CHAPTER 1

INTRODUCTION

1.1 Background of study

Sulfur in petroleum is one of the contributors to environmental pollution whereby it can produce harmful substances; sulfur dioxide (SO_2) upon combustion and hydrogen sulfide (H_2S) during refinery processes. These emissions of SO_2 and H_2S are one of the main sources of acid rain and air pollution [1]. Government from all over the world realize the importance of reducing any type of emissions to the environment; thus regulations were made to make sure that refineries adhere to reducing the sulfur content in their fuel product by improving their processing methods.

Table 1.1: US EPA sulfur regulations for diesel and jet fuels as of April 2003 **[2]**.

Category	**Year**			
	1989	**1993**	**2006**	**2010**
Highway diesel (ppmw)	5000 (maximum for no. 1D and 2D. with minimum cetane no. 40)	500 (current upper limit since 1993)	15 (regulated in 2001; exclude some small refineries)	15 (regulated in 2001; apply to all US refineries)
Non-road diesel (ppmw)	20000	5000 (current upper limit)	500 (proposed in 2003 for 2007)	15 (proposed in 2003 for 2010)
Jet fuel (ppmw)	3000	3000	3000 maximum	3000 maximum

At present, catalytic hydrodesulfurization is commonly used for sulfur removals from refinery products. This process involves high temperature exceeding 300^0C, elevated pressure over 2 MPa, precious metal catalyst, high hydrogen consumption and large reactors **[3]**. However, one of the sulfur species, dibenzothiophene, has been proven to be the most difficult to remove using hydrodesulfurization process unless an energy intensive process is applied **[1,3]**.

Therefore, research on reduction of the energy usage for desulfurization process that uses other non-hydrodesulfurization processes such as alkylation, extraction, precipitation, oxidation and adsorption can be conducted. Among these processes, oxidative desulfurization appears more promising since they can be applied at ambient pressure and temperature **[3]**. Oxidative desulfurization processes includes microbial oxidation, chemical oxidation and photooxidation where it generally leads to the formation of sulfoxides or sulfones that can be subsequently removed by conventional separation method such as extraction, adsorption or distillation. Interest has been focused on photooxidation because of the possibility of using atmospheric oxygen as an oxidizing agent for desulfurization process.

1.2 Problem statement

Sulfur present initially in the crude oil in the form of mercaptans, sulfides, disulfides, thiophene, benzothiophene and dibenzothiophene. These sulfur species in crude oil can be converted into SO_X by combustion or H_2S in plant process which is hazardous to living organisms and environment. In addition, high sulfur content in crude oil could affect the refinery performance; since sulfur is a poison to the reforming catalyst whereby it could lower the conversion of crude oil to fuel therefore reducing the yield of fuel oil. H_2S formed in the refinery process if emitted could promote formation of acid rain and could also cause air pollution. High emission of H_2S in a refinery could jeopardize the health of those nearby since H_2S can cause conjunctiva, irritation to skin and mucous membranes as well as reacting with enzymes in bloodstreams inhibiting cellular respiration resulting in pulmonary paralysis, sudden collapse and death (refer to MSDS for H_2S). Furthermore, sulfur in crude oil can promote corrosion to the equipment and pipelines of the refinery.

There is also interest by the government in environmental issues where regulations and laws have been developed to decrease dangerous emissions to the environment. Having high sulfur content in fuel oil could lead to more emission of SO_X to the air as a result from engine combustion. Japan’s regulation of sulfur content in Light Oil is tightened from 0.50 wt% in 1976, 0.20 wt% in 1992 and 0.05 wt% in 1997 [1]. US Environment Protection Agency (EPA) had called for new regulations in 2006 for new fuel standards for eventual reduction in sulfur content to below 30 ppm sulfur by mass for gasoline and 15 ppm for diesel **[4]**. Therefore to cater to these stricter regulations, research must be conducted to improve the sulfur removal efficiency for crude oil in refinery.

1.3 Objectives

As response to the restriction of several government regulations on the sulfur content in fuel and also for maintaining a safe working environment for refineries, this research is conducted with the following objectives;

- To develop Fe/TiO_2 photocatalyst for oxidation of sulfur species in model oil.
- To determine the efficiency of sulfur removal from model oil by integrating photooxidation and extraction processes.

1.4 Scope of study

This research is about investigating the usage of semiconductors as an oxidizing agent for sulfur species in the crude oil via photocatalytic oxidation. Photocatalytic oxidation of sulfur species is chosen based on its nature which can be conducted in ambient temperature and pressure together with the presence of a light source. This type of semiconductor photocatalyst will be synthesized in the laboratory and characterized using methods such as X-ray diffraction (XRD), Diffuse Reflectance UV-vis spectra and etc. to determine its physical properties. After characterization, performance of the photocatalyst will be evaluated; employing a sulfur component (dibenzothiophene) dissolved in dodecane (model oil). The experimental data were analyzed to determine the best semiconductor photocatalyst suitable for the photocatalytic desulfurization of crude oil.