

CATALYTIC OXIDATIVE DESULFURIZATION OF DIESEL FUEL UTILIZING
ALUMINA SUPPORTED COBALT MANGANESE OXIDES

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A Special Dedication to my Beloved Family...

Jasni Majed
Jama'ah Shamsuri
M Jaslan Ilmami Jasni.

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In the name of Allah, the Most Gracious, the Most Merciful,

All praise to Allah, for His Mercy has given me patience and strength to complete this work. All the praise to Allah again.

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ABSTRACT

The available technique of hydrodesulfurization (HDS) is no longer suitable in the purpose of achieving Euro-IV standard diesel due to high operational cost, low efficiency and operating at high temperature in the presence of hydrogen gas. In this study, the catalytic oxidative desulfurization was carried out in the presence of Co/Mn/Al₂O₃ catalyst and *tert*-butyl hydroperoxide (TBHP) as oxidant to achieve ultra low sulfur concentration in the model diesel fuel, Petronas commercial and crude diesel. The experimental variables involved were the effect of calcination temperatures of catalysts, dopant ratios, catalyst dopants, reaction times, reaction temperatures, extraction solvents, type of oxidants, reproducibility test and molar ratio of *tert*-butyl hydroperoxide/sulfur (TBHP/S) were studied to achieve optimum conditions for sulfur removal in the diesel fuel. From XRD analysis, the Co/Mn(10:90)/Al₂O₃ catalyst formed amorphous structure at 400°C while at 700°C and 900°C calcination temperature produced intermediate and highly crystalline structure, respectively. Further investigation by FESEM showed the particle size of as-synthesized Co/Mn (10:90)/Al₂O₃ catalyst reduced from the range of 70.3 - 90.2 nm to 50.6 - 52.6 nm after calcination at 400°C. For the EDX analysis, the chloride ions in as-synthesized Co/Mn (10:90)/Al₂O₃ catalyst reduced from 7.77% to 2.88% and 0.73% after calcination at 400°C and 900°C, respectively. Analysis using nitrogen adsorption showed that the surface area of Co/Mn (10:90)/Al₂O₃ as-synthesized catalyst was 103.8 m²g⁻¹ which was lower than Co/Mn(10:90)/Al₂O₃ after calcination at 400°C which was 128.2 m²g⁻¹. The optimum conditions for catalytic oxidative desulfurization of model diesel fuel was identified to perform at 60°C, with oxidant TBHP, molar ratio of TBHP/S = 3, in the presence of catalyst Co/Mn(10:90)/Al₂O₃ and using extraction solvent, dimethylformamide, where the sulfur contents was reduced from 600 ppm to 164 ppm. This optimum condition for oxidative desulfurization reaction was applied to the Petronas commercial diesel and Petronas crude diesel resulted in the reduction from 500 ppm to 127 ppm and 8269 ppm to 413 ppm of sulfur content respectively analyzed by Gas-Chromatography-Flame Photometric Detector.

