



CHAPTER I

INTRODUCTION

As a valuable source of energy and petrochemical feedstock, petroleum has made a big contribution to the livelihood of the populations of highly industrialized societies. Petroleum consists predominantly of various hydrocarbons and it also contains sulfur, nitrogen, oxygen, and organometallic compounds as impurities. The concentrations of these impurities are found in wide range depending on the source of crude oil. Sulfur compounds are generally the most prevalent in concentration and typically are found in the range from 0.5-8.0 wt% from most crudes [Drew, 1982].

The most important classes of organic sulfur compounds found in petroleum fractions and coal liquids are mercaptans, sulfides, disulfides, thiophenes, and thiophene derivatives such as benzothiophenes and dibenzothiophenes. The organic sulfur in petroleum fractions ranges from very simple identifiable compounds in lightest fractions to much more complicated compounds and much more concentrated, which are very difficult to identify, in heavier fractions. In light straight-run fractions, sulfur is typically present as aliphatic compounds and in heavier fractions, sulfur is present as heterocyclic compounds. In general, the aliphatic sulfur

compounds in petroleum are removed easier than heterocyclic sulfur compounds.

In petroleum products, sulfur compounds are objectionable because of their potential to cause corrosion, bad odor of light sulfur compounds, and toxic character of hydrogen sulfide. The presence of sulfur compounds in gasoline tends to lower the octane number and also decreases the susceptibility of gasolines to octane improvement by addition of tetraethyl or tetramethyl lead. The incentive is now strong for removal of sulfur from fuel oils, since combustion of sulfur-containing fuels is the primary cause of SO₂ pollution of atmosphere. This pollution is becoming a very acute problem to society. Furthermore, sulfur compounds poison noble metal catalysts. In catalytic reforming of naphthas and in isomerization of C₄ to C₆ paraffins, it is necessary to pretreat the feedstocks to lower sulfur contents down to a few parts per million to avoid catalyst deactivation.

Three methods are generally used to remove sulfur compounds from petroleum [Mcketta, 1982]: adsorption on molecular sieves, solvent extraction, and catalytic hydrodesulfurization (HDS). Adsorption on molecular sieves is widely used to remove sulfur compounds from natural gas. Solvent extraction removes entire sulfur-bearing molecules from hydrocarbon streams. Popular solvents for this purpose are aqueous of alcohol solutions of alkanolamines, and aqueous solutions of

alkali carbonates. The most broadly applicable process for sulfur removal is catalytic hydrodesulfurization, which involves the reaction of sulfur compounds with hydrogen in the presence of a catalyst, resulting in their decomposition into hydrogen sulfide and hydrocarbon remnants of the original sulfur compound. This process is effective for removing various sulfur compounds from products ranging from gasoline to heavy oils. Therefore, this process is chosen for sulfur removal in this study.

In the HDS processing of petroleum fractions, gas or liquid-phase oil is contacted cocurrently with hydrogen, flowing downward through solid catalyst particles in a fixed-bed reactor. The design of these reactors for new feedstocks is straightforward and often based on plant operation. Fluidized-bed or slurry-bed reactor is also used commercially in HDS, that catalyst particles are held in suspension by the upward velocity of the gas or liquid reactant through which hydrogen flows cocurrently.

The catalysts most commonly applied in HDS process are derived from alumina-supported oxides of cobalt and molybdenum, which are usually sulfided before operation. Catalysts of this type are commonly referred to as cobalt molybdate. Practical catalysts may contain as much as 10 to 20% of these metals, though lower metal contents are probably more common.

Poisoning of catalyst, which reduces activity of the catalyst, is caused by the impurity presented in the

feedstock. Nitrogen-containing compounds in feedstock have been claimed to be the most important compounds affecting the catalyst's HDS reactivity. Several reports [Kirch, 1959; Desikan and Amberg, 1964; Lipsch, 1969] reveal common and severe inhibitory effect of nitrogen-containing compounds on catalytic removal of sulfur. The presence of these species even at low concentrations may limit the observed catalytic activity and necessitate the use of higher pressures and temperatures to obtain desired conversions.

Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions occur simultaneously at severe conditions but at mild conditions, only HDS reaction occurs. As mentioned above, this research aims to study the effect of nitrogen compounds on HDS reaction at mild conditions.

Petroleum contains significant quantities of nitrogen compounds in addition to sulfur compounds. Nitrogen compounds are mainly heterocyclic. They are typically classed as basic compounds (pyridine, quinoline, and acridine) and nonbasic compounds (indole, pyrrole, and carbazole).

The intention of this study is to investigate the effects of temperature on catalytic hydrodesulfurization catalysts in the presence of nitrogen compound. In this present study, two commercial catalysts, CoMo/Al₂O₃ and NiMo/Al₂O₃, are used to study the effects of different kinds of active metal on sulfur removal. Thiophene and quinoline are chosen as model compounds which represent

some of the less reactive sulfur and nitrogen compounds, respectively. Toluene and hexane are used as liquid carrier. Liquid feed and product in each experiment are characterized for thiophene concentration by Gas Chromatography.