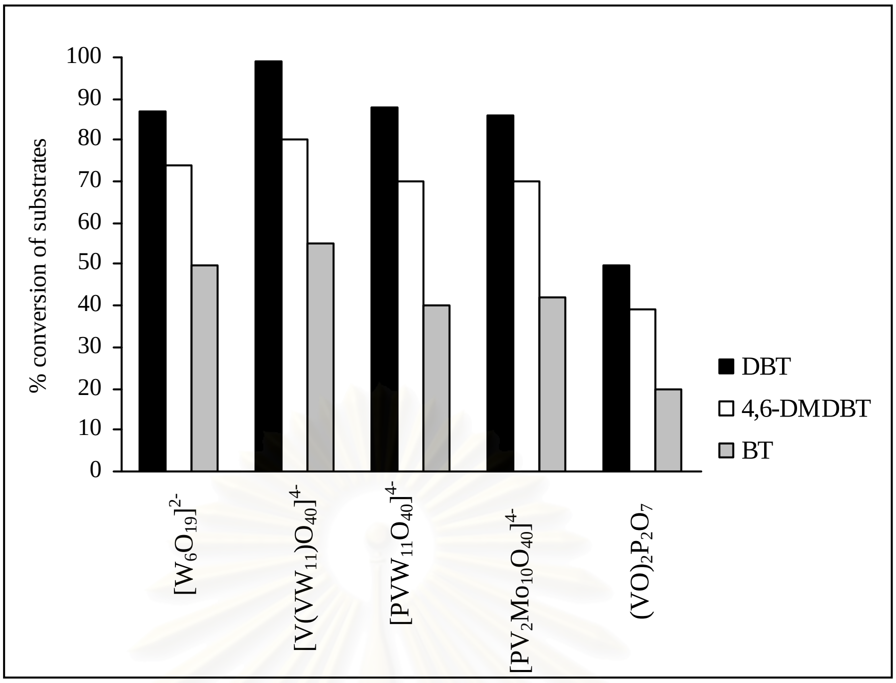


Figure 4.10 % Conversion using various catalysts

From the experimental data, it was shown that the reactivity of the sulfur compounds decreased in the order: DBT > 4,6-DMDBT > BT. Due to its methyl substitutes at the 4 and 6 position on dibenzothiophene rings , 4,6-DMDBT was harder to be oxidized. This shows that the steric effect is dominant as shown in Figure 4.11.

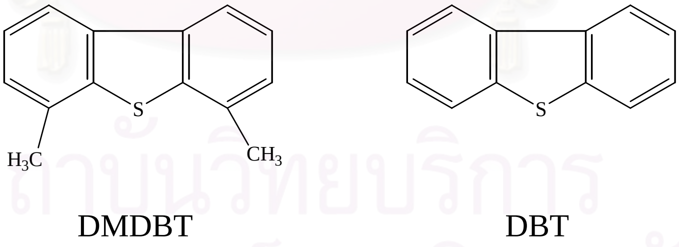


Figure 4.11 The steric hindrance of the methyl group.

Looking at the electronic effect of different substrate, the electron density on the sulfur atom was as shown in Figure 4.12. BT has less electron density therefore, it is harder to be oxidized compared with DBT.

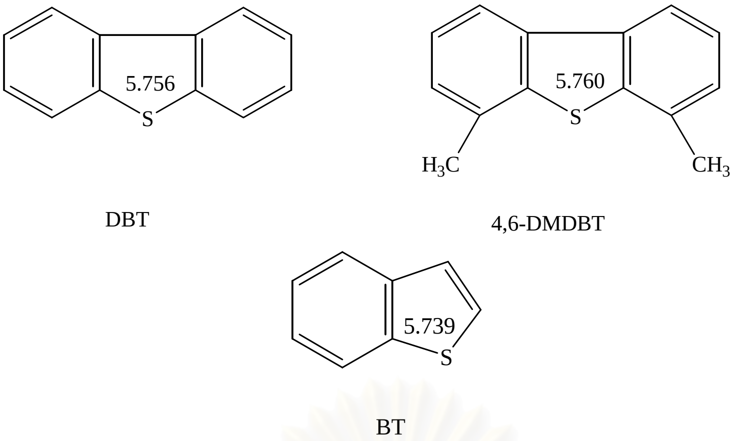


Figure 4.12 The electron density of sulfur atom in the compounds [32].

The effect of catalyst types are the same as previous section and the order of the catalyst activity is as follows: $[V(VW_{11})O_{40}]^{4-}$ > $[W_6O_{19}]^{2-}$ > $[PVW_{11}O_{40}]^{4-}$ ~ $[PV_2Mo_{10}O_{40}]^{4-}$ > $(VO)_2P_2O_7$.

It should be mentioned that in heterogeneous catalyst (metal on inorganic support), 16 wt% Mo/Al_2O_3/TBHP system [20, 24] or V/TiO_2/H_2O_2 system [39], the reactivity order of sulfur compounds decreases in the order: DBT > 4-MDBT > 4,6-DMDBT >> BT. The same reactivity trend was reported for the polyoxometalates/H_2O_2 system/surfactant [14].

4.3 Study on the oxidation of sulfur compounds in diesel fuel

In the previous section, it was shown that DBT in hexane solution can be effectively removed by using a H_2O_2-$[V(VW_{11})O_{40}]^{4-}$- CH_3COOH system. In order to investigate whether the oxidative desulfurization system is effective for diesel fuels, the oxidative desulfurization of a commercial diesel oil (containing 0.575 %wt of sulfur detectable by XRF method) was carried out. It was previously reported that the sulfone formed were still remained in the oil [6] so high polarity solvent was used to remove it. The most effective solvent for the removal was reported to be DMF but oil recovery was low [5]. In regard to oil recovery, acetronitrile is better than DMF [21]. Therefore in this work, oxidized product was removed by solvent extraction (CH_3CN) and alumina adsorption. The results are shown in Table 4.12 and Figure 4.13.

Table 4.12 %Sulfur conversion of diesel using various catalysts promoted with acid.

Entry	Catalyst	Sulfur content remained (wt%) By XRF	% conversion	Recovery of oil (%)
1	Peroxycetic acid	0.243	58	85
2	$[W_6O_{19}]^{2-}$	0.142	75	87
3	$[V(VW_{11})O_{40}]^{4-}$	0.055	90	87
4	$[PVW_{11}O_{40}]^{4-}$	0.098	83	86
5	$[PV_2Mo_{10}O_{40}]^{4-}$	0.129	78	87
6	$(VO)_2P_2O_7$	0.208	64	86

Condition: diesel (0.575 wt% S) 50 ml, catalyst 0.18 mmol, CH_3CN 50 ml, Al_2O_3 10 g, S/C = 50, O/S = 100, $[AcOH]/[H_2O_2]$ = 1, temp 70 °C 5 h.

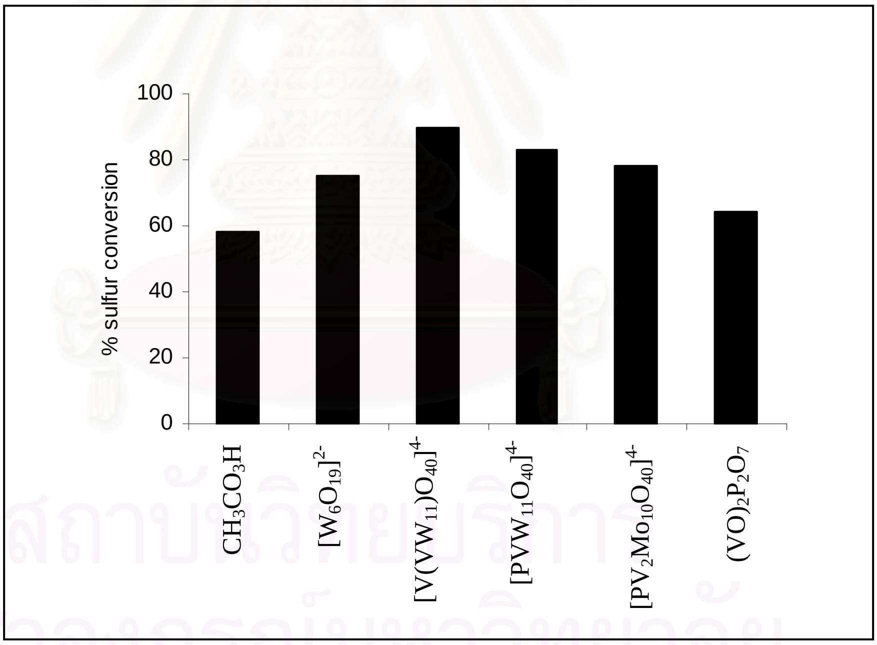


Figure 4.13 The effect of catalyst types in diesel fuel oxidation.

The results indicated that sulfur content of the oxidized diesel containing catalysts, hydrogen peroxide and acetic acid can be reduced more than that in the system without catalyst (entry 1). The reactivity order of catalysts is the same as that resulted from the sulfur model compounds in previous section. The treated oil after solvent extraction was passed through a glass column containing aluminum oxide to remove sulfones remained in the oil. The combination use of extraction and adsorption was also effective. The recovery of oil as a number of extraction and recovered ~ 86%. The resulting oil contained 0.055 wt% of sulfur that 90% of sulfur could be removed.

The diesel oil before and after oxidative treatment was checked with GC-FID. The chromatogram peaks were identified by comparison of their retention times with authentic compounds, the retention time are 6.961 min for BT, 10.420 min for DBT and 11.461 min for DMDBT. By calculating the peak areas, each sulfur compounds can be quantified and it was found that % removal of each sulfur compound is: BT (67%), DBT (86%) and DMDBT (87%), respectively. So, from the results obtained in this work, it was demonstrated that the catalyst can catalyze the oxidation reaction in 5 hours and can reduce sulfur content of diesel oil from 0.575 wt% S to 0.055 wt% S. For comparison, it should be mentioned that the oxidation of straight run light gas oil (1.35 wt% S) in the presence of high amount of oxidant (hydrogen peroxide) and formic acid, the removal of sulfur were 99 % in 46 hours [5].

4.4 Study on the kinetics of the model sulfur compounds

The reaction of the oxidation of benzothiophene (BT) was studied by using $[V(VW_{11})O_{40}]^{4-}$ as catalyst. BT (0.5 mmol) was dissolved in hexane (50 ml), hydrogen peroxide (50 mmol) were added to the flask. The flask immersed in the heating bath was stirred (50-70 °C). The catalyst (0.0065 mmol) and acetic acid (50 mmol) were added to initiate the reaction. Reaction samples were withdrawn at 1, 2, 3, 4 and 5 hours and quatified by GC. The BT conversions were plotted as a function of time. The reaction rates were then obtained from the corresponding slope according to equation 3.2.

4.4.1 Kinetics study of benzothiophene

The general oxidation procedure of benzothiophene using tungstovanadate $[V(VW_{11})O_{40}]^{4-}$ as catalyst was carried out. The BT conversions at different temperatures were summarized in Table 4.13 and plotted as a function of time in Figure 4.14, respectively.

