

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 characteristics 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: heterocyclics and non-heterocyclics. The latter comprises thiols, sulfides and disulfides. Heterocyclics 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

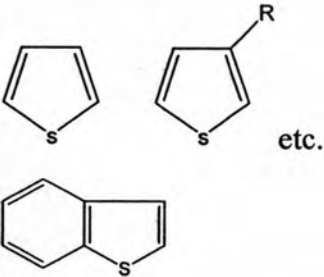
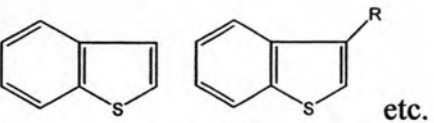
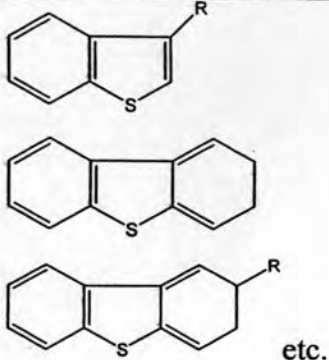
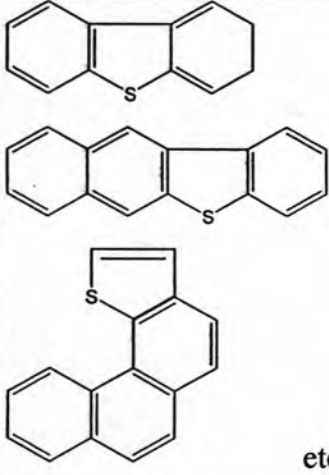
Common types	Compound class	Structure
Gasoline range: Naphtha, Fluid Catalytic Cracking (FCC)	mercaptanes	RSH
	sulfides	RSR'
	disulfides	RSSR'
	thiophene and its alkylated derivatives benzothiophene	 <p>etc.</p>
Jet fuel range: heavy naphtha, middle distillate	benzothiophene (BT) and its alkylated derivatives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

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 50 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.

2.1.2 Oxidizing agents [2]

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 (auto-oxidation). Usually, exposure to light, irradiation with ultraviolet light or catalysts are needed.

Oxygen (O₂), exists in two states. Stable ground-state oxygen (triplet oxygen) has two odd electrons with parallel spins. It behaves like a di-radical and is paramagnetic. In excited-state oxygen (singlet oxygen), the two odd electrons possess anti-parallel 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 (O₃), a blue gas or a dark blue liquid (bp. -106,-116 or -125°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°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 (H₂O₂), 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 non-polar 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** ((CH₃)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 high enantiomeric excesses.

Peroxyformic acid (performic acid), HCO₃H, 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), CH₃CO₃H, 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 bonds, 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 dibenzothiophene (DBT) to sulfoxide (DBTO) and sulfone (DBTO₂) under mild conditions.

Sodium hypochlorite, 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.

2.2 Literature reviews

2.2.1 Catalyst for oxidation of sulfur compounds

In 1989, Jame *et al.* [3] used sodium hypochlorite (NaOCl) as an 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 120 min, with high selectivity to the sulfoxide, compared to 5 h in its absence. Kinetic studies show the reaction occurs via transfer of OCl^- into the organic phase. Under certain conditions the transfer is rate limiting. The addition of a transition metal catalyst (tetraphenyl porphine manganese chloride, TPPMnCl) further increased the rate and led to the complete conversion of the sulfide to the sulfone.

In 1996, Brown *et al.* [4] investigated the oxidation of thiophene derivatives with hydrogen peroxide/methyltrioxorhenium (VII) (CH_3ReO_3). The 1:1 and 1:2 rhenium peroxides were formed and transferred an oxygen atom to the sulfur atom of thiophene derivatives. Complete oxidation to the sulfone occurred readily by way of its sulfoxide intermediate. The rate constants for the oxidation of the thiophenes are 2-4 orders of magnitude smaller than those for the oxidation of aliphatic sulfides. 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 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%) at 70 °C 36 h. The reaction was conducted with a mixture of hydrogen peroxide and formic acid. The sulfur compounds in SR-LGO and VGO appeared to be oxidized to a detectable levels (c.a., 0.01 wt% S) by GC-FID 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 recovery of oil was low.

In 2001, Hulea *et al.* [6] investigated the sulfoxidation of aromatic sulfur compounds with hydrogen peroxide and Ti-containing molecular sieves as catalyst. It was shown that the large pore catalytic materials, such as Ti-beta and mesoporous (hexagonal mesoporous silica), are active for the selective oxidation of thiophene derivatives to the corresponding sulfone, whereas the medium pore zeolites TS-1 (titanium silicalite) is totally inactive in the oxidation of polyaromatic sulfur compounds. For fuels, the best results was obtained using acetonitrile as solvent which is immiscible with the fuels. The benzo- and dibenzothiophene derivatives are oxidized into their corresponding sulfones which are then removed by simple liquid-liquid separation.