ABSTRAK

Kaedah hidropenyahsulfuran (HDS) pada masa ini tidak sesuai lagi digunakan untuk mencapai piawai minyak diesel Euro IV disebabkan oleh kos operasi yang tinggi, kurang efisien dan beroperasi pada suhu yang tinggi dengan kehadiran gas hidrogen. Dalam kajian ini, pemangkinan pengoksidaan penyahsulfuran telah dijalankan dengan kehadiran mangkin $\text{Co/Mn/Al}_2\text{O}_3$ dan *tert*-butil hidroperoksida (TBHP) sebagai pengoksida untuk mencapai kepekatan sulfur yang sangat rendah di dalam model diesel, minyak komersial dan minyak mentah diesel Petronas. Pemboleh ubah yang terlibat dalam kajian ini adalah kesan suhu pengkalsinan ke atas mangkin, nisbah pendopan, masa tindak balas, suhu tindak balas, pelarut pengekstrakan, jenis pengoksida dan ujian keboleholangan dan nisbah molar *tert*-butil hidroperoksida/sulfur (TBHP/S) untuk mencapai keadaan optimum penyahsulfuran dalam minyak diesel. Berdasarkan analisis XRD, mangkin $\text{Co/Mn/Al}_2\text{O}_3$ menunjukkan struktur amorfus pada suhu pengkalsinan 400°C , manakala pada suhu 700 dan 900°C , masing-masing menunjukkan struktur dalam bentuk pengantaraan dan sangat kristal. Kajian seterusnya oleh FESEM menunjukkan saiz zarah mangkin yang disintesis, $\text{Co/Mn/Al}_2\text{O}_3$ dalam julat $70.3 - 90.2$ nm berkurang kepada $50.6 - 52.6$ nm selepas pengkalsinan pada suhu 400°C . Berdasarkan analisis EDX, ion klorida dalam mangkin yang disintesis, $\text{Co/Mn/Al}_2\text{O}_3$ berkurang daripada 7.77% kepada 2.88% dan 0.73% setelah menjalani pengkalsinan pada suhu 400°C dan 900°C . Manakala analisis menggunakan kaedah penjerapan nitrogen menunjukkan luas permukaan mangkin yang disintesis, $\text{Co/Mn/Al}_2\text{O}_3$ adalah $103.8 \text{ m}^2/\text{g}$ lebih rendah berbanding mangkin $\text{Co/Mn/Al}_2\text{O}_3$ yang dikalsinkan pada suhu 400°C ($128.2 \text{ m}^2/\text{g}$). Keadaan optimum dalam kajian pemangkinan pengoksidaan penyahsulfuran telah dikenal pasti pada suhu 60°C dengan pengoksida TBHP, nisbah mol TBHP/S = 3, menggunakan mangkin $\text{Co/Mn/Al}_2\text{O}_3$ dan pelarut pengekstrakan dimetilformamida di mana kepekatan sulfur dapat dikurangkan daripada 600 ppm kepada 164 ppm. Keadaan optimum yang diperolehi kemudiannya diaplikasikan kepada minyak komersial dan minyak mentah diesel Petronas dan masing-masing menunjukkan pengurangan kepekatan kandungan sulfur daripada 500 ppm kepada 127 ppm dan 8269 ppm kepada 413 ppm setelah dianalisis oleh Kromatografi Gas Pengesan Fotometri Nyala.

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LIST OF ABBREVIATIONS

DBT	-	Dibenzothiophene
4, 6-DMDBT	-	4, 6-dimethyldibenzothiophene
EDX	-	Energy Dispersive X-ray Analysis
FESEM	-	Field Emission Scanning Electron Microscope
NA	-	Nitrogen Adsorption
XRD	-	X-ray Diffraction
GC-FPD	-	Gas Chromatography-Flame Photometric Detector
W-XRF	-	Wavelength-X-Ray Fluorescence
IWI	-	Incipient Wetness Impregnation techniques
TBHP	-	<i>tert</i> -butyl hydroperoxide
AcN	-	acetonitrile
DMF	-	dimethylformamide
NMP	-	1-methyl-2-pyrrolidone
MeOH	-	methanol
BET	-	Brunnauer, Emmet and Teller
BJH	-	Barret-Joyner-Halenda
c	-	cubic
h	-	hexagonal
d	-	pore diameter
hr	-	hour
ppm	-	part per million
wt%	-	weight percentage
UAODS	-	Ultrasonic Assisted Oxidative Desulfurization

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Petronas has just announced the introduction of Malaysia's first diesel fuel which called Dynamic Diesel that comply the Euro 2M sulfur requirements of 500 ppm on 1st September 2009 (Salian, 2009). However, the sulfur requirements of 500 ppm are still high as compared to the other countries such as Europe, North America, South America and Asia. For example, Euro IV standard has applied in the European Union since 2005, which specifies a maximum of 50 ppm of sulfur content in diesel fuel. Moreover, certain EU countries implemented Euro V containing less than 10 ppm beginning in 2009. Later on, a final target (to be confirmed by the European Commission) for the final reduction of sulfur to <5 ppm, which will be comply Euro VI fuel standard on 2014.

Malaysian Natural Resources and Environment Minister Dato' Seri Douglas Unggah Embas established clear roadmap for diesel fuel standards and quality towards Euro 4M standards that will be implemented by 2011 due to the increasingly stringent environmental regulations on sulfur content in transportation fuels (Salian, 2009). Table 1.1 shows the international diesel fuel quality standard and Table 1.2 shows the sulfur content in different types of diesel. Therefore, oxidative desulfurization (ODS) technique was introduced as an interesting alternative to remove sulfur compounds in diesel fuel in order to meet the challenges of introducing Euro 4M, especially with sulfur content lower than 50 ppm.