Table 4.13 Oxidation reaction conversion of BT at 50-70°C

Entry	Time (min)	% conversion		
		50°C	60°C	70°C
1	0	0	0	0
2	60	23	39	40
3	120	43	71	82
4	180	56	88	91
5	240	73	97	98
6	300	82	98	99

Condition: BT = 0.5 mmol, $[V(VW_{11})O_{40}]^{4-}$ = 0.0065 mmol, oxidant = 50 mmol, S/C = 80, O/S = 100, hexane 50 ml, $[H_2O_2]/[AcOH]$ = 1.

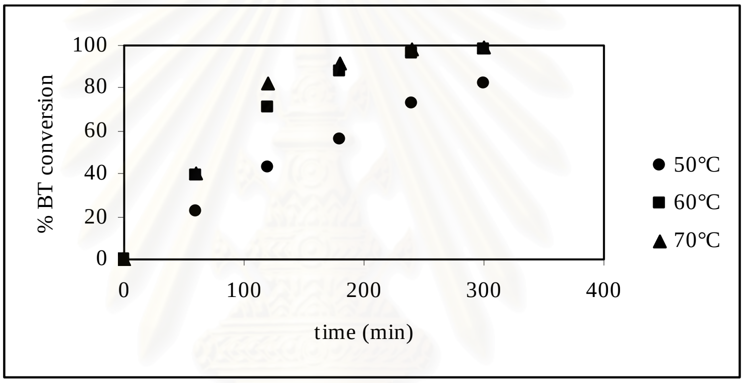


Figure 4.14 Oxidation conversion of BT at 50-70°C using $[V(VW_{11})O_{40}]^{4-}$.

It was found that the time around 3 hours (180 min) period of time was adequate for oxidation of benzothiophene at 70°C. The BT conversions were plotted as a function of time (t). The reaction rates (*k*) were then obtained from the corresponding slope. The empirical expression is shown in equation 3.2. A plot of ln(Ct/Co) versus reaction time displayed a linear relationship that confirmed the pseudo first order reaction kinetics was shown in Figure 4.15.

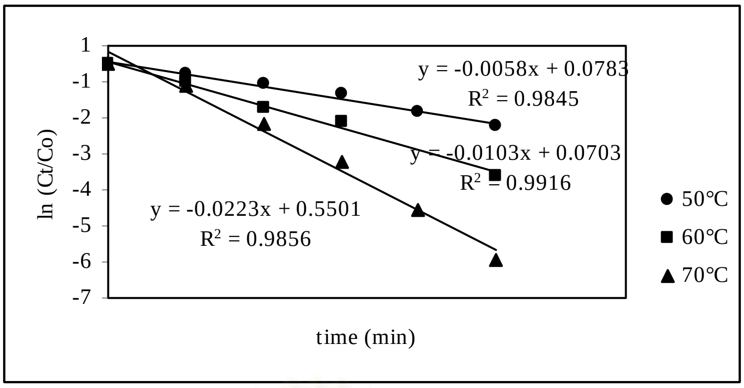


Figure 4.15 Pseudo first order oxidation of BT at 50-70°C using $[V(VW_{11})O_{40}]^{4-}$.

4.4.2 Kinetics study of dibenzothiophene

The same procedure as in section 4.4.1 was performed, except that benzothiophene was replaced with dibenzothiophene. The DBT conversions at different temperatures were summarized in Table 4.14 and plotted as a function of time in Figure 4.16, respectively.

Table 4.14 Oxidation reaction conversion of DBT at 50-70°C

Entry	Time (min)	% conversion		
		50°C	60°C	70°C
1	0	0	0	0
2	60	42	52	62
3	120	73	81	94
4	180	85	94	99
5	240	93	98	100
6	300	96	100	100

Condition: DBT = 0.5 mmol, $[V(VW_{11})O_{40}]^{4-}$ = 0.0065 mmol, oxidant = 50 mmol, S/C = 80, O/S = 100, hexane 50 ml, $[H_2O_2]/[AcOH]$ = 1.

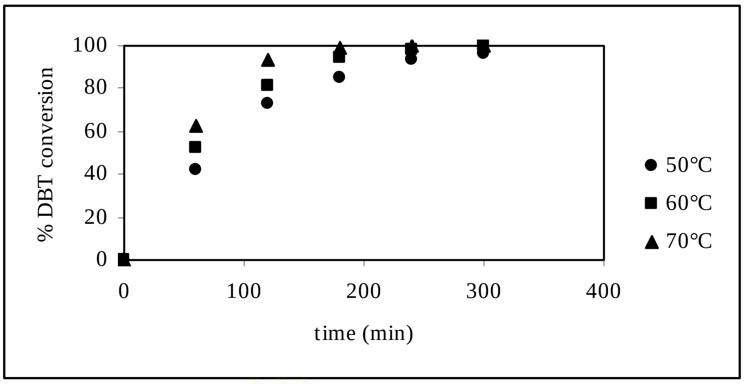


Figure 4.16 Oxidation of DBT at 50-70°C using $[V(VW_{11})O_{40}]^{4-}$.

It was found that 4 hours (240 min) period of time was adequate for oxidation of dibenzothiophene at 70 °C. The DBT conversions were plotted as a function of time (t). The reaction rates (*k*) were then obtained from the corresponding slope. The empirical expression is shown in equation 3.2. A plot of ln (Ct/Co) versus reaction time displayed a linear relationship that confirmed the pseudo first order reaction kinetics was shown in Figure 4.17.

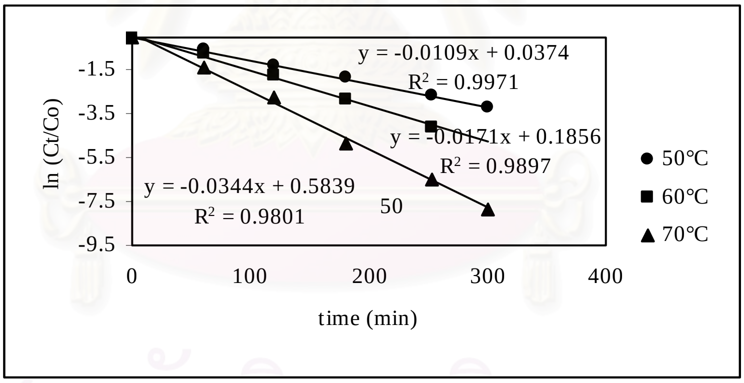


Figure 4.17 Pseudo first order oxidation of DBT at 50-70°C using $[V(VW_{11})O_{40}]^{4-}$.

4.4.3 Kinetics study of dimethyldibenzothiophene

The same procedure as in section 4.4.1 was performed, except that benzothiophene was replaced with dimethyldibenzothiophene. The 4,6-DMDBT conversions at different temperatures were summarized in Table 4.15 and plotted as a function of time in Figure 4.18, respectively.

Table 4.15 Oxidation reaction conversion of 4,6-DMDBT at 50-70°C

Entry	Time (min)	% conversion		
		50°C	60°C	70°C
1	0	0	0	0
2	60	21	43	51
3	120	42	75	84
4	180	60	88	96
5	240	75	97	98
6	300	83	99	100

Condition: DMDBT = 0.5 mmol, $[V(VW_{11})O_{40}]^{4-}$ = 0.0065 mmol, oxidant = 50 mmol, S/C = 80, O/S = 100, hexane 50 ml, $[H_2O_2]/[AcOH]$ = 1.

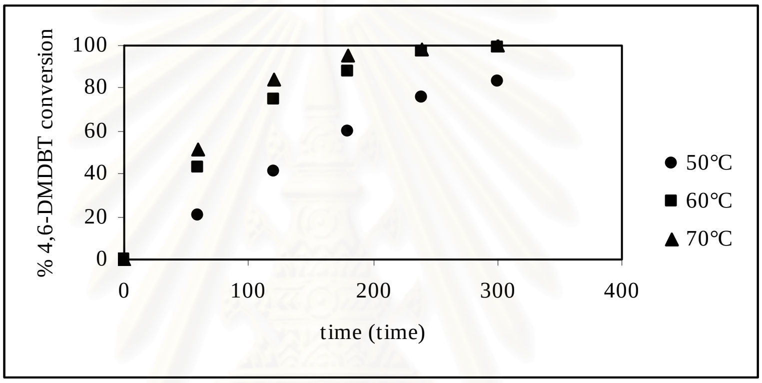


Figure 4.18 Oxidation of 4,6-DMDBT at 50-70 °C using $[V(VW_{11})O_{40}]^{4-}$.

It was found that 4 hours period of time was adequate for oxidation of 4,6-DMDBT at 70 °C. The DMDBT conversions were plotted as a function of time (t). Reaction rates (*k*) were then obtained from the corresponding slope. A plot of ln (Ct/Co) versus reaction time displayed a linear relationship that confirmed the pseudo first order reaction kinetics was shown in Figure 4.19.

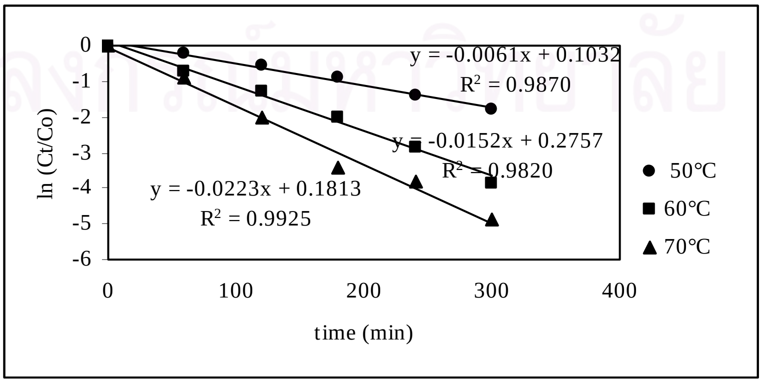


Figure 4.19 Pseudo first order oxidation of 4,6-DMDBT at 50-70°C using $[V(VW_{11})O_{40}]^{4-}$.

The reaction data of BT (Figure 4.14), DBT (Figure 4.16) and 4,6-DMDBT (Figure 4.18) at 50-70°C also fitted well with pseudo first order reaction kinetics. The rate constants (*k*) generated are summarized in Table 4.16.

Table 4.16 BT, DBT and 4,6-DMDBT rate constants at different temperatures

Substrates	Reaction temperature (°C)	Rate constants (min^{-1})	Correlation factor R^2
BT	50	0.0058	0.9845
	60	0.0103	0.9916
	70	0.0223	0.9856
DBT	50	0.0109	0.9971
	60	0.0171	0.9897
	70	0.0344	0.9801
4,6-DMDBT	50	0.0061	09870
	60	0.0152	0.9820
	70	0.0223	0.9925

Condition: substrates = 0.5 mmol, $[V(VW_{11})O_{40}]^{4-}$ = 0.0065 mmol, oxidant = 50 mmol, S/C = 80, O/S = 100, hexane 50 ml, $[H_2O_2]/[AcOH]$ = 1.

A plot of –ln *k* versus 1/*T* allows us to calculate the activation energy *E*a (slope = -*E*a/*R*). The Arrhenius plots are shown in Figure 4.20 and the activation energies are listed in Table 4.17.

