CHAPTER 1

INTRODUCTION

1.0 Overview

Atmospheric sulfur emission from vehicle exhaust is becoming a significant environmental issue and is being dealt with stringent regulation of allowable maximum sulfur limit in fuels. By 2015, it is expected that many countries around the world will enforce the new limit of 10 ppm of sulfur content in fuel. The removal of sulfur compounds from fuel is necessary because these compounds are a threat to the environment due to their hazardous nature. Compound such as SO_2 and SO_3, which are produced during fuel combustion process, have been identified as among the compounds that contribute to acid rain, air contamination and ozone depletion. Acid rain for example has harmful effects on plants, aquatic animals and infrastructures (*Li et al. 2009; Shakirullah et al. 2010*).

Apart from that, the current fuel combustion engines and exhaust-cleaning catalyst are quite sensitive to sulfur; high sulfur level can cause faster deterioration of the engine and catalyst (*Kuhlmann et al. 2009*). Sulfur compound will cause detrimental effect by poisoning the metal catalysts and lowering the efficiency of catalytic converters in automobiles (*Kulkani and Afonso, 2010; Taib and Murugesan, 2011*).

The push for lower sulfur content in vehicle fuel consequently creates pressure for refineries either to improve the existing desulfurization process or to replace it with completely new desulfurization process. Currently, the desulfurization of various products from middle distillate or vacuum distillation unit is carried out in hydrotreating unit as shown in Figure 1.1.
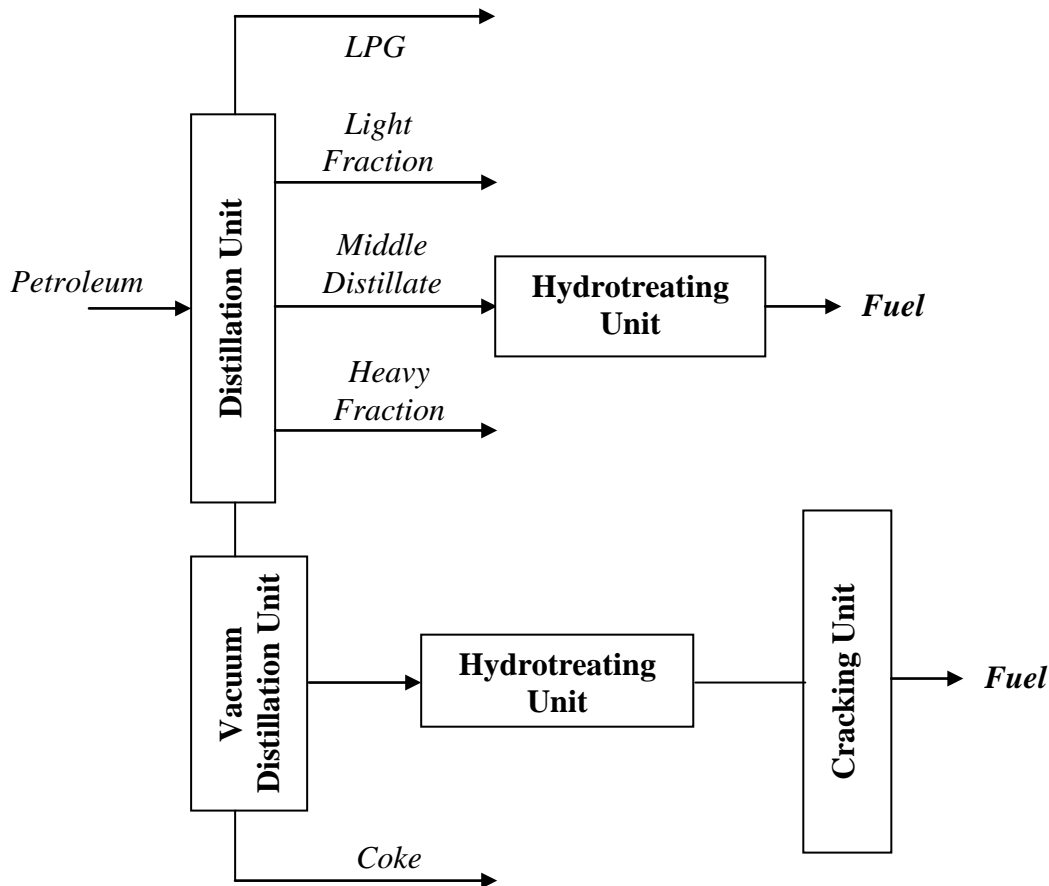
Figure 1.1: A simplified schematic diagram of fuel processing from petroleum
(*Moulijn et al. 2001*)

Industrially, desulfurization of fuel is carried out in hydrotreating unit by means of catalytic hydrodesulfurization (HDS) process. However, the application of existing HDS technology to effectively remove sulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT) and their derivatives needs very high pressure and temperature (*Holbrey et al. 2007; Gao et al. 2008*), which makes the HDS technology as no longer viable economically.