Table 1.1: International diesel fuel quality standard

Countries	Sulfur Content (ppm)
Indonesia	>2000
Brazil	2000
Argentina	2000
Malaysia	500
Mexico	500
North Africa	500
China	350
Chile	50
Morocco	50
United State	10 or 15
Canada	10 or 15
France	10 or 15
Spain	10 or 15
Australia	10 or 15

Source: International Fuel Quality Centre, September 2011

Table 1.2 Sulfur content in different types of diesel

Types of Diesel	Sulfur Content (ppm)
Euro II (Low Sulfur Diesel)	500
Euro IV (Ultra Low Sulfur Diesel)	50
Euro V (Green Diesel)	10
Euro VI (Very Low Sulfur Diesel)	<5

1.2 Desulfurization of Diesel Fuel Methods

In previous study, the hydrodesulfurization (HDS) method was commonly used in order to reduce sulfur compounds in diesel fuel. However, this method will cause the high operating cost thus it is impractical in industrial scale. Because of that, oxidative desulfurization (ODS) method was introduced as a modern technology which has many advantages as compared to HDS method. Beside of these two methods, there are many other methods or technologies that can be applied on desulfurization of diesel fuel such as selective adsorption for removing sulfur (SARS), combination of SARS and HDS, ionic liquid, adsorption and biodesulfurization.

1.2.1 Hydrodesulfurization Method

Hydrodesulfurization is the conventional method for removal of organosulfur compounds by using H₂ gas in order to convert organic sulfur into hydrogen sulfide as shown in Equation 1.1 (Garcia-Gutierrez *et al.*, 2006).



This process successfully removes most sulfur compounds such as thiols, sulfides, disulfides and some thiophene derivatives. Unfortunately, HDS method ineffectively removes dibenzothiophene derivatives due to the steric hindrance on the sulfur atom (refractory organosulfur compounds), such as 4, 6-dimethyldibenzothiophene (4, 6-DMDBT), which are present in diesel fuel (Ali *et al.*, 2006). This method requires temperatures above 643 K, pressures of the order of 79 bar and LHSV below 1.5 h⁻¹ in order to remove such compounds. These operating conditions gave worst effect such as consumption of large hydrogen and a reduction of catalyst life, thus increasing significantly the operating expenses (Caero *et al.*, 2005).

1.2.2 Selective Adsorption for Removing Sulfur (SARS) Method

In order to further reduce the sulfur concentration in liquid hydrocarbon fuels such as diesel fuel, selective adsorption for removing sulfur (SARS) was introduced and applied for adsorption desulfurization of diesel fuel at room temperature. The SARS process can successfully remove sulfur compounds in the liquid hydrocarbon fuels at ambient temperature under atmospheric pressure with low investment and operating cost. The challenge of this method is to attract and selectively adsorb sulfur compounds onto the surface of the solid adsorbent (transition metal supported in silica gel) but untouched the aromatic and olefinic hydrocarbons of diesel fuel since they have framework and electronic properties (Ma *et al.*, 2002).

1.2.3 Combination of SARS and HDS Method

In 2003, a new approach for integrated deep desulfurization of liquid hydrocarbon fuels (gasoline, diesel fuel and jet fuel) process which combines the selective adsorption of the sulfur compounds (SARS unit) and the hydrodesulfurization (HDS) was reported. Since HDS method cannot remove refractory organosulfur compounds, selective adsorption that using a transition metal compound successfully removes those compounds in the diesel fuel at ambient temperature under atmospheric pressure with low investment and operating cost (Song and Ma, 2003).

1.2.4 Ionic Liquid Method

Ionic liquids (ILs) are organic salts that are in liquid form at temperatures below 100°C. Ionic liquids such as imidazolium based ionic liquids ([BMIM][PF₆], [EMIM][BF₄], [BMIM][MeSO₄], [BMIM][AlCl₄], [BMIM][OcSO₄]) are predicted to

take the place of organic solvents because they have no measurable vapor pressure below their decomposition temperature. Although chlorometallate ILs such as [BMIM][AlCl₄] shows good selectivity for removal of sulfur compounds, they have some weakness which are very sensitive to air and moisture and may cause alkene polymerization in fuel. Bigger anions such as [OcSO₄]⁻ could extract DBTs more effectively than smaller anions (e.g. [PF₆]⁻ or [CF₃SO₃]⁻). It was reported that imidazolium ions with larger alkyl substitution groups are better solvents for DBT removal. The purpose of research on ILs in future refineries is to minimize desulfurization energy requirements and decrease CO₂ production that is associated with HDS. Organic solvent extraction techniques can be used to recycle or recover ILs. However, loss of solvents during the extraction process is unavoidable and undesirable. (Soleimani *et al.*, 2007).