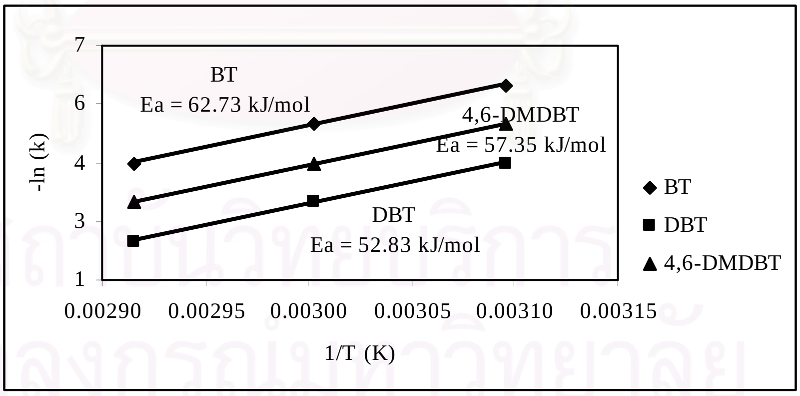


Figure 4.20 Arrhenius activation energies for DBT 4,6-DMDBT and BT oxidation.

Table 4.17 Apparent activation energies for oxidation BT, DBT and 4,6-DMDBT

Substrates	*E*a (kJ/mol)	Correlation factor R^2
BT	62.73	0.9849
DBT	52.83	0.9943
4,6-DMDBT	57.35	0.9963

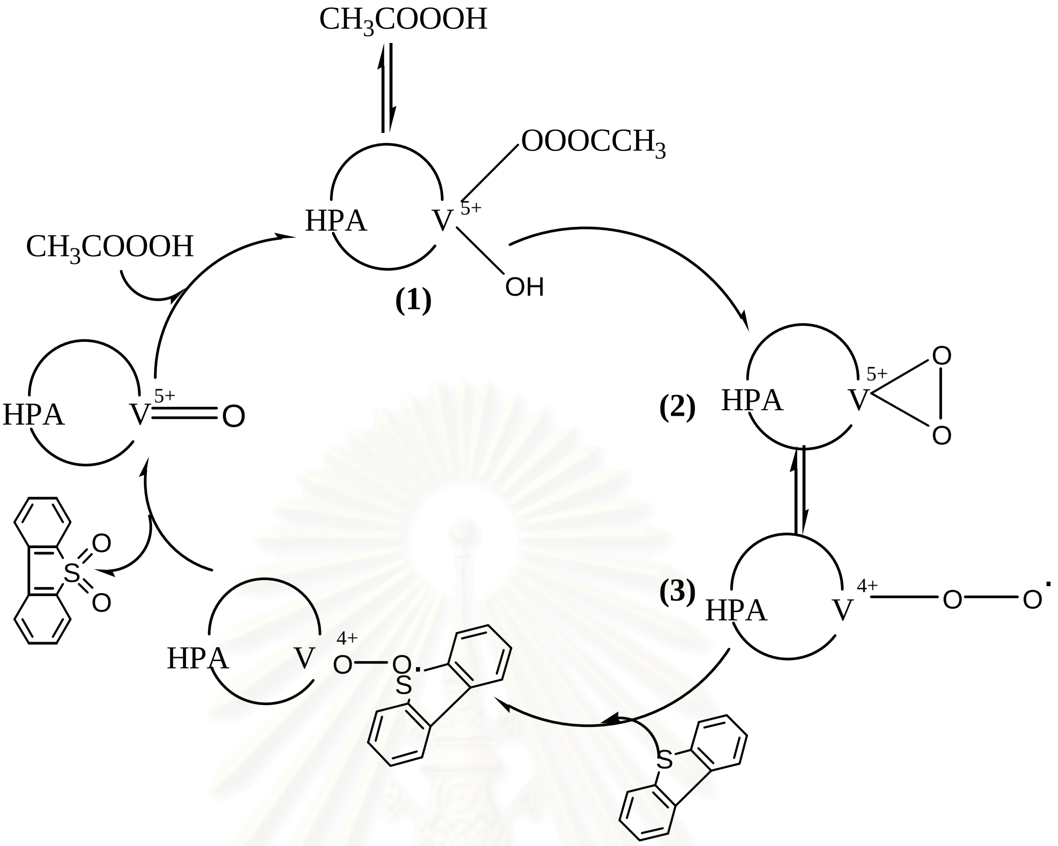
Condition: substrate = 0.5 mmol, $[V(VW_{11})O_{40}]^{4-}$ = 0.0065 mmol, oxidant = 50 mmol, S/C = 80, O/S = 100, hexane 50 ml, $[H_2O_2]/[AcOH]$ = 1, 50-70 °C.

From data in Table 4.17 and Figure 4.20, apparent activation energy of pseudo first order reaction for BT, 4,6-DMDBT and DBT were determined to be 62.73, 57.35 and 52.83 kJ/mol respectively. The activation energy data showed the reactivity order of DBT > 4,6-DMDBT > BT which is consistent with that in the previous section.

It should be noted that the apparent activation energy obtained from this work is in good agreement with those reported. For the polyoxometalate/H_2O_2 system the apparent activation energy of DBT, 4-MDBT and 4,6-DMDBT were 53.8 56.0 and 57.41 kJ/mol, respectively [14]. In the formic acid/H_2O_2 system the apparent activation energy of DBT was 60 kJ/mol [32]. In a biphasic system of diesel and acetronitrile using H_2O_2/Na_2CO_3, the apparent activation energy of 4,6-DMDBT was 57.1 kJ/mol [25].

4.5 Proposed mechanism for catalyzed oxidation of sulfur compounds

From the obtained results, sulfone is found as a main product from sulfur compounds oxidation, it was confirmed by gas chromatography (some trace of sulfoxide was observed with $(VO)_2P_2O_7$ catalyst). % Conversion increased with time. Mechanism of sulfur compounds oxidation was proposed as shown in Scheme 4.1.



Scheme 4.3 Mechanism for the vanadium-CH_3CO_3H catalyzed oxidation of sulfur compounds.

In this work, it was proposed that when the catalyst was reacted with oxidizing agent, the electrophilic intermediate **(1)** is formed after the exchange of V^{5+} with CH_3CO_3H (from combination of H_2O_2 and CH_3COOH) and this process may be reversible. After that the intermediate **(1)** was transformed into either V(5+)-peroxo (**2**) or V(4+)-superoxo **(3)** intermediates. It reacted with sulfur compound by forming O-S bond, then to give rise to sulfone product. As only sulfone was detected without sulfoxide found, the oxidation is believed to proceed with fast rate.

4.6 Characterization of product

4.6.1 Fourier transform infrared spectroscopy (FT-IR)

The infrared spectroscopy is an effective method to identify sulfur compound. It is sufficient to characterize the functional groups of sulfoxide and sulfone in the wave number of 1070-1030 and 1160-1140, 1230-1150 cm^{-1}. The IR spectrum for the product obtained demonstrated absorption bands at 1130 and 1280 cm^{-1} which are attributable to sulfone group. The spectra of benzothiophene and its oxidized products are shown in Figure 4.21.

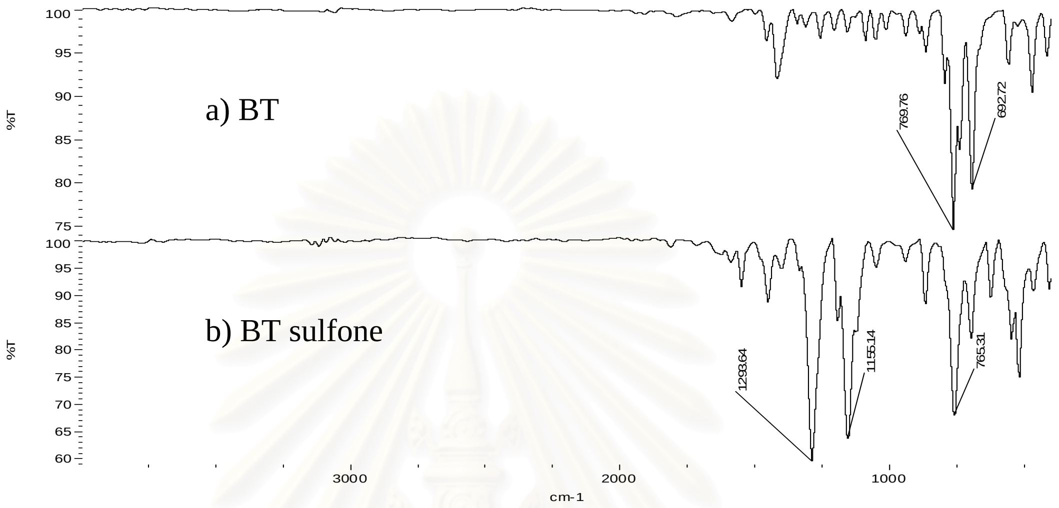


Figure 4.21 FT-IR spectra of BT and its oxidized product.

From the IR spectrum of benzothiophene sulfone (Figure 4.21 b) as comparing with benzothiophene (Figure 4.21 a), it could be observed the absorption band of SO_2 stretching of sulfone at 1155 and 1293 cm^{-1}.

Table 4.18 FT-IR data of the benzothiophenes, and its oxidized products.

Wave number (cm^{-1})	Assignment
700-600	C-S stretching
1160-1140 1230-1150	S=O stretching of sulfone
1600-1500	C=C stretch (aromatic)

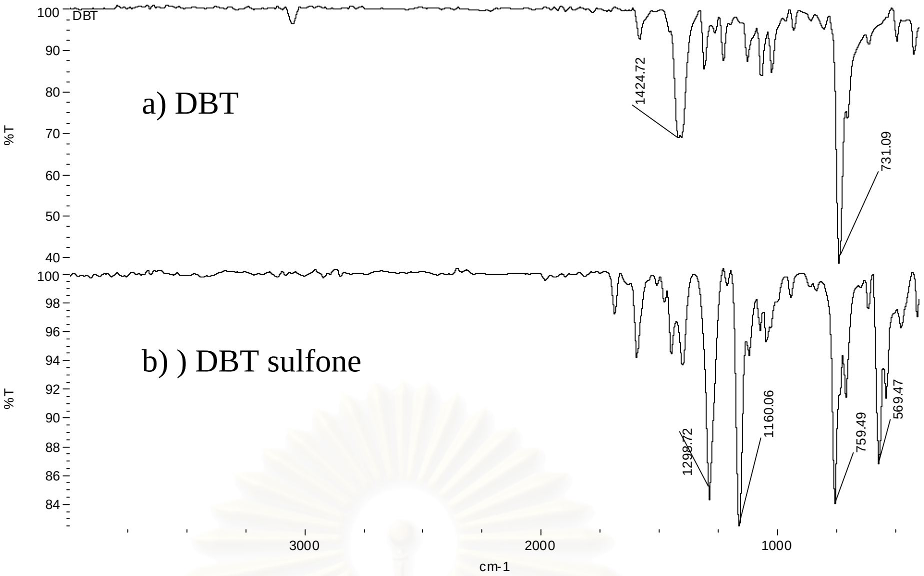


Figure 4.21 FT-IR spectra of DBT and its oxidized products.

From the IR spectrum of dibenzothiophene sulfone (Figure 4.22, b) as comparing with dibenzothiophene (Figure 4.22, a), it could be observed that the absorption band of SO_2 stretching of sulfone were clearly observed at 1160 and 1298 cm^{-1} respectively [6, 40].