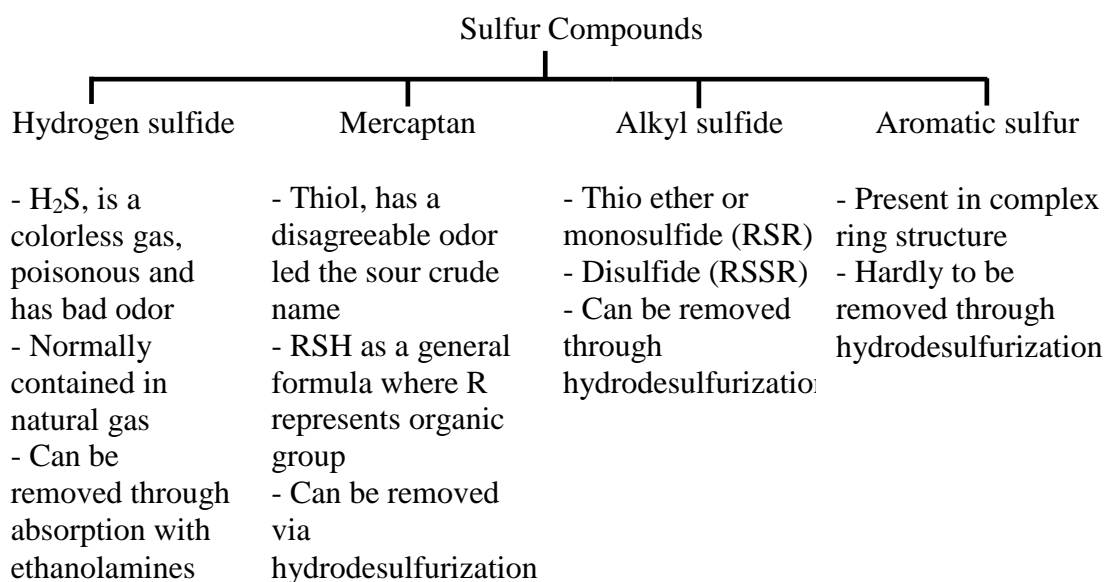### 1.1 Sulfur Compound in Petroleum

Sulfur compounds are commonly found as a natural part of fossil fuel, coal, natural gas and petroleum (*Stanislaus et al. 2010*). Nearly all naturally occurring petroleum contains compounds in which sulfur, nitrogen, and/or oxygen elements are combined with carbon and/or hydrogen. A typical elemental analysis of petroleum is given in

Table 1.1. The sulfur content in petroleum varies considerably. In some petroleum, the sulfur content may be as low as less than 0.1 wt % (sweet crude), while in some it can go extremely high up to 7 wt% (sour crude). Apparently, the density of petroleum increases as the sulfur content increases.

Table 1.1: Elemental analysis of typical petroleum (*McCain, 1990*)

| Element	Percentage by weight
Carbon	84 – 87
Hydrogen	11 – 14
Sulfur	0.06 – 2.0
Nitrogen	0.1 – 2.0
Oxygen	0.1 – 2.0

The properties of petroleum fluids, 2nd Edition

Sulfur Compounds

Hydrogen sulfide	Mercaptan	Alkyl sulfide	Aromatic sulfur
- H_2S, is a colorless gas, poisonous and has bad odor - Normally contained in natural gas - Can be removed through absorption with ethanolamines	- Thiol, has a disagreeable odor led the sour crude name - RSH as a general formula where R represents organic group - Can be removed via hydrodesulfurization	- Thio ether or monosulfide (RSR) - Disulfide (RSSR) - Can be removed through hydrodesulfurization	- Present in complex ring structure - Hardly to be removed through hydrodesulfurization

Figure 1.2: Classification of typical sulfur compounds in petroleum (*McCain, 1990*)