1.2.5 Adsorption Method

Adsorption is an another method for motor fuel desulfurization and the idea behind this method is to selectively separate less than 1 wt% of fuel mass using selective adsorption for removing sulfur compounds and untouched the 99 wt% of non-sulfur containing fuel mass. As compared to HDS process, the removal of sulfur compounds by adsorption method seems very efficient in term of energy consumption since adsorption can be conducted at low temperature and pressure and the sulfur content in fuels can be reduced to a very low level. Activated carbons and zeolites have been widely used as adsorbents in the separation and purification processes for gaseous or aqueous solution systems. Activated carbons have high adsorption capacity towards some organic and inorganic compounds due to large specific surface area, high adsorbate adsorbent physical and chemical attraction. Zeolites can be effectively used for the selective adsorption of polar or polarizable molecules such as water and CO₂ and sulfur-containing molecules from some petroleum fractions (Muzic *et al.*, 2010)

1.2.6 Biodesulfurization

Another method to produce ultra-low fuels is biodesulfurization (BDS) which can selectively remove sulfur from DBTs. Sulfur atom forms 0.5–1% of bacterial cell dry weight. Microorganisms require sulfur compounds for their growth and biological activities. Microorganisms, depending on their enzymes and metabolic pathways, may have the capability to provide their required sulfur from different sources. Some microorganisms can consume thiophenic compounds such as DBT and reduce the sulfur concentration in diesel fuel. The advantage of desulfurization by microorganisms is it capable carried out in mild temperature and pressure conditions which it is considered as an energy-saving process (an advantage over HDS). Secondly, in biological activities, biocatalysts (enzymes) are involved where the desulfurization would be highly selective (Soleimani *et al.*, 2007).

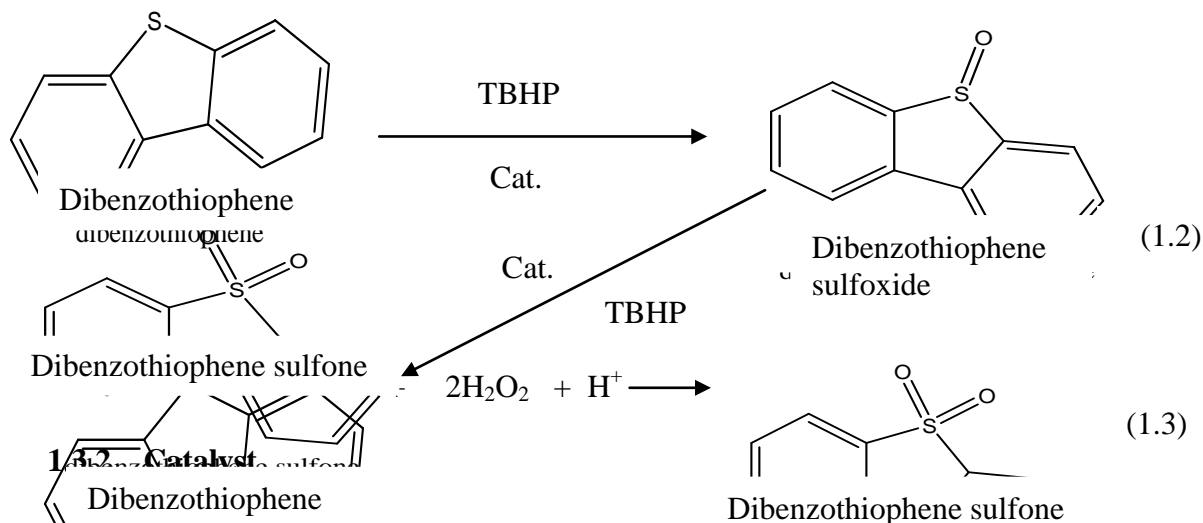
1.3 Oxidative Desulfurization Method

The oxidative desulfurization (ODS) is considered to be one of the promising new approaches for deep desulfurization of diesel fuel. The oxidative desulfurization is basically a two-stage processes where the oxidation of sulfur compounds to corresponding sulphoxides and sulphones by suitable oxidant was followed by liquid extraction by using non-miscible solvent such as acetonitrile. Oxidative desulfurization are more preferred method as compared to hydrodesulfurization (HDS) method since the sulfur compounds such as dibenzothiophene (DBT) and 4, 6-DMDBT can be oxidized under mild conditions to sulfoxides or sulfones in high yields and these products are removed by extraction and adsorption (Garcia-Gutierrez *et al.*, 2006). The process involves an oxidizing agent, catalyst, phase transfer agent and extraction solvent.

