CHAPTER I

Introduction

In the present day, there is an increasing demand of petroleum as a feedstock of refinery and petrochemical processes. The petroleum usually contains impurities, mainly responsible for the catalyst deactivation during the catalytic hydroprocessing. Removal of the impurities is necessary for improving hydrocarbon feedstock before further processes. The impurities consist of asphaltene, sulfur, nitrogen and oxygen compounds, and metal impurities such as nickel, vanadium and iron etc., especially mercury.

Mercury is metal compound found in wide range of petroleum such as natural gas, condensate and crude oil. Chemistry structure and quantity of mercury depend on the source and type of petroleum feedstock (Sarrazin, 1993). The mercury which is found in the condensate is presented in various chemical states; elemental, ionic and organometallic (Yamada et al., 1995).

The presence of mercury in condensate and crude oil can cause major problems such as reduction of catalyst life (Sokolskii et al., 1982) and corrosion (Leeper, 1980). Mercury-induce corrosion on aluminum heat exchanger has resulted in at least four long term industrial complex shutdowns, one each in Algeria, The United States, Indonesia, and Thailand (Stockwell, 1993). Furthermore, mercury can also cause the environmental problems.

Several methods for removal of mercury from both gas and liquid hydrocarbon have been proposed. These methods can be classified into two groups: chemical treatment and adsorption. In chemical treatment, mercury reacts with some chemical and converts to a mercuric sulfide that is insoluble and easy to remove from hydrocarbon feedstock. The chemical substance used is usually a sulfur compound, such as alkali polysulfide. By this method, sulfur compound contacts directly to hydrocarbon and reacts with mercury compounds in hydrocarbon and converts to a mercuric sulfide.

On the other hands, adsorption is a present common method that is used to remove mercury because this method provides a high efficiency of mercury removal and does not contaminate with other chemical substance. This method comprises of contacting hydrocarbon-containing mercury with an adsorbent.

However, some methods combine between chemical reaction and adsorption. The sulfur supported on the adsorbents such as activated carbon and alumina can be used. By this method mercury reacts with sulfur supported on the adsorbents and converts to a mercuric sulfide depositing. In addition, hydrodemetallation is a method for removing metal from liquid hydrocarbon by using hydrogen to contact with an organometallic compound at the surface of the hydrodemetallation catalyst and produce a metal sulfide and hydrocarbon.

$$\text{R-M} + \text{hydrogen} + \text{Catalyst} \rightarrow \text{M-Catalyst} + \text{RH}$$

It is the method that combines between chemical reaction and adsorption. Hydrodemetallation reaction is the one reaction in the hydrotreating process.

Hydrotreating is a process commonly used in most modern oil refining operation (Satterfield, 1980). It is a process to saturate olefins and/or reduce the sulfur, nitrogen, oxygen, halides, and trace metal by reacting them with hydrogen on catalyst (Gary and Handwerk, 1994). Hydrotreating consist of several classes of reactions, which occur simultaneously: hydrogenation, hydrodesulfurization (HDS), hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), hydrodehalogenation, hydrocracking, and hydrodemetallation (HDM).

Hydrodemetallation has high efficiency to remove organometallic compounds from liquid hydrocarbon such as iron, nickel and vanadium etc. However nobody studied the removal of mercury compounds from natural gas condensate by hydrodemetallation.

Catalysts developed for hydrotreating include cobalt and molybdenum oxides on alumina, nickel oxide, nickel thiomolybdate, tungsten and nickel sulfides, and vanadium oxide. Cobalt and molybdenum oxides on alumina catalysts are most generally used for hydrotreating catalysts (Gary and Handwerk, 1994). Because they are proven to be highly selective, easy to regenerate, and resistant to poisons. Converting the hydrogenation metals from the oxide to the sulfide form must activate them. Furthermore, the chemical structures of the metals in the feed are a very important determinant in the metals deposition process and in the potential effects on catalyst activity (Silbernagel and Riley, 1980). As mention above, the mercury found in condensate is presented in various chemical states, elemental, ionic and organometallic. However nobody studied the effect of chemical structure of mercury compounds to remove mercury from natural gas condensate by hydrodemetallation.

Thus the objectives of this research are to study the effect of chemical structure of mercury compounds and temperature that are suitable for the removal of mercury from liquid hydrocarbon by hydrodemetallation. $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ are used as hydrotreating catalysts. Toluene containing mercury compounds is used as the feed model. Toluene is used because of its solubility. Mercuric chloride is used as mercuric compound in inorganic form. Diphenylmercury is used as mercuric compound in organometallic form. Liquid product and spent catalysts are digested with permanganate-persulfate solution, nitric acid, and sulfuric acid which applied from ASTM D-3223 to obtain the ionic form in aqueous phase and reduce analytical interference before analysis by atomic absorption spectrometry. Flow Injection Analysis Mercury Hydride system is a technique for measurement mercury in water. Total surface area, total pore volume and pore size distribution of each fresh and spent catalysts are analyzed by BET method.