In 2001, Sato *et al.* [7] 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 , $Na_2WO_4 \cdot 2H_2O$ 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 bi-phase conditions sulfone was obtained in 96% yield. The oxidation can also be performed with hexane, toluene, or ethyl acetate as co-solvent.

In 2002, Shiraishi *et al.* [8] investigated the desulfurization process for light oils. Sulfur-containing 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 deulfurization 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, Rapas *et al.* [9] investigated the process for desulfurization 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 a oxidizing/extracting solution of formic acids and a small amount of hydrogen peroxide. The organic sulfones were removed by adsorption on alumina and eluted by methanol.

In 2003, Shiraishi *et al.* [10] investigated the ODS process for light oil using a vanadosilicate molecular sieve as the catalyst and H_2O_2 . The catalytic activities of 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 from 425 ppm to less than 50 ppm. However, the vanadosilicate could not be reused. This is owing to the dissolution of vanadium species in the silica framework into the acetonitrile solution.

In 2003, Wang *et al.* [11] investigated the oxidation of dibenzothiophene in kerosene, using *t*-BuOOH as an oxidant in the presence of Mo catalysts supported on Al_2O_3 . The results show that the oxidation of DBT increased with increasing Mo content up to 16wt%. The oxidation of different sulfur compounds: benzothiophene

(BT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) dissolved in decalin was also carried out. The order of oxidation reactivities of these sulfur compounds was found as follows: DBT > 4-MDBT > 4,6-DMDBT >> BT.

In 2003, Anisimov *et al.* [12] studied the oxidation of sulfur compounds and diesel fuel desulfurization, catalyzed by vanadium peroxo complexes/hydrogen peroxide in biphasic system. All vanadium complexes show high activity in oxidation of diphenylsulfide and phenylbenzyl sulfide to the corresponding sulfoxides. The oxidation of diesel fuel (0.86 wt% S) with this catalyst system reduces the amount of sulfur in the fuel to 0.2 wt%.

In 2004, Murata *et al.* [13] studied the oxidative desulfurization of diesel fuels with molecular oxygen using cobalt salts and aldehydes. A mixture of benzene, dibenzothiophene, n-octanal and cobalt acetate was stirred at 40 °C under atmospheric pressure of oxygen. Dibenzothiophene sulfone produced could be easily removed from the model oils by alumina adsorption. Sulfur containing compounds in the diesel fuel were oxidized at 40°C for 16 h, removed by alumina adsorption. The resulting oil contained less than 5 ppm of sulfur (more than 97% sulfur removal).

In 2004, Shiraihi *et al.* [14] investigated the oxidative desulfurization of vacuum gas oil (VGO) using hydrogen peroxide/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.

In 2004, Ramirez-Verduzco *et al.* [15] investigated the desulfurization of diesel using 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 30 wt% hydrogen peroxide in heterogeneous WO_x/ZrO_2 catalyst (15 wt% W). The experiments were done in a batch reactor at 60°C. 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 2005, Ishihara *et al.* [16] investigated the oxidation of sulfur compounds present in light gas oil (LOG; sulfur content: 39 ppm) with *tert*-butyl hydroperoxide (*tert*-BuOOH) 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 was increased up to 15. The reactivity decreased in the order: DBT >> 4,6-DMDBT > C₃-DBT irrespective of the temperature. The sulfur in the treated light oil was further removed by adsorption over a silica gel. The total sulfur content could be decreased after oxidation/adsorption to less than 5 ppm.

In 2005, Despande *et al.* [17] reported on the oxidation of refractory sulfur compound 4,6-dimethyldibenzothiophene (4,6-DMDBT) in a biphasic system, using hydrogen peroxide and sodium carbonate in the presence of ultrasonic. The application of an ultrasonic pulse was used for good contact between phase. This technique removed >90% of 4,6-DMDBT from diesel phase. The use of mild condition and the absence of hydrogen at high pressure make it an attractive process.

In 2006, Caero *et al.* [18] studied oxidative desulfurization of a synthetic diesel at mild conditions (atmospheric pressure and 60 °C) in presence of V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts. Results show that activity was improved when using hydrogen peroxide as oxidant and V_2O_5/Al_2O_3 , as catalyst. This result was attributed to the high decomposition of peroxide due to the presence of catalyst. In presence of nitrogen compounds, the ODS activity decreases in the order: quinoline > indole > carbazole.