1.3.1 Oxidizing Agent

In recent study, potassium ferrate (VI) was used as an oxidizing agent for oxidation desulfurization of diesel fuel. The function of oxidizing agent is to oxidize sulfur compounds to the sulfones. Unfortunately, this oxidizing agent was easily converted to other compounds in the presence of water (Liu *et al.*, 2008). Therefore, the concentrations of sulfur remain high because the oxidizing agent was not effective to oxidize sulfur compounds. Moreover, the preparation of this oxidizing agent is long and lead to high operating cost.

For an alternative to potassium ferrate (VI), hydrogen peroxide and tert-butyl hydroperoxide (TBHP) were used as the oxidizing agent. Both oxidants have their own advantage where TBHP does not show deactivation during reactive cycles meanwhile hydrogen peroxide is cheap, nonpolluting, not strongly corrosive and commercially available (Gonzalez-Garcia and Caero, 2009). The most important, both oxidants can soluble in the oil. The mechanism for the reaction involving TBHP and hydrogen peroxide is shown in Equation 1.2 and 1.3 (Chica *et al.*, 2006):



Catalyst is also an important component in the oxidative desulfurization reaction of diesel fuel. From the previous study, it was proven that the manganese and cobalt

oxide catalysts supported on alumina ($\gamma\text{-Al}_2\text{O}_3$) are highly effective for catalytic oxidation of the refractory sulfur compounds in diesel fuel as compared to W, Ni, V, Fe and Cu (Sampanthar *et al.*, 2006). However, the precursor of the catalyst (manganese (II) acetate) was quite expensive compared to our catalyst (manganese (II) chloride). Meanwhile, this catalyst can be well performed at high temperature of oxidation reaction (130-180°C).

In this study, we report the use of catalytic oxidative desulfurization technique for the removal of sulfur compounds in diesel utilizing effective and inexpensive manganese oxide based catalyst. The advantage of this catalyst is it can be effectively produced at low temperature of calcination and well performed at low oxidation reaction temperature (60°C). According to Zapata *et al.* (2005), the removal of sulfur compounds is quite similar while manganese oxide based catalyst (precursor used: manganese (II) nitrate) calcined at 300 and 950°C.

1.3.3 Phase Transfer Agent

Phase transfer agent such as tetraethylammonium bromide has an important role in the oxidative desulfurization of diesel fuel. Phase transfer agent is surface active species that lower the surface tension or reduce the boundary of organic phase (Anisimov *et al.*, 2003). It has been proven that tetraethylammonium bromide has ability to permit the oxidized sulfur or sulfones to be removed from diesel phase to the solvent phase by oxidation and extraction process (Liu *et al.*, 2008).

1.3.4 Extraction Solvent

In the oxidation reaction process, the oxidizing agent will oxidize the sulfur compounds present in the diesel fuel to produce the corresponding sulfones. From the

previous study, these sulfones which are highly polarized will be extracted from the diesel fuel by water-soluble polar solvent such as 1-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), acetonitrile (AcN) and methanol (MeOH) (Sampanthar *et al.*, 2006).

1.4 Problem Statement

The presence of sulfur in diesel fuel is a major source that leads to environment pollution. The sulfur from the diesel fuel will react with oxygen in the combustion system and generates sulfur dioxide (SO_2), which reacts with atmospheric water and oxygen to produce sulfuric acid (H_2SO_4). The sulfuric acid is a component of acid rain where the pH is around 2 to 3. Acid rain will kill individual fish, reduce fish population numbers and completely eliminate fish species from the lakes. As acid rain flows through soils into the lakes, aluminium will dissolve and brought together with acid rain. As such, the pH of the lake will decrease and the aluminium level increased and directly toxic to the fish. Moreover, the acid rain will affect the trees by damaging their leaves and limiting the nutrients necessary. This happened when hydrogen ion from the acid rain will replace the elements (calcium and magnesium ions) in the fertilizers and reduced its effectiveness. The acidic condition also will kill the organism in the soil that needed by the plant. Therefore, a solution needed in order to reduce the sulfur concentration in the diesel fuel.

Regarding to the problem stated above, we develop a new catalyst called $\text{Co/Mn/Al}_2\text{O}_3$ in order to accelerate the catalytic activity, thus increasing the sulfur removal in the diesel fuel. Beside that, the production of $\text{Co/Mn/Al}_2\text{O}_3$ catalyst is more economical in industrial scale in term of the price of catalyst precursors and this catalyst effectively can be produced at low calcination temperature.