Sulfur may be present in many forms within petroleum such as hydrogen sulfide (H_2S), mercaptan, alkyl sulfide and aromatic sulfur, as shown in Figure 1.2. Mercaptan, alkyl sulfide and aromatic sulfur are also known as organosulfur where they consist of organic part and sulfur element. During distillation process, various petroleum products together with various organic sulfur compounds will be produced at different fractionation temperatures. In order to comply with the product

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specifications, the sulfur compounds are removed from the petroleum products through treatment process. However, some compounds of the refractory sulfur such as thiophene (TS), benzothiophene (BT) and dibenzothiophene (DBT) with their derivatives are difficult to be removed using the present treatment process due to their steric hindrance. Figure 1.3 shows the structures of typical refractory sulfur compounds that are generally present in petroleum product streams. It is reported that after the treatment process, some of the petroleum products may contain BT, alkyl-BT, DBT and alkyl-DBT whereas alkyl-DBT with substitution at 4, or 6, or both 4,6 positions and their derivatives contribute to 39, 20 and 26 wt% of the total sulfur, respectively (*Dhir et al. 2009*).


| Thiophene | Benzothiophene | Dibenzothiophene |

4-methyldibenzothiophene   4,6-dimethyldibenzothiophene
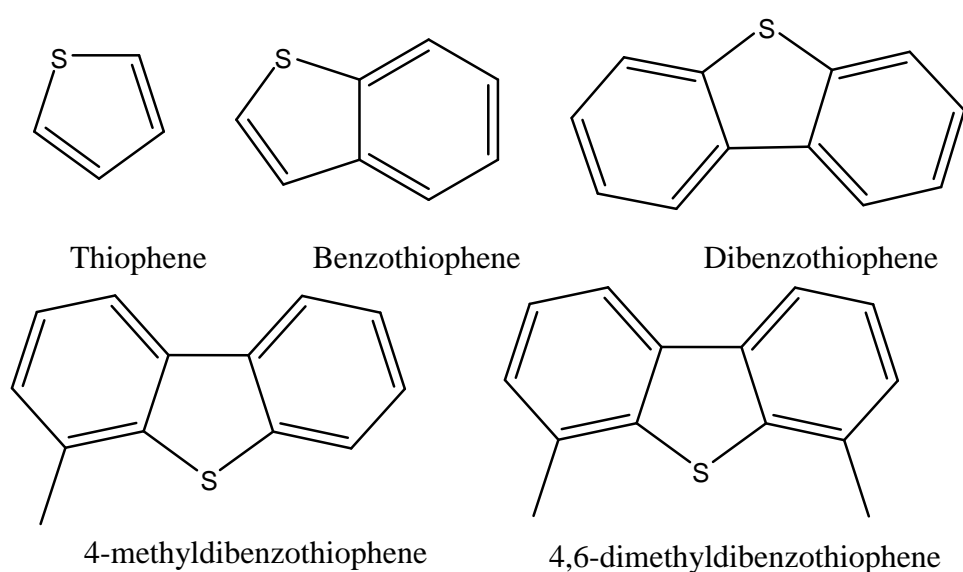
Figure 1.3: Structures of refractory sulfur compounds

Organosulfur and its derivatives are major sulfur compounds in fuel with boiling point higher than 100°C, where they usually contribute up to 50-80% of the total sulfur content in diesel (*Dai et al. 2008*). Therefore, the removal of these sulfur compounds from petroleum products such as diesel is one of the prime important processes in petroleum refining industry (*Khenkin and Neumann, 2011*). As mentioned earlier, in petroleum refining industry, the removal of sulfur compound is carried out by a catalytic HDS but the process requires both high temperatures and pressures of hydrogen gas, which leads to high operating cost.