From the IR spectrum of DMDBT sulfone (Figure 4.23 b) as comparing with DBT (Figure 4.23, a), it could be observed the absorption band of SO_2 stretching of sulfone at 1155, 1283 and 1586 cm^{-1}.

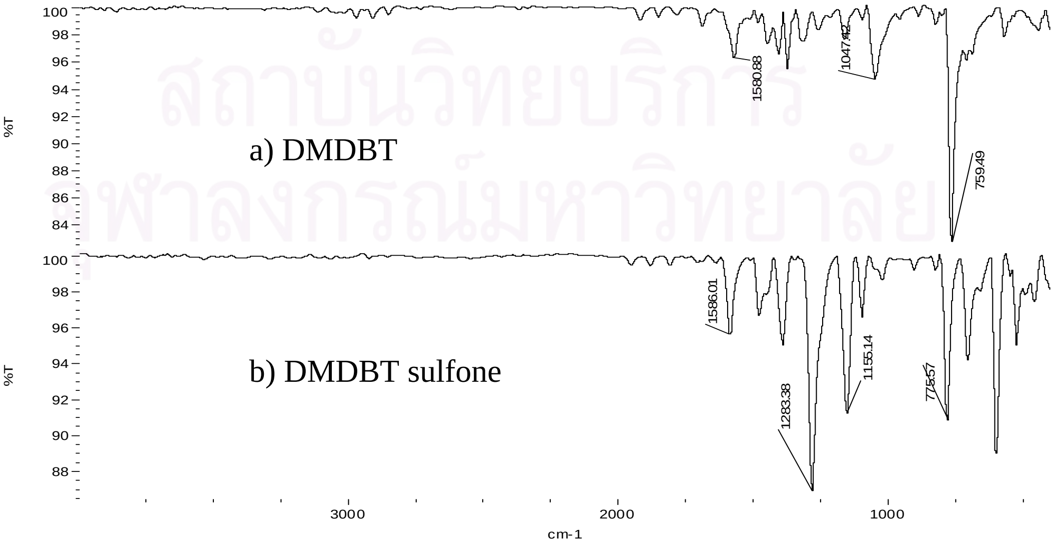


Figure 4.23 FT-IR spectra of 4,6-DMDBT and its oxidized product.

4.4.3 Nuclear magnetic resonance spectroscopy (NMR)

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy is a tool for molecular structure analysis. The chemical shifts of the benzothiophene, dibenzothiophene and dimethyldibenzothiophene and their corresponding sulfones were presented in Figures 4.24-4.29.

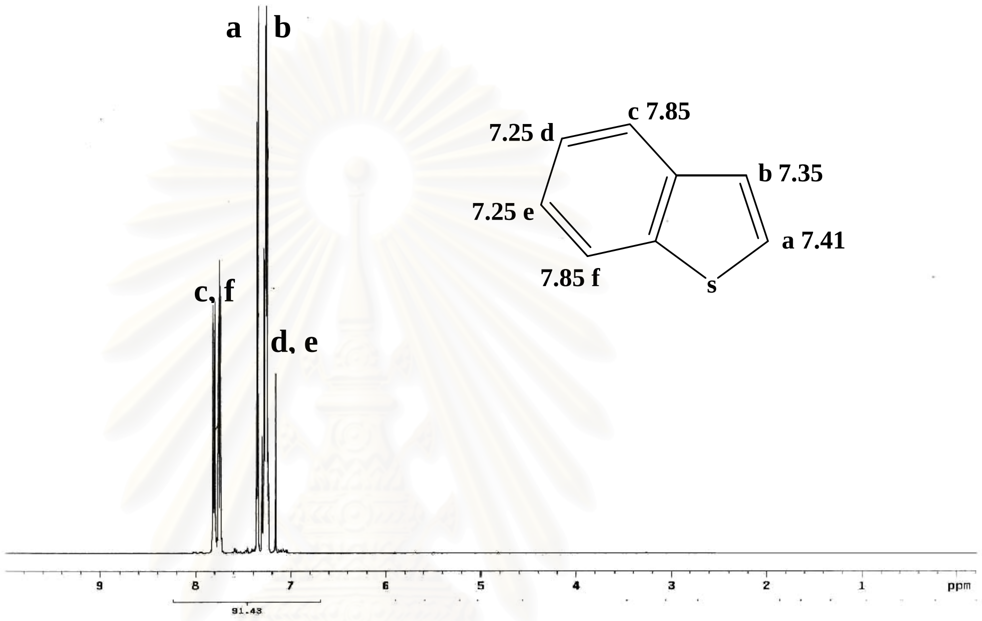


Figure 4.24 ^{1}H NMR spectrum of the benzothiophene ($CDCl_3$).

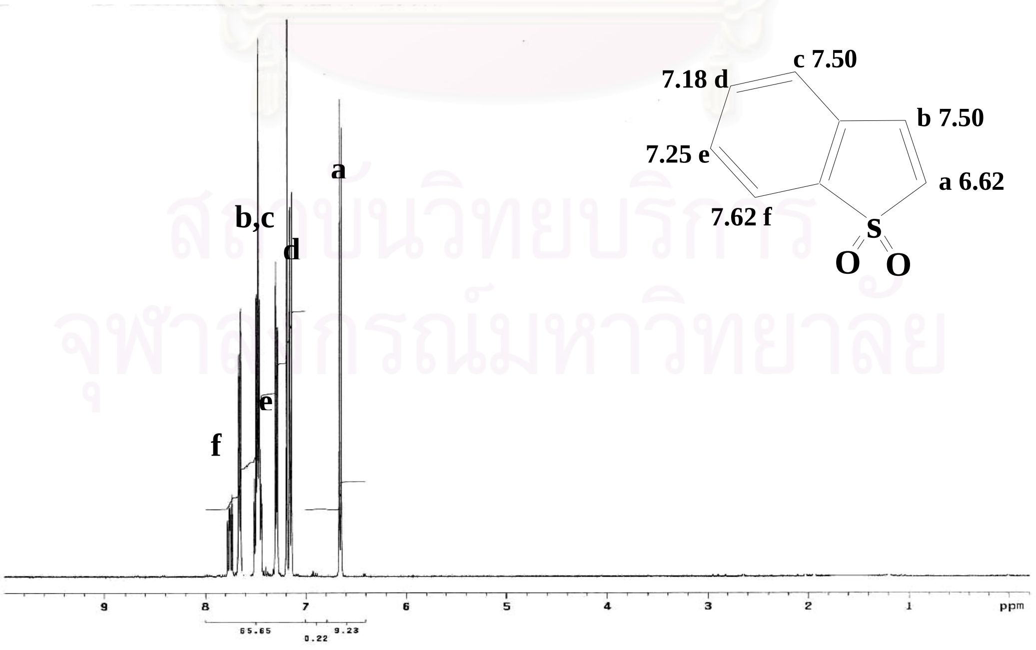


Figure 4.25 ^{1}H NMR spectrum of the benzothiophene sulfone ($CDCl_3$).

The NMR spectra of sulfones revealed that a proton near the S shifted upfield. This can be explained by the electron withdrawing effect of O atom which caused the deshielding.

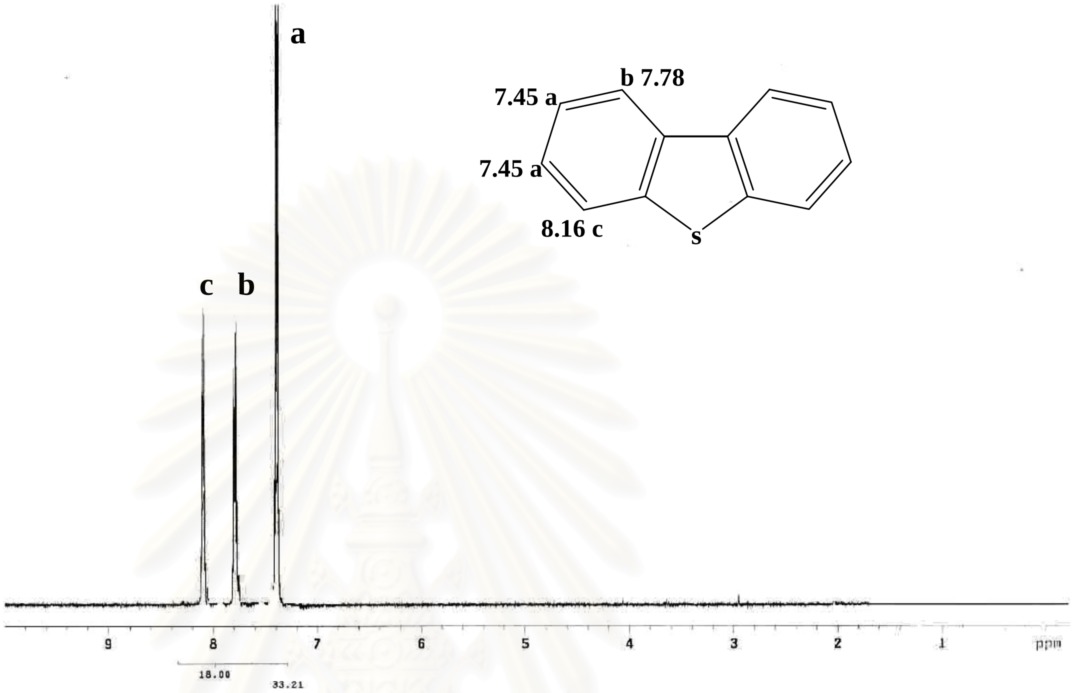


Figure 4.26 ^{1}H NMR spectrum of the dibenzothiophene ($CDCl_3$).

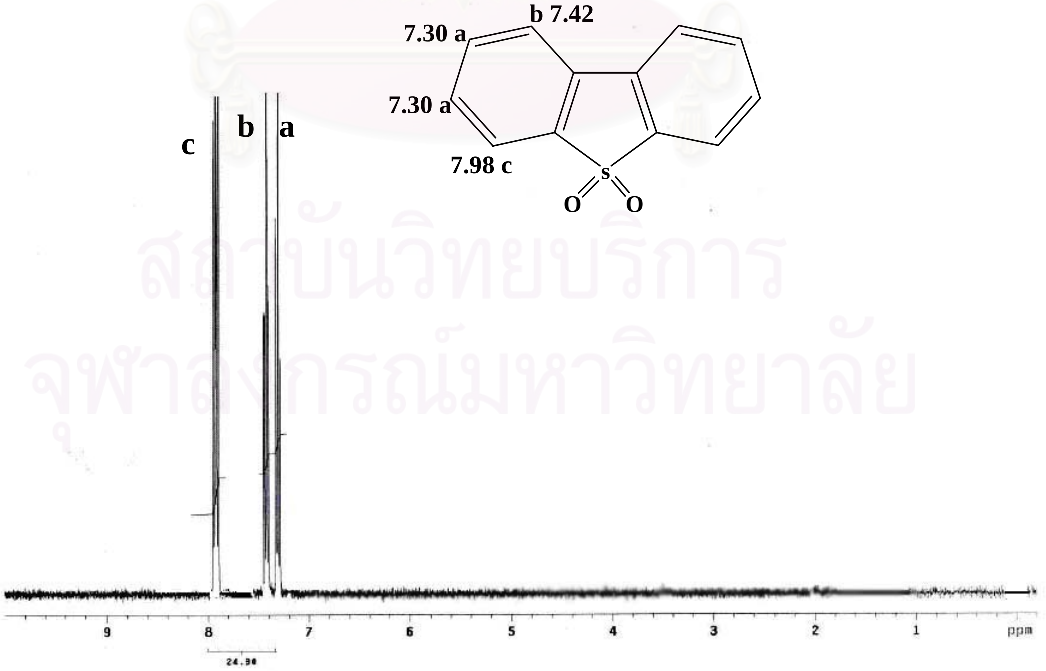


Figure 4.27 ^{1}H NMR spectrum of the dibenzothiophene sulfone ($CDCl_3$).