Therefore, an oxidative desulfurization (ODS) process assisted with metal oxide catalyst have been develop as an alternative more energy-efficient desulfurization process where the operation conducted at low reaction temperature and pressure.

1.5 Objective of Research

The objectives of the research are:

- 1) To synthesis the Co/Mn/Al₂O₃ catalyst with various type of dopants precursors, dopant ratios at varying calcination temperatures.
- 2) To study the effect of oxidants, molar ratio of oxidant, reaction time, extraction solvents, reaction temperature, and catalysts in oxidative desulfurization process of model diesel.
- 3) To characterize the prepared catalyst by different characterization methods
- 4) To optimize the condition for the oxidative desulfurization process in model diesel that will be applied to the Petronas commercial and crude diesel.

1.6 Scope of Research

In this project, the transition metals such as manganese and cobalt were used to prepare the catalysts by using incipient wetness impregnation method. After oxidation and extraction process, the model diesel, treated Petronas commercial and crude diesel will be analyzed by Gas Chromatography-Flame Photometric Detector (GC-FPD).

The potential catalysts, Co/Mn/Al₂O₃ (Catalyst I) was also characterized by Field Emission Scanning Electron Microscopy - Energy Dispersive Analysis of X-Ray (FESEM - EDX), X-Ray Diffraction (XRD) and Nitrogen Adsorption (NA).

Then, the treated Petronas crude diesel was analyzed for diesel specification parameters such as density, kinematic viscosity, pour point, flash point, volatility distillation, sulfur content, colour, ash content, carbon residue, water content and cetane index.

REFERENCES

- Abdalla Z.E.A., Li, B. and Tufail, A. (2009). Preparation of Phosphate Promoted $\text{Na}_2\text{WO}_4/\text{Al}_2\text{O}_3$ Catalyst and Its Application for Oxidative Desulfurization, *Journal of Industrial and Engineering Chemistry*. **15**, 780-783.
- Ali, M.F., Al-Malki, A., El-Ali, B., Martinie, G. and Siddiqui, M.N. (2006). Deep Desulphurization of Gasoline and Diesel Fuels using Non-Hydrogen Consuming Techniques, *Fuel*. **85**, 1354–1363.
- Ali, M.F., Al-Malki, A. and Ahmed, S. (2009). Chemical Desulfurization of Petroleum Fractions for Ultra-Low Sulfur Fuels, *Fuel Processing Technology*. **90**, 536-544.
- Al-Shahrani, F., Xiao, T., A. Llewellyn, S., Barri, S., Jiang, Z., Shi, H., Martinie, G. and Green, M.L.H. (2007). Desulfurization of Diesel via the H_2O_2 Oxidation of Aromatic Sulfides to Sulfones using a Tungstate Catalyst, *Applied Catalysis B: Environmental*. **73**, 311-316.
- Anisimov, A.V., Fedorova, E.V., Lesnugin, A.Z., Senyavin, V.M., Aslanov, L.A., Rybakov, V.B. and Tarakanova, A.V. (2003). Vanadium Peroxocomplexes as Oxidation Catalysts of Sulfur Organic Compounds by Hydrogen Peroxide in Bi-Phase Systems, *Catalyst Today*. **78**, 319-325.
- Caero, L.C., Hernandez, E., Pedraza, F. and Murrieta, F. (2005). Oxidative Desulfurization of Synthetic Diesel using Supported Catalysts Part I. Study of the Operation Conditions with a Vanadium Oxide Based Catalyst, *Catalysis Today*. **107-108**, 564-569.
- Caero, L.C., Jorge, F., Navarro, A. and Gutierrez-Alejandre, A. (2006). Oxidative Desulfurization of Synthetic Diesel using Supported Catalysts Part II. Effect of Oxidant and Nitrogen-Compounds on Extraction–Oxidation Process, *Catalysis Today*. **116**, 562-568.