1.2 Sulfur Limitation in Petroleum Product

In every oil refinery, the central separation step is distillation process where petroleum is separated into various fractions according to their volatility. Figure 1.4 shows a schematic diagram of a simple crude oil distillation unit.
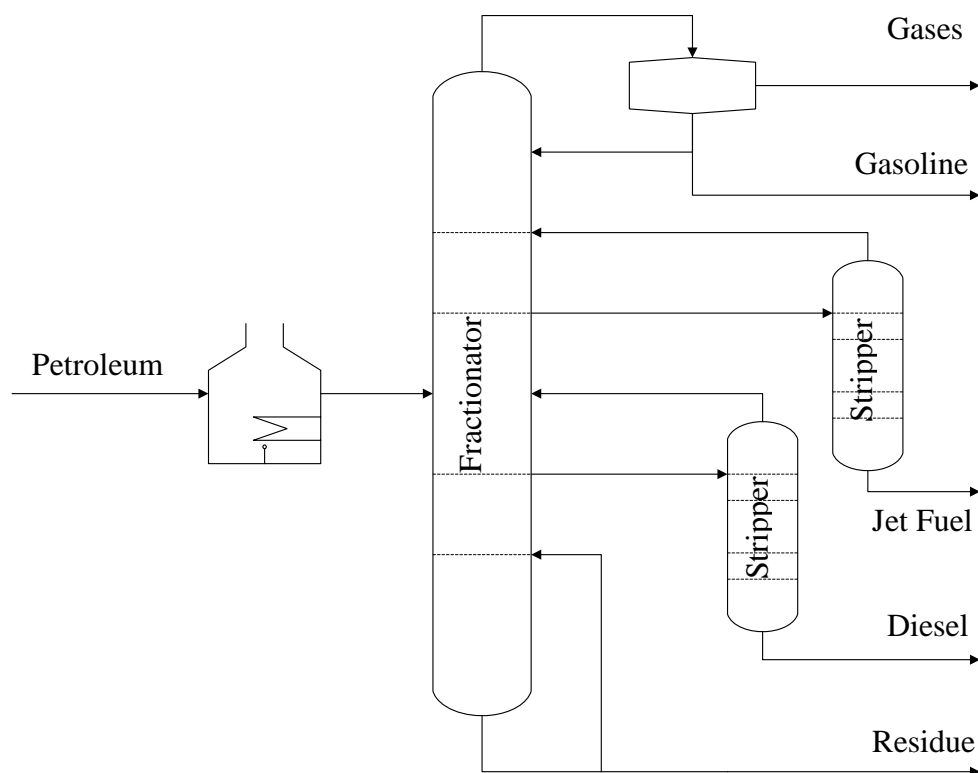
Figure 1.4: Simple crude oil distillation (*Moulijn et al. 2001*)

Unfortunately, the sulfur compounds present in the crude oil will also be collected in the fractionated distillation products. In order to meet market regulation, the sulfur content in each product obtained from different fractionation temperatures is required to be removed. For commercial diesel especially, due to the tightening of air quality act all over the world, the maximum allowable limit of sulfur content has been reduced drastically, as shown in Table 1.2.

Table 1.2: Diesel regulatory outlook in some countries*

Year of implementation	Sulfur (ppm)	Country
2008	50	Argentina
2008	50	Bahrain
2008	50	Iran
2008	50	Lebanon
2008	50	Oman
2009	50	Brazil
2010	50	Chile
2010	50	China
2010	50	India
2010	50	Kuwait
2010	50	Peru
2010	50	Russia
2010	50	Thailand
2010	15	USA
2008	10	Canada
2008	10	Japan
2009	10	Australia
2009	10	New Zealand
2009	10	Hong Kong
2010	10	Singapore
2013	10	Saudi Arabia
2010	< 10	Denmark
2010	< 10	France
2010	< 10	Germany
2010	< 10	Sweden

Lo et al. 2003; Lu et al. 2007; Zhao et al. 2007; Dai et al. 2008; Liu[b] et al. 2008; Rheinberg et al. 2008; Zhao et al. 2008; Li et al. 2009; Adzamic et al. 2009; Kulkani and Afonso, 2010; Taib and Murugesan, 2011; Wang et al. 2011

For instance, European Union (EU) imposed a restriction on sulfur content in fuels at 350 ppm in 2004, followed by a drastic reduction to 50 ppm in 2006, when later reduced it further to 10 ppm in 2010. In general, after 2010, the limit for sulfur content in fuel has been reduced to within the range of 15 to 10 ppm in Japan, United States of America (USA), Canada, Australia, New Zealand, Singapore and Hong Kong. Currently, many of the other countries in the world, especially those with high fuel consumption such as China, India, Russia, Brazil and Iran, are taking steps to follow the standard fuel product specification that is presently in place in the USA and

Europe. Some countries in Asia, Middle East and South America such as Thailand, Bahrain, Oman, Kuwait, Argentina, Chile and Peru are currently contemplating a more drastic action in ratcheting down the standards which would bring them at par with the USA Environmental Protection Agency (EPA) and Euro IV standard, where the limit for sulfur content is 50 ppm.