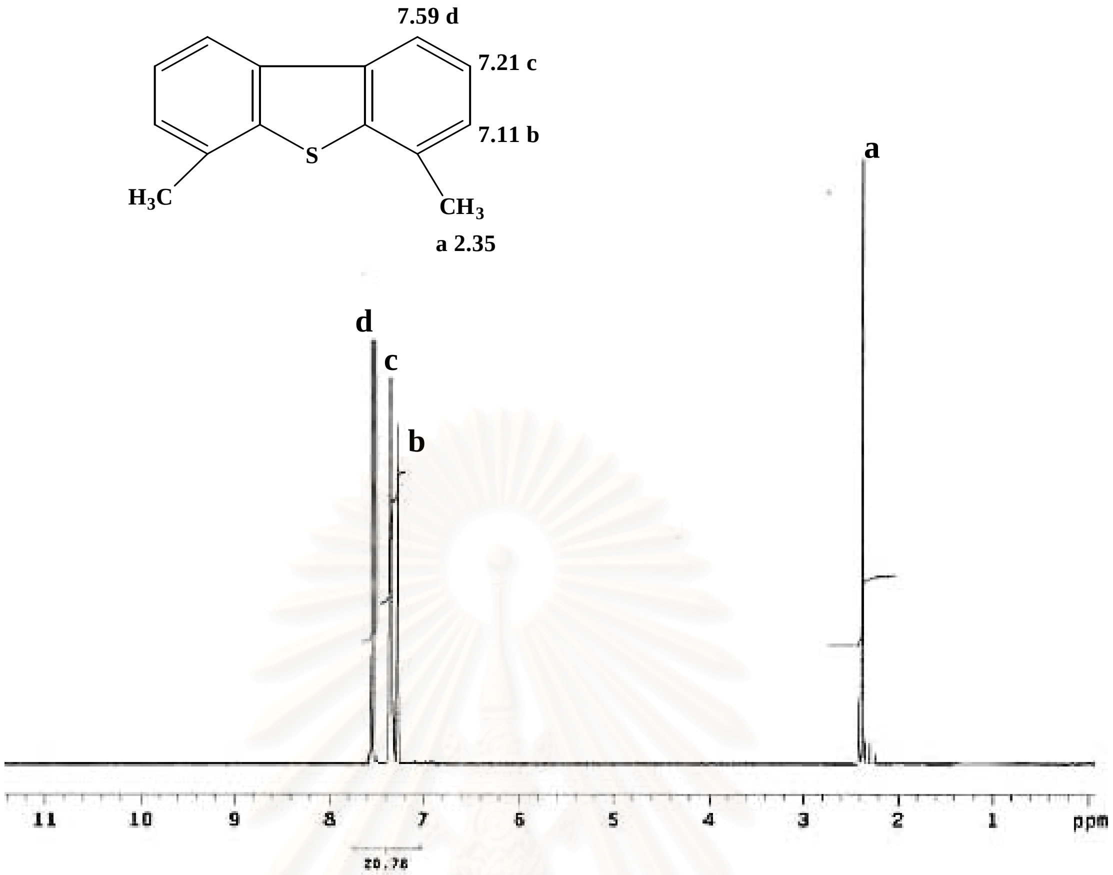


Figure 4.29 ^{1}H NMR spectrum of the dimethyldibenzothiophene (CDCl$_3$).

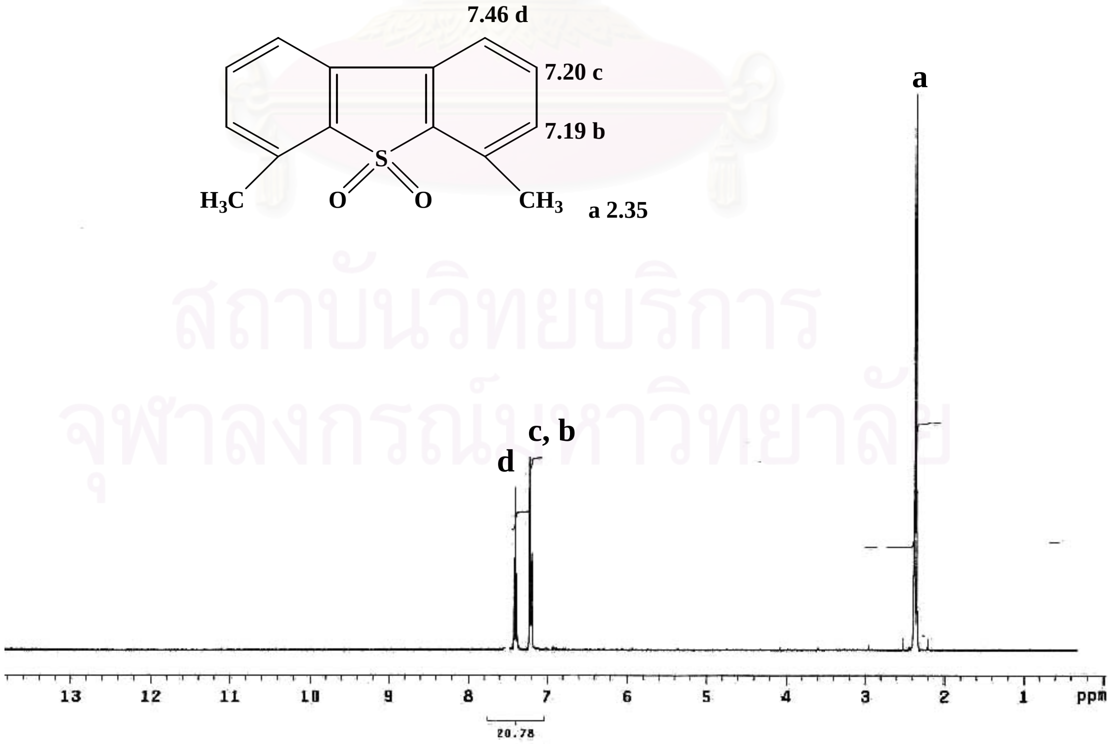


Figure 4.30 ^{1}H NMR spectrum of the dimethyldibenzothiophene sulfone (CDCl$_3$).

CHAPTER V
CONCLUSION AND SUGGESTION

The main objective of this research is to search for the catalytic system for oxidative desulfuruzation of sulfur compounds (benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene) using mild condition. The objective is achieved by using polyoxometalates catalysts. To find optimum condition for the oxidation reaction, reaction parameters were studied and it was found that the reaction should be performed using hydrogen peroxide as oxidizing agent in hexane solvent at 70°C, the suitable extraction solvent is DMF.

Among several catalysts tested in this work were $[V(VW_{11})O_{40}]^{4-}$, $[W_6O_{19}]^{2-}$ $[PVW_{11}O_{40}]^{4-}$, $[PV_2Mo_{10}O_{40}]^{4-}$ and $(VO)_2P_2O_7$, the highest active is $[V(VW_{11})O_{40}]^{4-}$. The activity is increased by adding acetic acid (the suitable acid/oxidizing agent mole ratio is 1.5). The sulfone products were characterized by gas chromatography, fourier transform infrared spectroscopy and nuclear magnetic resonance.

The best catalyst $[V(VW_{11})O_{40}]^{4-}$ was utilized for fuel oil oxidation with hydrogen peroxide and acetic acid. The oxidation with simultaneous extraction was performed at 70 °C 5 h. Further removal of oxidized product was done using alumina adsorption. The sulfur content of oil was decreased successfully up to 90%, from 0.575 %wt sulfur to 0.055 %wt sulfur.

The kinetics study was performed using gas chromatography technique. It can be found that the rate of dibenzothiophene (DBT) oxidation was faster than that of dimethyldibenzothiophene (DMDBT) and benzothiophene (BT) oxidation. Apparent activation energies were 52.83, 57.35, and 62.73 kJ/mol, respectively. Order of the oxidation reaction rate was: DBT > DMDBT > BT.

Suggestion for the future work

From all aforementioned results and discussion, the future work to improve the system should be focused on the following:

1. The modification of catalyst, especially the vanadium containing one should be attempted.
2. The detailed study of mechanism of the oxidation reaction should be further investigated.

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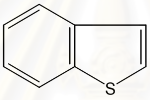
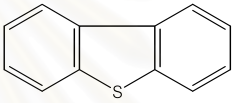
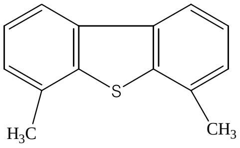
APPENDICES

APPENDIX A

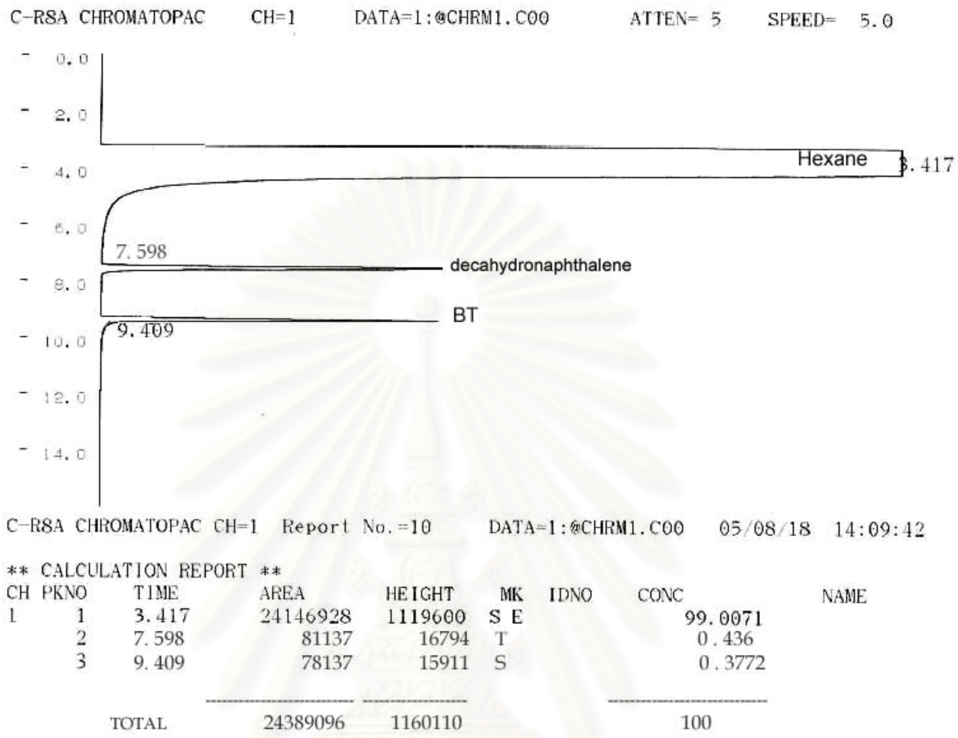
APPENDIX A

Table A1 Properties of the model sulfur compounds

property	benzothiophene	dibenzothiophene	4,6-dimethyl dibenzothiophene
Chemical formula	C_8H_6S	$C_{12}H_8S$	$C_{14}H_{12}S$
Molecular weight	134.3	184.3	212.3
Melting poit (C°)	28-32	97-100	153-157
Physical	liquid	white crystal	pale yellow crystal
Boiling point (C°)	221	332	366
Chemical structure			

