

## CHAPTER 1



### INTRODUCTION

Traditional environmental concern about sulfur which contains in fuels of all types is linked to its transformation to sulfur dioxide during combustion; this has led to legislation in almost all parts of the world that has gradually diminished the maximum allowable sulfur content, particularly in middle distillates and residual fuels. Recently, fuel sulfur has been conclusively shown to adversely effect particulate emissions from diesel engines and this has led to new legislation in Thailand which limits the sulfur content of diesel fuel to 0.05% maximum.

Two general methods of reducing the amount of sulfur have been developed. One method involves solvent extraction of the sulfur compounds and another is about decomposition of sulfur compounds using catalyst to be hydrogen sulfide and hydrocarbon remnants. The solvent extraction processes are not as cheap or effective as the catalytic processes in the removal of sulfur because they remove the entire sulfur-bearing molecule and at the same time certain hydrocarbons, particularly those with aromatic rings. Thus, when the removal of aromatic hydrocarbons and sulfur are desirable, the solvent processes should be superior. Sulfuric acid has long been used in dissolving or removing sulfur, and furfural are mentioned more frequently.

The accepted method for reducing the sulfur which is contained in petroleum derived fuels is catalytic hydrodesulfurization (HDS), which removes sulfur from the fuel molecules by transforming it to hydrogen sulfide:



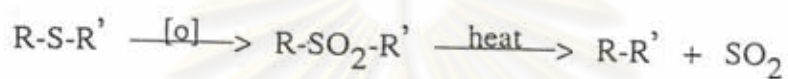
Catalytic hydrodesulfurization (hydrorefining) is of great importance in oil refining and generally in the technology of liquid fuel. The target of catalytic hydrodesulfurization is hydrogenation of and sulfur removal (desulfurization) from different oil fractions. Under hydrodesulfurization conditions hydrogenolysis of C-S bonds proceeds with sulfur removal as hydrogen sulfide. At the same time under these conditions hydrogenolysis of C-O and C-N bonds also takes place with oxygen and nitrogen elimination as  $H_2O$  and  $NH_3$ , respectively. The process is carried out in the presence of various catalysts which are stable to the action of sulfur compounds (mainly molybdenum or cobalt oxides on  $Al_2O_3$  or nickel and tungsten sulfides as well as miscellaneous mixed catalysts) under hydrogen pressure at 150-600°C but mainly at 300-400°C.

The relative susceptibility of organosulfur compounds to hydrodesulfurization depends greatly on their structures. For instance, among sulfides desulfurization, benzyl sulfides proceeds more easily than alkyl aryl sulfides and diaryl sulfides are the most stable. Thiophene compounds are generally more resistant to desulfurization than sulfides. For illustration one devoted to the kinetics of hydrodesulfurization on  $CoO-MoO_3-Al_2O_3$  catalysts which gave the sequence of the reaction rates.

The need to produce low sulfur fuels will necessitate a large number of new desulfurization units and will greatly increase the demand for hydrogen, which is necessary for the HDS process. Traditionally, there is a hydrogen balance in refinery operations in which the catalytic reformers produce the hydrogen which is necessary for HDS process and other processes such as hydrocracking. This source of hydrogen will not be able to meet the needs of the new units, however, particularly since the limits that have recently been put on the maximum aromatic content of gasolines preclude the expansion of reformer operations. Thus the quantities of hydrogen will have to be produced by steam reforming of light hydrocarbons or partial oxidation of heavy petroleum components; this will not only incur a substantial investment and operating

cost, but will also release to the atmosphere a large quantity of by-product carbon dioxide.

It is evident from the above that a process for reducing fuel sulfur without the additional hydrogen would be highly desirable as a supplement to hydrodesulfurization. To that end, various chemical processes for removing sulfur were tried in the past but with different success. The only promising approach, termed oxo-desulfurization, took advantage of the fact that the divalent sulfur of the sulfide group can be oxidized to the hexavalent of the sulfone group, which upon thermal treatment can eject sulfur dioxide:



The above procedure does achieve the goal of sulfur removal without recourse to hydrogen, but suffers from the fact that the temperatures for decomposition of sulfones are in excess of 500 °C, which leads to substantial (and undesirable) thermal cracking of the rest of the fuel molecules.

Another feature of the sulfur atom is that it renders slightly more polar than hydrocarbon molecules in which it occurs; this permits the selective removal of sulfur compounds by solvent extraction.

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## 1.1 OBJECTIVES

In the present study, desulfurization of high speed diesel using hydroperoxide and peroxy acid as oxidants and solvent extraction are to be investigated. The main objective of this work are as follow:

- 1.1.1 To study desulfurization of high speed diesel by using oxidation reaction.
- 1.1.2 To study seperation of sulfur compounds after oxidized by solvent extraction.
- 1.1.3 To study physical properties of high speed diesel after desulfurization process.

## 1.2 SCOPE OF WORK

The scope of work is as follow;

- 1.2.1 To study and compare efficiency of two oxidants, Hydroperoxide and Peroxy acid to desulfurization of high speed diesel by oxidation reaction.
- 1.2.2 To study and compare efficiency of solvent, Methanol, Acetic acid, Ammonia and Ethanolamine to solvent extraction process.
- 1.2.3 To study and compare the samples of High speed diesel taken from refinery before desulfurization unit.

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