In Malaysia, since 2006 petroleum companies have adopted Euro II standard where the sulfur content is kept at 500 ppm. However, due to stringent environmental requirement imposed by the government recently, petroleum refineries are forced to comply with a new requirement to further reduce the sulfur content up to 50 ppm in accordance to Euro IV requirement which will commence in 2015 (*ACFA, 2012*).
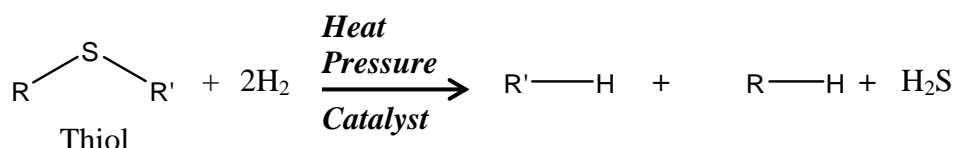
1.3 Sulfur Removal Technology

The process of removing sulfur can be divided into three groups based on the way in which the sulfur compounds are transformed during the process; these are decomposed sulfur compounds, separated sulfur compounds from product stream without decomposition, or both separated and then decomposed. When sulfur compounds are decomposed, gaseous or solid sulfur products are formed and separated from the hydrocarbon part (*Corma et al. 2001*). HDS is the most typical example of this type of process which is currently being used to remove most of the sulfur compounds (*Garcia-Cruz et al. 2008*; *Li et al. 2009*). But, it is difficult to achieve ultralow sulfur levels by HDS due to the presence of some refractory aromatic sulfurs such as BT, DBT and 4,6-dialkyl substituted DBTs as mentioned in the previous section. Attributing to their steric hindrance, severe operating conditions and large capital cost are required for HDS to achieve ultralow sulfur level in fuels (*Li et al. 2009*).

Subsequently, non-HDS technology including oxidative, reactive, adsorption, biodesulfurization and extraction desulfurization was developed (*Wang et al. 2011*). Some of these technologies have shown a good result in removing sulfur compounds from fuels, but needs to be investigated. Therefore, further removal of residual sulfur compounds from diesel is expected to significantly increase the cost of treatment and

by considering that, alternative methods of sulfur removal are of particular interest (*Nefedieva et al. 2010*).

1.3.1 Hydrodesulfurization (HDS)

HDS is a catalytic process in which the petroleum feedstock is reacted with H_2 to reduce the sulfur content in petroleum product. The schematic reaction of HDS process is shown in Figure 1.5.

$$R \overset{S}{\diagup} R' \ + \ 2H_2 \ \xrightarrow[\textit{Catalyst}]{\textit{Heat} \ \textit{Pressure}} \ R'\text{——}H \ + \ R\text{——}H + \ H_2S$$

Thiol

Figure 1.5: A typical reaction during hydrodesulfurization

Industrially, most sulfur compounds are removed through HDS in which H_2 gas is used to form hydrocarbon and hydrogen sulfide (H_2S). Most sulfur compounds from petroleum stream products such as thiols, sulfide, disulfide and thiothers can be easily removed by HDS process but it becomes difficult when dealing with refractory sulfurs such as thiophene, BT and DBT; even harder for their alkyl-substituted and derivatives due to steric hindrance of these compounds which prevents adsorption on the catalyst surface. As a result these sulfur compounds still remain in the diesel (*Garcia-Cruz et al. 2008*; *Adzamic et al. 2009; Gao et al. 2009; Khenkin and Neumann, 2011*; *Yu et al. 2011*).

At present, the HDS process for removing sulfur compounds in diesel is a very complex problem in petroleum industry as the industry is being challenged to minimize further the sulfur content in the product, thus minimizing sulfur pollution from exhaust gas. In order to bring down the sulfur content in diesel to within the required level, researchers have been making several efforts such as developing new catalyst, or enhancing existing catalyst activity and changing HDS operating conditions. For that, the removal of sulfur in diesel through HDS process which requires more severe conditions including the use of higher temperature (>300°C), higher H_2 gas pressure (>4 MPa), more H_2 gas consumption, more active catalysts and

longer residence time is needed (*Shen et al. 2005; Wang et al. 2011*). These severe operating conditions combined with expensive catalyst are other disadvantages of the HDS process (*Song, 2003*; *Shakirullah et al. 2010*).