Calculation of the correction factor

Correction factor of benzothiophene (BT) :



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** CALCULATION REPORT **
CH PKNO     TIME        AREA        HEIGHT     MK  IDNO     CONC              NAME
1     1     3.417       24146928    1119600    S E              99.0071
      2     7.598          81137      16794    T                 0.436
      3     9.409          78137      15911    S                 0.3772

                    ------------------ ------------           --------------------
           TOTAL        24389096     1160110                    100
```

Figure A-1 A gas chromatogram of BT for correction factor calculation.

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section) decahydronaphthalene was used as internal standard.

A1: exact amount of BT prepared = 1.0 x 10^{-4} mol
B1: exact amount of internal standard added = 1.50 x 10^{-5} mol
C1: peak area of BT prepared = 78137
D1: peak area of the internal standard = 81137
Total volume of the reaction = 10 ml.

The calculation of the correction factor can be described as follows:

The amount of BT from the reaction mixture

= (B1 x C1 / D1) = E1

= 1.50 x 10^{-5} x 78137 / 81137

= 1.44 x 10^{-5}

The amount of BT in 10 ml (total volume of the reaction)

= E1 x 10 = F1

= 1.44 x 10^{-5} x 10

= 1.44 x 10^{-4}

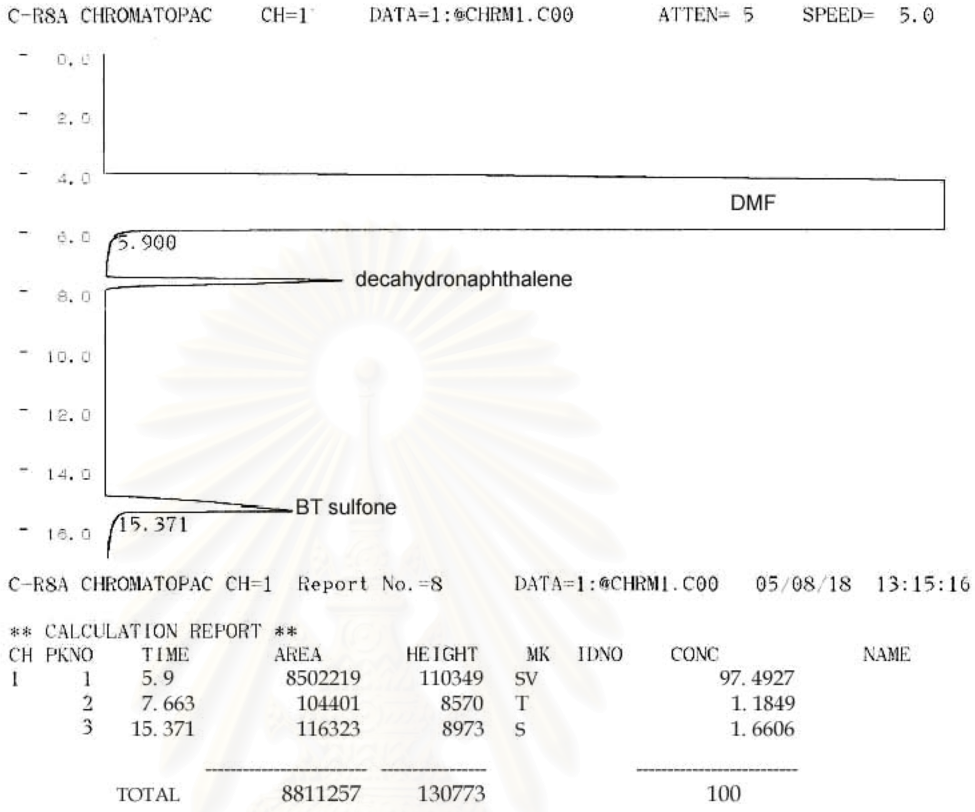
Thus, the correction factor of BT can be calculated as:

= A1 / F1

= 1.0 x10^{-4} / 1.44 x 10^{-4}

= 0.69

Correction factor of benzothiophene (BT sulfone):



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** CALCULATION REPORT **
CH PKNO     TIME        AREA        HEIGHT     MK   IDNO      CONC              NAME
1     1      5.9         8502219     110349    SV                  97.4927
      2      7.663        104401       8570    T                    1.1849
      3     15.371        116323       8973    S                    1.6606
                       ----------  ----------               ----------
          TOTAL          8811257     130773                      100
```

Figure A-2 A gas chromatogram of BT sulfone for correction factor calculation.

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section) decahydronaphthalene was used as internal standard.

G1: exact amount of BT sulfone prepared = 0.85×10^{-4} mol

H1: exact amount of internal standard added = 0.957×10^{-5} mol

I1: peak area of BT sulfone prepared = 104401

J1: peak area of the internal standard = 116323

Total volume of the reaction = 10 ml.

The calculation of the correction factor can be described as follows:

The amount of BT sulfone from the reaction mixture

= (H1 x I1 / J1) = K1

= $0.957 \times 10^{-5} \times 104401 / 116323$

= 0.859×10^{-5}

The amount of BT sulfone in 10 ml (total volume of the reaction)

= K1 x 10 = L1

= $0.859 \times 10^{-5} \times 10$

= 0.859×10^{-4}

Thus, the correction factor of BT sulfone can be calculated as:

= G1 / L1

= $0.85 \times 10^{-4} / 0.859 \times 10^{-4}$

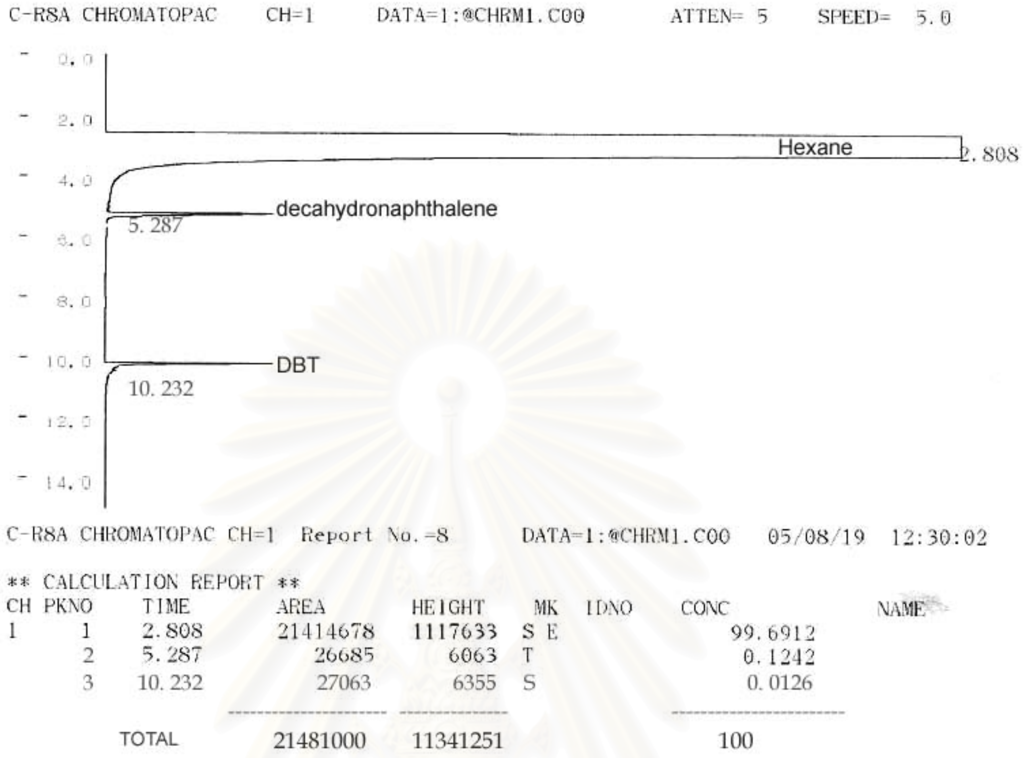
= 0.99

The correction factors of chemicals are listed as follows:

BT = 0.69

BT sulfone = 0.99

Correction factor of dibenzothiophene (DBT):



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** CALCULATION REPORT **
CH PKNO    TIME       AREA       HEIGHT     MK  IDNO    CONC              NAME
1     1    2.808    21414678    1117633    S E              99.6912
      2    5.287       26685       6063    T                 0.1242
      3   10.232       27063       6355    S                 0.0126
                    ---------------  -----------        ----------------
           TOTAL    21481000    11341251                  100
```

Figure A-3 A gas chromatogram of DBT for correction factor calculation.

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section) decahydronaphthalene was used as internal standard.

A2: exact amount of BT prepared = 1.2×10^{-4} mol
B2: exact amount of internal standard was added = 1.45×10^{-5} mol
C2: peak area of BT prepared = 27063
D2: peak area of the internal standard = 26685
Total volume of the reaction = 10 ml.

The calculation of the correction factor can be described as follows:

The amount of DBT from the reaction mixture

= (B2 x C2 / D2) = E2

= $1.45 \times 10^{-5} \times 27063 / 26685$

= 1.47×10^{-5}

The amount of DBT in 10 ml (total volume of the reaction)

= E2 x 10 = F2

= $1.47 \times 10^{-5} \times 10$

= 1.47×10^{-4}

Thus, the correction factor of DBT can be calculated as:

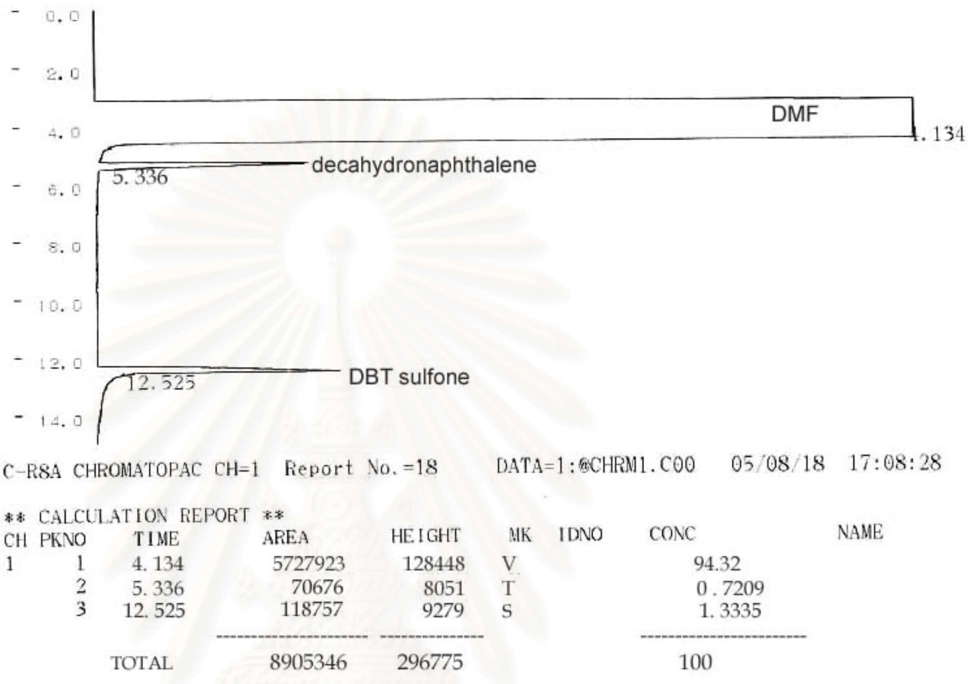
= A2 / F2

= $1.20 \times 10^{-4} / 1.47 \times 10^{-4}$

= 0.86

Correction factor of dibenzothiophene sulfone:

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section) decahydronaphthalene was used as internal standard.



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** CALCULATION REPORT **
CH PKNO    TIME        AREA       HEIGHT    MK  IDNO     CONC          NAME
1    1    4.134      5727923      128448    V              94.32
     2    5.336        70676        8051    T              0.7209
     3   12.525       118757        9279    S              1.3335
                   ----------  ----------             -----------
         TOTAL       8905346      296775                 100
```