In 2006, Zhou *et al.* [19] studied the catalytic oxidative desulfurization of dibenzothiophene (DBT) in decahydronaphthalene (decalin) using the oil-soluble oxidant cyclohexanone peroxide (CYHPO) with a molybdenum oxide (MoO_3) catalyst supported on macroporous polyacrylic cationic exchange resin of weak acid series. The influence of the reaction temperature, reaction time, the molar ratio of CYHPO/DBT, and catalyst reuse was investigated. The conversion of DBT to DBT sulfone was up to 100% at 100°C in 40 min. The different oil-soluble alkyl peroxides, i.e., *tert*-butyl hydroperoxide (TBHP) and *tert*-amyl hydroperoxide (TAHP) were also used in comparison with the CYHPO. The results showed that the activity of alkyl peroxides decreases in the order $\text{CYHPO} > \text{TAHP} > \text{TBHP}$.

In 2006, Xiaoliang *et al.* [20] investigated the ODS of liquid hydrocarbon fuels. The system combines a catalytic oxidation step (using oxygen) with an adsorption step using activated carbon. The ODS of a model jet fuel was conducted in a batch system at ambient conditions. It was found that oxidation reaction with Fe(III) salts was able to convert the thiophenic compounds to the corresponding sulfone. The oxidation reactivity of sulfur compounds decreases in the order of 2-methylbenzothiophene > 5-methylbenzothiophene > benzothiophene >> dibenzothiophene.

In 2006, Mondal *et al.* [21] investigated the oxidation of dibenzothiophene-derivatives in homogeneous and two-liquid phase systems by hydrogen peroxide with Fe-TAML, an iron containing tetraamido macrocyclic ligand catalyst. They used *tert*-BuOOH as a co-solvent. The catalytic process was applied to commercial diesel fuel, under mild conditions: temperature 50 °C in 3 h. It was shown that > 75% of the total sulfur content of the fuel can be removed.

In 2006, Lu *et al.* [22] investigated the oxidation of sulfur-containing compounds in diesel (water in oil [W/O]) using 30 wt% hydrogen peroxide, and an amphiphilic catalyst $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_4\text{[H}_2\text{NaPW}_{10}\text{O}_{36}]$. This catalyst in the W/O emulsion system exhibits very high catalytic activity. The catalytic oxidation reactivity of sulfur compounds was found to be in the following order: benzothiophene < 5-methylbenzothiophene < dibenzothiophene < 4,6-dimethyldibenzothiophene. The sulfone product can be readily separated from diesel

by an extractant. The sulfur level of a prehydrotreated diesel and a straight-run diesel can be lowered from 500 to 0.1 ppm and 6000 to 30 ppm, respectively.

In 2006, Komintarachat *et al.* [23] synthesized several polyoxometalates catalysts. $[W_6O_{19}]^{2-}$, $[V(VW_{11})O_{40}]^{4-}$, $[PVW_{11}O_{40}]^{4-}$, and $[PV_2Mo_{10}O_{40}]^{5-}$ as tetrabutylammonium salts. They were used as catalyst for the oxidative desulfurization of model compounds (benzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene) with hydrogen peroxide/acetic acid. The experimental results show that the most active catalyst is $[V(VW_{11})O_{40}]^{4-}$. The method was also used for the treatment of diesel oil. The combination of solvent extraction and alumina adsorption can efficiently remove sulfone products. The resulting oil contained less than 0.055% sulfur, and this corresponds to 90% sulfur removal.

In 2007, Yang *et al.* [24] studied the oxidation adsorption desulfurization of model fuel composed of dibenzothiophene (DBT) and isooctane using *tert*-butyl hydroperoxide (*tert*-BuOOH) as oxidant. A series of catalysts included SBA-15 modified with $H_3PW_{12}O_{40}$ (HPWA). HPWA-SBA-15 has both catalytic oxidation ability and adsorption ability. The DBT can be converted into polar DBT sulfone that is easily absorbed on HPWA-SBA-15. The catalytic process was performed at 70°C and the total desulfurization was up to 90%.

In 2008, Lanju *et al.* [25] studied the model sulfur compounds: thiophene (C_4H_4S) and 3-methylthiophene (3-MC₄H₄S) that exist in gasoline from fluid catalytic cracking (FCC) process. The sulfur compounds were oxidized by hydrogen peroxide and formic acid using silica gel loaded-copper and cobalt (1:1) catalyst. Tetrabutylammonium bromide was also added in the oxidation system. The sulfur removal of both sulfur compounds was 100% in the oil layer after extraction with *N,N*-dimethylformamide.

In our research group, Komintarachat [23] synthesized several polyoxometalates catalysts. $[W_6O_{19}]^{2-}$, $[V(VW_{11})O_{40}]^{4-}$, $[PVW_{11}O_{40}]^{4-}$, and $[PV_2Mo_{10}O_{40}]^{5-}$ as tetrabutylammonium salts and used them as catalyst for the oxidative desulfurization of diesel oil. The removal of sulfur were 90%. Therefore, in this work, the catalytic performance of many more different polyoxometalate catalysts

are done. Refractory sulfur compounds exist in actual diesel: benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene are chosen for the study. The suitable catalysts are further utilized for the oxidation of diesel fuels.