1.3.2 Oxidative Desulfurization

Mei et *al.* (2003) investigated ultrasound techniques for possible use to enhance oxidative desulfurization using oxidants and catalysts. Through the use of catalytic oxidation and ultrasonication followed by solvent extraction, the removal efficiency of sulfur compounds in diesel can reach up to 99% in a short time at ambient temperature and atmospheric pressure. Figure 1.6 shows the schematic of a typical reaction during oxidative desulfurization.

4,6-dimethyldibenzothiophene   4,6-dimethyldibenzothiophene sulfone
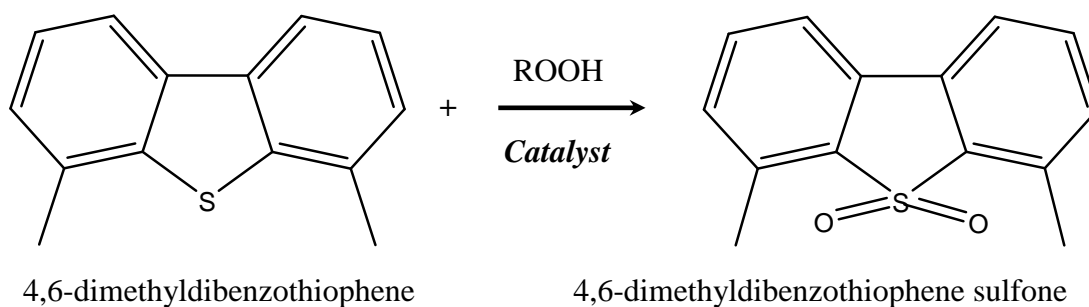
Figure 1.6: A typical reaction during oxidative desulfurization (*Mei et al. 2003*)

Even though this removal process sounds promising, some issues have arisen particularly in the waste management of sulfone compounds at the end of the process. An excess amount of oxidant is required to convert sulfur to sulfone compounds which increased the operation cost, and could limit the feed flexibility for refineries when targeting for a cost effective process (*Ito and van Veen, 2006*).

1.3.3 Reactive Desulfurization

Reactive desulfurization employs chemical interaction of the sulfur compounds generally with the presence of a catalyst. A new method was reported for deep desulfurization where the condensation reaction of sulfur compound with formaldehyde occurred in the pore spaces of activated carbon catalyzed by sulfuric

acid. Because the reaction occurred in the pore spaces, the desulfurization function was locally intensified and the reaction products were absorbed by activated carbon. The total sulfur content of the commercial fuel dropped from 1697 ppm to 14 ppm (*Dai et al. 2008*). However, the drawbacks of this technique are side reaction between the hydrocarbon with formaldehyde, corrosive reaction condition due to the use of sulfuric acid and difficulty in regeneration of activated carbon. Recently in 2011, Khenkin and Neumann reported that $H_5PV_2Mo_{10}O_{40}$ polyoxometalate can convert sulfur compounds into insoluble sulfur-containing polymers at 120°C after a five hours reaction; the sulfur-containing polymers were claimed to be easily extracted from the fuel phase. However, this method is not suitable for removing sulfur from diesel due to the high viscosity of diesel; a high temperature would be required to reduce the viscosity to enable diesel to penetrate into the pore spaces.

1.3.4 Adsorption in Desulfurization

Ma et *al.* (2002) reported that the desulfurization process called selective adsorption for fuels such as gasoline, jet fuel and diesel which have been investigated at ambient temperature and atmospheric pressure, are effective in removing sulfur compounds with low investment and operating cost. Generally, the selective adsorption process involves the use of porous materials which provide huge interface area for the collection of dilute species (*Ma et al. 2002; Dai et al. 2008)*. However, the main limitation of this process is quick overloading of adsorbent in the case of high sulfur content in refinery streams.