Figure A-4 A gas chromatogram of DBT sulfone for correction factor calculation

G2: exact amount of DBT sulfone prepared = 1.50×10^{-4} mol

H2: exact amount of internal standard added = 1.50×10^{-5} mol

I2: peak area of DBT sulfone prepared = 118757

J2: peak area of the internal standard = 70676

Total volume of the reaction = 10 ml.

The calculation of the correction factor can be described as follows:

The amount of DBT sulfone from the reaction mixture

= (G2 x I2 / J2) = K2

= 1.50 x 10^{-5} x 118757/70676

= 2.52 x10^{-5}

The amount of DBT sulfone in 10 ml (total volume of the reaction)

= K2 x 10 = L2

= 2.52 x10^{-5}x 10

= 2.52 x10^{-4}

Thus, the correction factor of DBT sulfone can be calculated as:

= G2 / L2

= 1.50 x10^{-4} / 2.52 x 10^{-4}

= 0.59

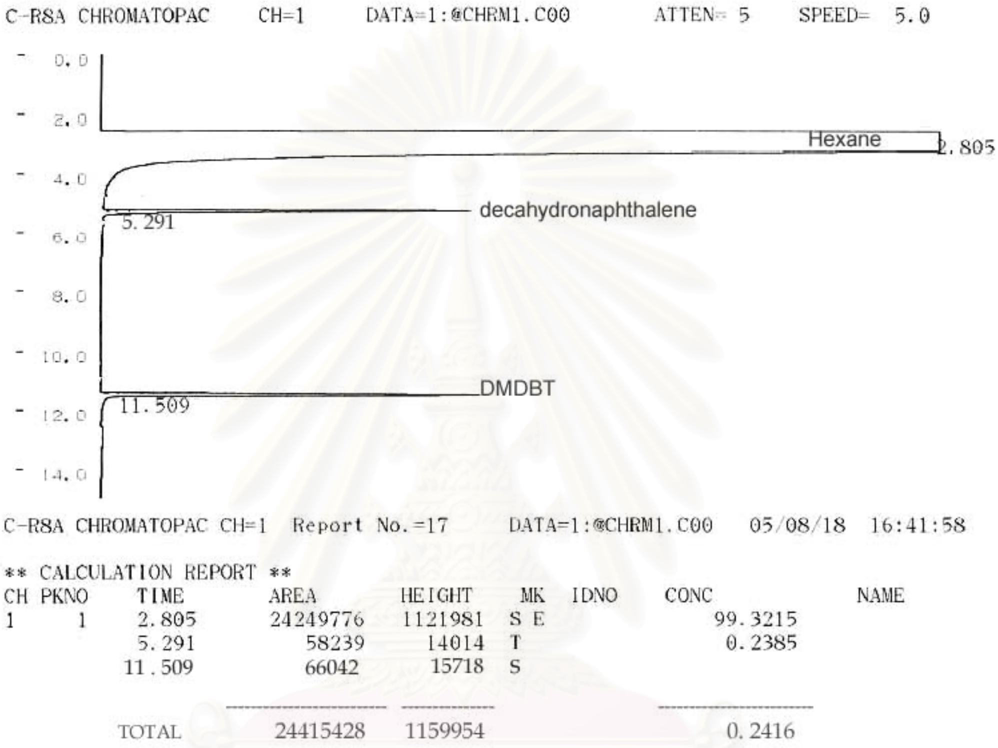
The correction factors of chemicals are listed as follows:

DBT = 0.86

DBT sulfone = 0.59

Correction factor of dimethyldibenzothiophene (DMDBT) :

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section) decahydronaphthalene was used as internal standard.