- Chica, A., Corma, A. and Dómine, M.E. (2006). Catalytic Oxidative Desulfurization (ODS) of Diesel Fuel on a Continuous Fixed-Bed Reactor, *Journal of Catalysis*. **242**, 299-308.
- Dai, Y., Qi, Y., Zhao, D. and Zhang, H. (2008). An Oxidative Desulfurization Method using Ultrasound/Fenton's Reagent for Obtaining Low and/or Ultra-Low Sulfur Diesel Fuel, *Fuel Processing Technology*. **89**, 927-932.
- Dai, Y., Zhao, D. and Qi, Y. (2011). Sono-Desulfurization Oxidation Reactivities of FCC Diesel Fuel in Metal Ion/H₂O₂ Systems, *Ultrasonics Sonochemistry*. **18**, 264-268.
- Dehkordi, A.M., Kiaei, Z. and Sobati, M.A. (2009). Oxidative Desulfurization of Simulated Light Fuel Oil and Untreated Kerosene, *Fuel Processing Technology*. **90**, 435-445.
- Duarte, F.A., Mello, P.D.A., Bizzi, C.A., Nunes, M.A.G., Moreira, E.M., Alencar, M.S., Motta, H.N., Dressler, V.L. and Flores, E.M.M. (2011). Sulfur Removal from Hydrotreated Petroleum Fractions using Ultrasound-Assisted Oxidative Desulfurization Process, *Fuel*. **90**, 2158-2164.
- Gall, R., Faraj, M. and Hill, C. (1994). Role of Water in Polyoxometalate –Catalyzed Oxidations in Nonaqueous Media. Scope, Kinetics and Mechanism of Oxidation of Thioether Mustard (HD) Analogs by *Tert*-Butyl Hydroperoxide Catalyzed by H₅PV₂Mo₁₀O₄₀, *Inorganic Chemistry*. **33(20)**, 5015-5021.
- Garcia-Gutierrez, J.L., Fuentes, G.A., Hernandez-Teran, M.E., Murrieta, F., Nararete, J. and Jimenez-Cruz, F. (2006). Ultra-Deep Oxidative Desulfurization of Diesel Fuel with H₂O₂ Catalyzed under Mild Conditions by Polymolybdates Supported on Al₂O₃, *Applied Catalysis A*. **305**, 15–20.
- Garcia-Gutierrez, J.L., Fuentes, G.A., Maria Eugenia Hernandez-Tera'n, M.E., Garcí'a, P., Murrieta-Guevara, F. and Jimé'nez-Cruz, F. (2008). Ultra-Deep Oxidative Desulfurization of Diesel Fuel by the Mo/Al₂O₃-H₂O₂ System: The Effect of System Parameters on Catalytic Activity, *Applied Catalyst A: General*. **334**, 366-373.

- Gonzalez-Garcia, O. and Caero, L.C (2009). V-Mo Based Catalysts for Oxidative Desulfurization of Diesel Fuel, *Catalysis Today*. **148**, 42-48.
- Guo, W., Wang, C., Lin, P. and Lu, X. (2011). Oxidative Desulfurization of Diesel with TBHP/Isobutyl Aldehyde/Air Oxidation System, *Applied Energy*. **88**, 175-179.
- Ishihara, A., Wang, D., Dumeignil, F., Amano, H., Weihua Qian, E. and Kabe, T. (2005). Oxidative Desulfurization and Denitrogenation of a Light Gas Oil using an Oxidation/Adsorption Continuous Flow Process
- Jia, Y., Li, G. and Ning, G. (2011). Efficient Oxidative Desulfurization (ODS) of Model Fuel with H₂O₂ Catalyzed by MoO₃/γ-Al₂O₃ under Mild and Solvent Free Conditions, *Fuel Processing Technology*. **92**, 106-111.
- Jian, Z., Xiumei, B., Xiang., L., Anjie, W. and Xuehu, MA. (2009). Preparation of MoO₃-CeO₂-SiO₂ Oxidative Desulfurization Catalysts by a Sol-Gel Procedure, *Chinese Journal of Catalysis*. **30**, 1017-1021.
- Jiang, X., Li, H., Zhu, W., He, L., Shu, H. and Lu, J. (2009). Deep Desulfurization of Fuels Catalyzed by Surfactant-Type Decatungstates using H₂O₂ as Oxidant, *Fuel*. **88**, 431-436.
- Liu, S., Wang, B., Cui, B. and Sun, L. (2008). Deep Desulfurization of Diesel Oil Oxidized by Fe (VI) Systems, *Fuel*. **87**, 422-428.
- Lu, H., Gao, J., Jiang, Z., Jing, F., Yang, Y., Wang, G. and Li, C. (2006). Ultra-Deep Desulfurization of Diesel by Selective Oxidation with [C₁₈H₃₇N(CH₃)₃]₄[H₂NaPW₁₀O₃₆] Catalyst Assembled in Emulsion Droplets, *Journals of Catalysis*. **239**, 369-375.
- Ma, X., Sun, L. and Song, C. (2002). A New Approach to Deep Desulfurization of Gasoline, Diesel Fuel and Jet Fuel by Selective Adsorption for Ultra-Clean Fuels and For Fuel Cell Applications, *Catalysis Today*. **77**, 107-116.
- Mei, H., Mei, B.W. and Yen, T.F. (2003). A New Method for Obtaining Ultra-Low Sulfur Diesel Fuel via Ultrasound Assisted Oxidative Desulfurization, *Fuel*. **82**, 405-414.
- Muzic, M., Sertic-Bionda, K., Gomzi, Z., Podolski, S. and Telen, S. (2010). Study of Diesel Fuel Desulfurization by Adsorption, *Chemical Engineering Research and Design*. **88**, 487-495.