1.3.5 Biodesulfurization

Biodesulfurization is a non-invasive biological approach that can specifically remove sulfur from refractory hydrocarbons under mild conditions. However, the highest activity obtained is still insufficient to fulfill the industrial requirements. The possibility of degrading non-sulfur aromatic compounds still needs further research (*Oldfield et al. 1998*; *Soleimani et al. 2007*). Figure 1.7 depicts the schematic of biodesulfurization process by bacteria.
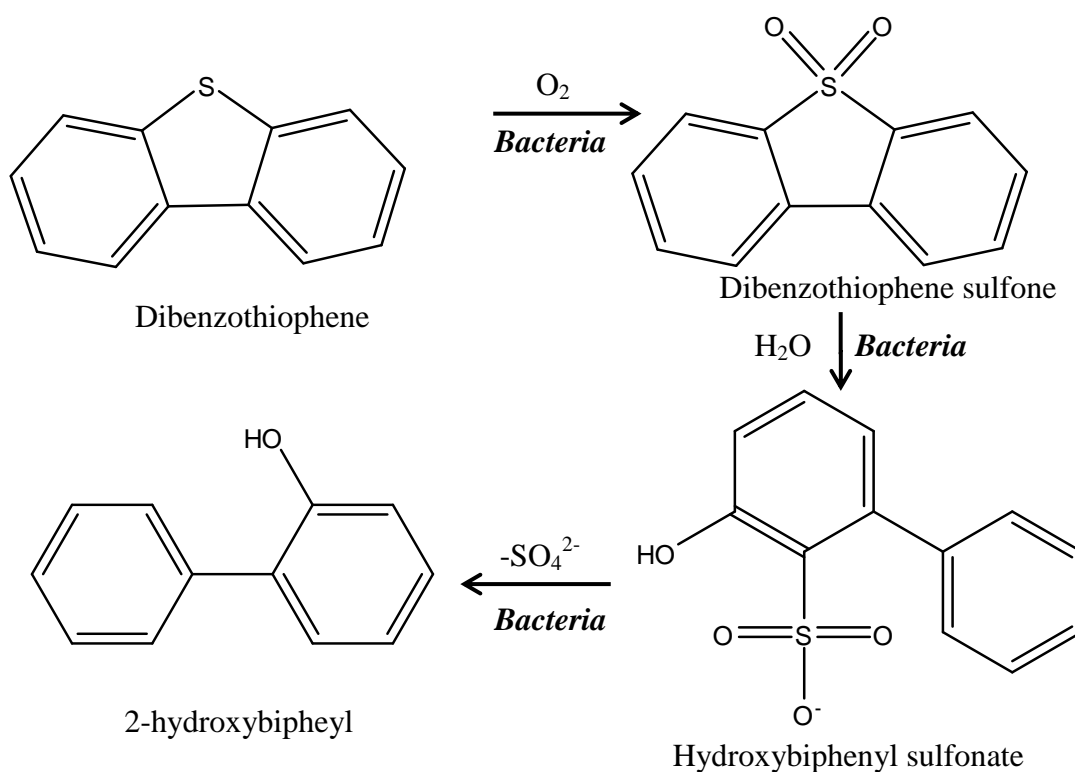
Figure 1.7: A reaction route of biodesulfurization by bacteria (*Soleimani et al. 2007*)

1.3.6 Extractive Desulfurization

Chemical industry has to reduce the use of solvents while focusing more on the development of a sustainable green chemistry (*Revelli et al. 2010*). In petroleum refining industry, sulfolane and furfural are commercial extraction solvents that are mostly used for aromatics extraction from different petroleum fraction. Since part of the sulfur in petroleum is present in the form of aromatic compounds, these two solvents are suitable for extractive desulfurization (*Adzamic et al. 2009; Adzamic et al. 2010*). However, the regeneration of used solvents is much harder and not economically feasible due to volatility limitations.

1.4 Problem Statement

Driven by regulatory requirements to reduce the content of sulfur in fuels, the demand to find an alternative process to HDS is on the rise. Other technologies that have a high potential to be considered as alternatives are adsorption, liquid-liquid

extraction (LLE), oxidative desulfurization, biodesulfurization and etc. (*Rang et al. 2006; Soleimani et al. 2007*). Among these technologies, LLE is of practical interest considering the fact that it is a well-established technology and can be operated at ambient conditions (*Zhang and Zhang, 2002; Eβer et al. 2004*). However, the key to the success of LLE process is efficient extractant which features the following attributes: better extractive ability for sulfur compounds, ease of regeneration of used extractant, non-contaminant to diesel, non-toxic and environmentally benign, and recyclability for repetitive uses. Ionic liquids (ILs), also known as a designer solvent, have been reported to have these characteristics and are considered as a promising extractant for LLE process of desulfurizing some petroleum products (*Gao et al. 2008; Eβer at al. 2004; Zhang et al. 2004; Letcher et al. 2005; Palou et al. 2010; Taib and Murugesan, 2011*).