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** CALCULATION REPORT **
CH PKNO    TIME       AREA       HEIGHT    MK  IDNO    CONC             NAME
1     1    2.805      24249776   1121981   S E              99.3215
           5.291         58239     14014   T                 0.2385
          11.509         66042     15718   S
                 --------------  ----------          ----------------
          TOTAL     24415428   1159954                       0.2416
```

Figure A-4 A gas chromatogram of DMDBT for correction factor calculation.

A3: exact amount of DMDBT prepared = 5×10^{-4} mol

B3: exact amount of internal standard added = 5.124×10^{-5} mol

C3: peak area of DMDBT prepared = 66042

D3: peak area of the internal standard = 58239

Total volume of the reaction = 10 ml.

The calculation of the correction factor can be described as follows:

The amount of DMDBT from the reaction mixture

= (B3 x C3 / D3) = E3

= $5.124 \times 10^{-5} \times 66042/58239$

= 5.81×10^{-5}

The amount of DMDBT in G ml (total volume of the reaction)

= E3 x 10 = F3

= $5.81 \times 10^{-5} \times 10$

= 5.81×10^{-4}

Thus, the correction factor of DMDBT can be calculated as:

= A3 / F3

= $5.0 \times 10^{-4}/5.81 \times 10^{-4}$

=0.86

The correction factors of chemicals are listed as follows:

DMDBT = 0.86

APPENDIX B

Table B1 Oxidation of benzothiophene at 50°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	*Ct* (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	$\ln \frac{Ct}{Co}$
1	0	0.4617	0.0000	0	1.0000	0.0000
2	60	0.3569	0.2270	23	0.7656	-0.2672
3	120	0.2650	0.4260	43	0.5684	-0.5649
4	180	0.2037	0.5588	56	0.4369	-0.8280
5	240	0.1239	0.7316	73	0.2658	-1.3251
6	300	0.0823	0.8217	82	0.1765	-1.7342

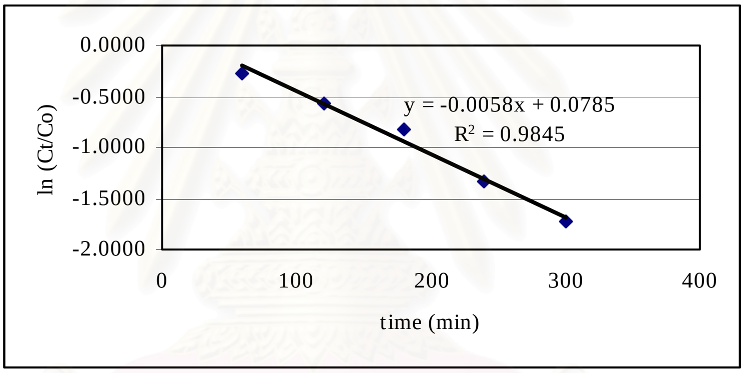

Figure B1 ln (*Ct/Co*) of BT as a function of reaction time at 50°C.

Table B2 Oxidation of benzothiophene at 60°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	Ct (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	$\ln\frac{Ct}{Co}$
1	0	0.4229	0.0000	0	1.0000	0.0000
2	60	0.2587	0.3883	39	0.6117	-0.4915
3	120	0.1231	0.7089	71	0.2911	-1.2341
4	180	0.0840	0.8014	80	0.1986	-1.6163
5	240	0.0349	0.9175	92	0.0825	-2.4946
6	300	0.0190	0.9551	96	0.0449	-3.1027

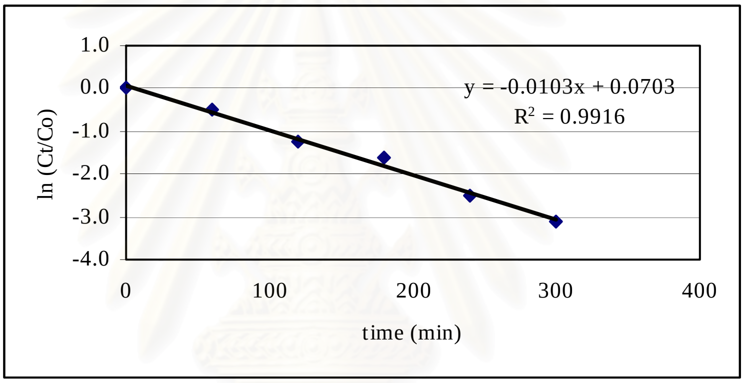

Figure B2 ln (*Ct/Co*) of BT as a function of reaction time at 60°C.

Table B3 Oxidation of benzothiophene at 70°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	*Ct* (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	$\ln \frac{Ct}{Co}$
1	0	0.5412	0.0000	0	1.0000	0.0000
2	60	0.3013	0.4434	44	0.5566	-0.5858
3	120	0.1000	0.8152	82	0.1848	-1.6886
4	180	0.0350	0.9353	94	0.0647	-2.7384
5	240	0.0095	0.9824	98	0.0176	-4.0425
6	300	0.0023	0.9957	100	0.0043	-5.4565

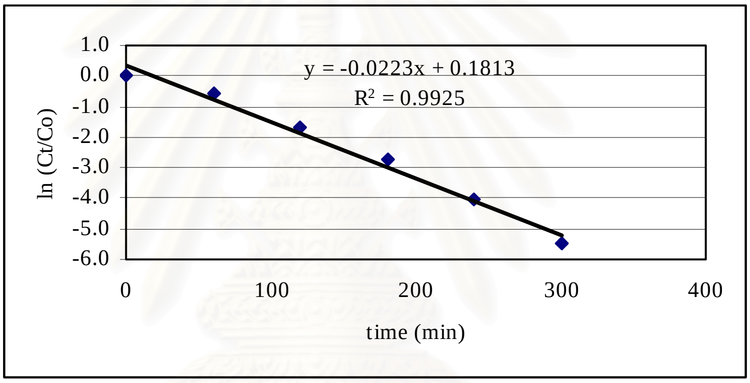

Figure B3 ln (*Ct/Co*) of BT as a function of reaction time at 70°C.

Table B4 Oxidation of dibenzothiophene at 50°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	*Ct* (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	$\ln \frac{Ct}{Co}$
1	0	0.4611	0.0000	0	1.0000	0.0000
2	60	0.2691	0.4164	42	0.5836	-0.5385
3	120	0.1236	0.7319	73	0.2681	-1.3166
4	180	0.0709	0.8462	85	0.1538	-1.8723
5	240	0.0321	0.9304	93	0.0696	-2.6648
6	300	0.0190	0.9588	96	0.0412	-3.1892

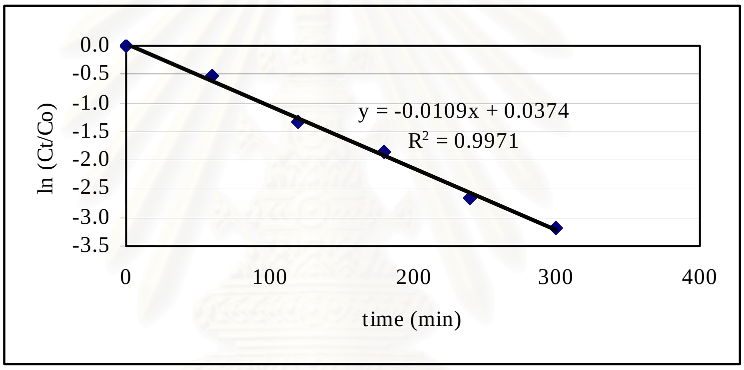

Figure B4 ln (*Ct/Co*) of DBT as a function of reaction time at 50°C.

Table B5 Oxidation of dibenzothiophene at 60°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	*Ct* (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	ln $\frac{Ct}{Co}$
1	0	0.5536	0.0000	0	1.0000	0.0000
2	60	0.2654	0.5206	52	0.4794	-0.7352
3	120	0.0978	0.8233	82	0.1767	-1.7335
4	180	0.0321	0.9420	94	0.0580	-2.8476
5	240	0.0094	0.9830	98	0.0170	-4.0757
6	300	0.0010	0.9983	100	0.0017	-6.3573

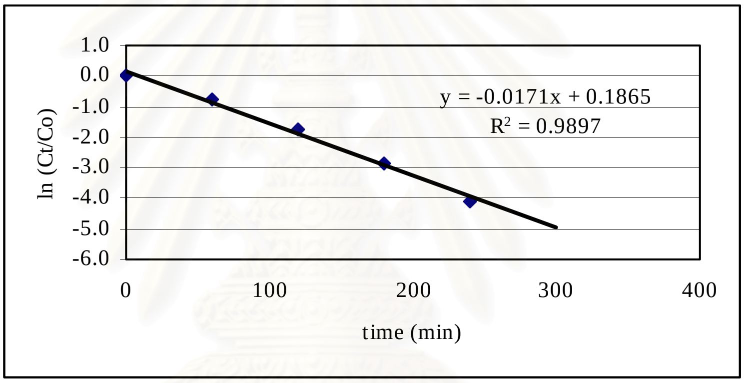

Figure B5 ln (*Ct/Co*) of DBT as a function of reaction time at 60°C.

Table B6 Oxidation of dibenzothiophene at 70°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	*Ct* (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	$\ln \frac{Ct}{Co}$
1	0	0.5377	0.0000	0	1.0000	0.0000
2	60	0.2031	0.6223	62	0.3777	-0.9736
3	120	0.0332	0.9383	94	0.0617	-2.7848
4	180	0.0030	0.9944	99	0.0056	-5.1887
5	240	0.0002	0.9996	100	0.0004	-7.8967
6	300	0.0001	0.9999	100	0.0001	-8.8776

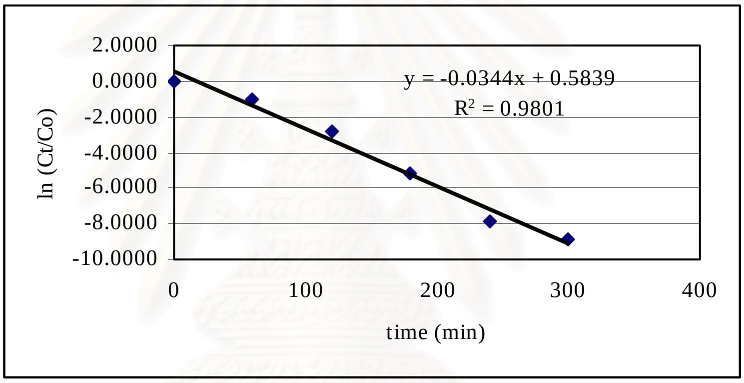

Figure B6 ln (*Ct/Co*) of DBT as a function of reaction time at 70°C.

Table B7 Oxidation of dimethyldibenzothiophene at 50°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	*Ct* (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	ln $\frac{Ct}{Co}$
1	0	0.5359	0.0000	0	1.0000	0.0000
2	60	0.4236	0.2096	21	0.7904	-0.2352
3	120	0.3133	0.4154	42	0.5846	-0.5368
4	180	0.2130	0.6025	60	0.3975	-0.9227
5	240	0.1325	0.7528	75	0.2472	-1.3974
6	300	0.0890	0.8339	83	0.1661	-1.7953

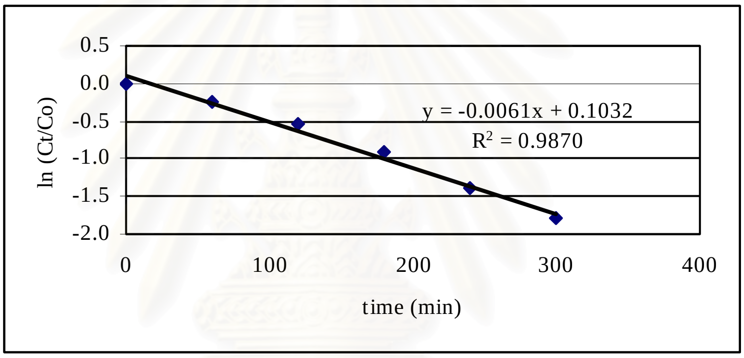

Figure B7 ln (*Ct/Co*) of DMDBT as a function of reaction time at 50°C.

Table B8 Oxidation of dimethyldibenzothiophene at 60°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	*Ct* (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	ln $\frac{Ct}{Co}$
1	0	0.5873	0.0000	0	1.0000	0.0000
2	60	0.2813	0.5210	52	0.4790	-0.7360
3	120	0.1647	0.7196	72	0.2804	-1.2714
4	180	0.0798	0.8641	86	0.1359	-1.9960
5	240	0.0341	0.9419	94	0.0581	-2.8462
6	300	0.0124	0.9789	98	0.0211	-3.8586

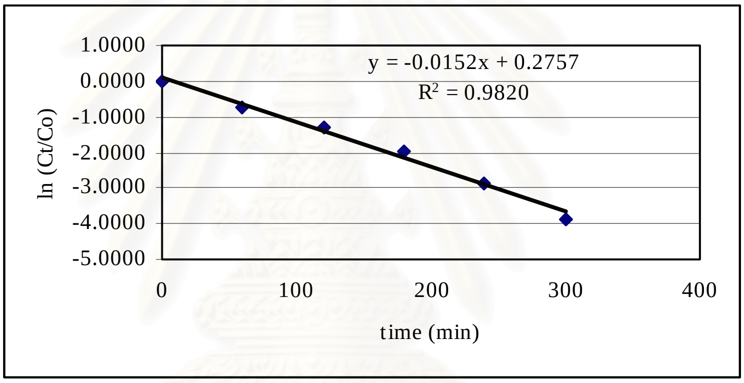

Figure B8 ln (*Ct/Co*) of DMDBT as a function of reaction time at 60°C.

Table B9 Oxidation of dimethyldibenzothiophene at 70°C using $[V(VW_{11})O_{40}]^{4-}$

Entry	Time (min)	*Ct* (mmol)	$\frac{Co-Ct}{Co}$	% conversion	$\frac{Ct}{Co}$	$\ln \frac{Ct}{Co}$
1	0	0.5463	0.0000	0	1.0000	0.0000
2	60	0.3123	0.5973	60	0.4027	-0.9000
3	120	0.2031	0.7748	77	0.2252	-2.0000
4	180	0.1000	0.9433	94	0.0567	-3.4000
5	240	0.0500	0.9671	97	0.0329	-3.8000
6	300	0.0100	0.9897	99	0.0103	-4.9000

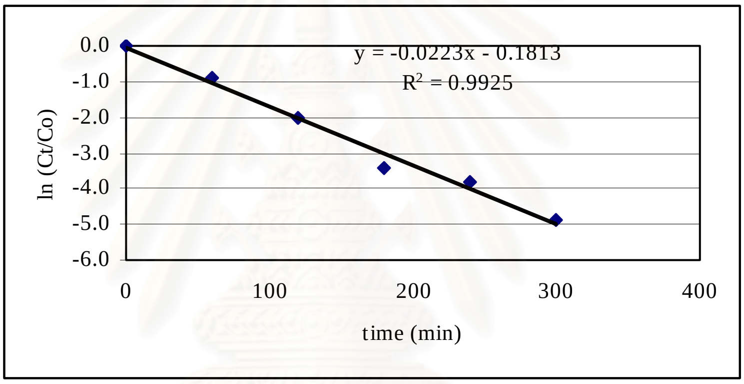

Figure B9 ln (*Ct/Co*) of DMDBT as a function of reaction time at 70°C.

Table B10 BT, DBT and 4,6-DMDBT rate constants at different temperatures

Substrates	Reaction temperature (°C)	Rate constants (min^{-1})	Correlation factor R^2
BT	50	0.0058	0.9845
	60	0.0103	0.9916
	70	0.0223	0.9856
DBT	50	0.0109	0.9971
	60	0.0171	0.9897
	70	0.0344	0.9801
4,6-DMDBT	50	0.0061	09870
	60	0.0152	0.9820
	70	0.0223	0.9925

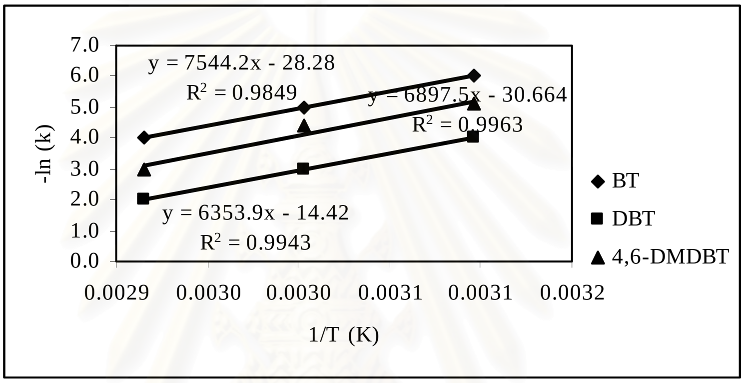

Figure B10 Arrhenius activation energy of sulfur compounds.

VITA

Miss Cholada Komintarachat was born on April 8, 1980 in Sakonnakorn. She received the B. Sc.Degree in General Science at Kasetsart University in 2002. Since then, she has been a graduate student studying in the program of Petrochemistry and Polymer Science at Faculty of Science, Chulalongkorn University and finished her study in 2005.

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