- Nurunnabi, M., Murata, K., Okabe, K., Inaba, M. and Takahara, I. (2007). Effect of Mn Addition on Activity and Resistance to Catalyst Deactivation for Fisher-Tropsch Synthesis over Ru/Al₂O₃ and Ru/SiO₂ Catalysts, *Catalysis Communications*. **8**, 1531-1537.
- Prasad, V.V.D.N., Jeong, K.E., Chae, H.J., Kim, C.U. and Jeong, S.Y. (2008). Oxidative Desulfurization of 4, 6-dimethyl Dibenzothiophene and Light Cycle Oil over Supported Molybdenum Oxide Catalysts, *Catalysis Communications*. **9**, 1966-1969.
- Qiu, J., Wang, G., Danlin Zeng, D., Tang, Y., Wang, M. and Li, Y. (2009). Oxidative Desulfurization of Diesel Fuel using Amphiphilic Quaternary Ammonium Phosphomolybdate Catalysts, *Fuel Processing Technology*. **90**, 1538-1542.
- Salian, S. (2009, August 21). Petronas Dagangan Lancar Dynamic Diesel. *Berita Harian*. p. 13.
- Sampanthar, T.S., Xiao, H., Dou, J., Nah, T.Y., Rong, X. and Kwan, W.P.(2006). A Novel Oxidative Desulfurization Process to Remove Refractory Sulfur Compounds from Diesel Fuel, *Applied Catalysis B: Environmental*. **63**, 85-93.
- Soleimani, M., Bassi, M. and Margaritis, A. (2007). Biodesulfurization of Refractory Organic Sulfur Compounds in Fossil Fuels, *Biotechnology Advances*. **25**, 570-596.
- Song, C. (2003). An Overview of New Approaches to Deep Desulfurization for Ultra-Clean Gasoline, Diesel Fuel and Jet Fuel, *Catalysis Today*. **86**, 211-263.
- Song, C. and Ma, X. (2003). New Design Approaches to Ultra-Clean Diesel Fuels by Deep Desulphurization and Deep Dearomatization, *Applied Catalysis B: Environmental*. **41**, 207-238.
- Vicenta, M.A., Belver, C., Trujillano, R., Rives, V., Alvarez, A.C., Lambert, J.F., Korili, S.A., Gandia, L.M. and Gil, A. (2004). Preparation and Characterisation of Mn- and Co- Supported Catalysts Derived from Al-Pillared Clays and Mn- and Co-Complexes, *Applied Catalysis A*. **267**, 47-58.
- Wan, M.W. and Yen, T.F. (2007). Enhance Efficiency of Tetraoctylammonium Fluoride Applied to Ultrasound-Assisted Oxidative Desulfurization (UAOD) Process, *Applied Catalysis A*. **319**, 237-245.

- Xue-min, Y., Gao-shen, S. and Lin, X. (2009). Oxidative Desulfurization of Diesel Oil over Ag-Modified Mesoporous HPW/SiO₂ Catalyst, *Journal of Fuel Chemistry and Technology*. **37**, 318-323.
- Yu, G., Lu, S., Chen, H. and Zhu, Z. (2005). Diesel Fuel Desulfurization with Hydrogen Peroxide Promoted by Formic Acid and Catalyzed by Activated Carbon, *Carbon*. **43**, 2285-2294.
- Zapata, B., Pedraza, F. and Valenzuela, M.A. (2005). Catalyst Screening for Oxidative Desulfurization using Hydrogen Peroxide, *Catalysis Today*. **106**, 219-221.
- Zhang, J., Wang, A., Li, X. and Ma, X. (2011). Oxidative Desulfurization of Dibenzothiophene and Diesel over [Bmim]3PMo₁₂O₄₀, *Journal of Catalysis*. **279**, 269-275.
- Zhao, D., Wang, Y., Duan, E. and Zhang, J. (2010). Oxidation Desulfurization of Fuel using Pyridinium-Based Ionic Liquids as Phase-Transfer Catalysts, *Fuel Processing Technology*. **91**, 1803-1806.