The efficiency of an extraction process mostly depends on the correct solvent selection, which means that a compromise must be reached between solvent selectivity and capacity including environmental restriction (*Laus et al. 2005; Wang[a] et al. 2007; Abe et al. 2008; Liu et al. 2009; Adzamic et al. 2009*). The existing methods for selecting the appropriate combination of cations and anions of an ILs rely on experimental works (*Bosmann et al. 2001; Eβer et al. 2004; Nie et al. 2006)* which are costly and time consuming. On the other hand, predicting the combination of cations and anions using simulated software such as COSMO-RS (*Kumar and Banerjee, 2009*), usually demonstrated poor results of experimental desulfurization. Therefore, no proper selection criteria or method has been proposed thus far. However, by a judicious combination of cations and anions, it is possible to screen potential ILs that might meet the required extraction performance. This new method of selecting ILs is based on interaction mechanism. In the present study, a complimentary method is suggested by means of aromaticity index (AI) and double bond equivalent (DBE) for preliminary selection of an appropriate combination of cation and anion for fuel desulfurization.

Although various kinds of ILs have been used as extractive solvent, their direct applications for sulfur removal have not been extensively studied due to lack of information on the behaviour of ILs with different type of hydrocarbons. This also

hampers efforts in designing and selecting appropriate ILs for extractive desulfurization of fuels. In addition, the information on cross-miscibility between ILs and hydrocarbon is still limited, and needs to be addressed before possible applications such as desulfurization of petroleum products such as diesel can be implemented (*Davis and Forrester, 1999; Tian et al. 2007; Liu[a] et al. 2008*). Taking this into consideration, the present study also investigated phase equilibrium and miscibility regions of aliphatic and aromatic hydrocarbons.

1.5 Research Objective

This work has been carried out with the main objective of removing sulfur compounds from diesel using imidazolium-based ILs that operates under mild conditions without requiring H_2, O_2, catalyst and oxidant as potential alternative to HDS. These are sequence of the research objective:

➢ to identify, select and validate the potential cations/anions combination based on COSMO-RS database using aromaticty index (AI) and double bond equivalent (DBE) approach,

➢ to synthesize and characterize the potential ILs for extractive desulfurization,

➢ to conduct and optimize desulfurization process conditions based on model oil,

➢ to develop ternary diagram between studied hydrocarbon, ILs and BT for cross-miscibility study,

➢ to classify desulfurization capability of the selected ILs on model fuel and actual diesel and lastly conduct the regeneration process of spent ILs.

1.6 Thesis Organization

This thesis consists of six chapters. This chapter (Introduction) includes a brief introduction on sulfur compounds in petroleum, sulfur limitation in petroleum product, current technologies on sulfur removal and HDS process which is the current industrially practice. This chapter also includes problem statement which provides basis and rational research direction together with research objectives and thesis organization.

The second chapter (Literature Review) reviews on ILs, their interaction mechanisms and their selection for extractive desulfurization process. The influence of various parameters on extractive desulfurization of model oil, model fuel and actual diesel are discussed. Ternary systems are investigated in order to explain the behaviour of model fuel and actual diesel later on. A general review and discussion on existing regeneration processes of ILs are given. Finally, the statistical approach study on optimization, data mapping and correlation is also covered.

The third chapter (Methodology) describes the detail of the materials and chemicals used in the present study. The overall experimental flowchart is presented. The detail of the experimental work from screening, synthesizing, characterizing of ILs, extraction process based on model oil, model fuel and actual diesel is elaborated in this chapter. The statistical approach on optimization, data mapping and correlation procedures are detailed out. Regeneration technique for ILs is discussed at the end of the chapter.

The fourth chapter focused on interaction mechanism by comparing experimental results obtained using Raman spectroscopy against predicted results by COSMO-RS simulations, aromaticity index (AI) and double bond equivalent (DBE) calculations, in order to understand the exact extraction mechanism between ILs and aromatic sulfur. Suggested ILs were synthesized and characterized, and their thermophysical properties were also calculated.

The fifth chapter deals with extractive desulfurization process on batch system where seven parameters were evaluated and optimized. The optimized parameters obtained were further used in model fuel and actual diesel extraction process. This fifth chapter also covers the details on data validation, data mapping and correlation using statistical approach, ternary diagram and regeneration study.

The sixth chapter (Conclusion) concludes the findings from the research. This chapter contents are arranged accordingly to the sequence of the main studies.

The seventh chapter (Recommendation) proposes future studies in the related field. These recommendations are given due to their significance and importance related to the current studies.