CHAPTER I

INTRODUCTION

Hydrocarbon feedstocks for refinery and petrochemical production may contain some impurities. These impurities are usually found in the form of sulfur, nitrogen, oxygen and metal compounds. Mercury is one of metal impurities which can be found. Trace amount of mercury can present in wide range of petroleum such as natural gas, condensate and crude oils. The quantities of mercury are found in various ranges, depending on the source of petroleum feedstocks. For example, natural gas and associated condensate from one field are found to have mercury contents of 15-450 (Yan, 1987) and 10-3000 ppb (Sarrazin, 1993), respectively. Low level of mercury can be found in crude oils at range of 0.5-10 ppb (Yan, 1990).

Mercury in natural gas is generally in elementary form. Natural gas condensate is very different. There are various mercury species in condensate: elemental Hg, ionic and organometallic compounds. Ionic and organic forms are commonly found more than elemental mercury. In crude oil, California Tertiary crude oil, mercury is found in a nonphophyrin form (Filby, 1975). However, it is now known that mercury, which is detected in the gas and the associated condensate, does not result from well drilling and does not result by accident. The mercury is

produced in association with the gas and the condensate. This mercury is thought to originate from geologic deposits in petroleum reservoirs.

Although mercury is found in trace quantity, it can be a potential cause of problems. Catalyst used in catalytic processes such as catalytic hydrogenation, is susceptible to mercury poisoning (Sokol'skii, 1983). Recently refiners and petrochemical producers have experienced in a serious increment of catalyst poisoning caused by mercury. In addition mercury can also be a major source of concern in liquefied natural gas plants. This may lead to a plant having to shut down for repairs and maintance at a cost of millions of bahts. Mercury-induced corrosion on aluminium heat exchangers has resulted in at least four long term industrial complex shutdowns, one each in Algeria, The United States, Indonesia and Thailand (Stockwell, 1993). All four shutdowns required costly replacements and from several weeks to several months of lost production, resulting in major financial losses. When mercury contaminated in transportation fuels is released into atmosphere with exhaust gas after combustion, it can affect plants, human and animal life. Because of its highly toxicity, it is necessary to remove or reduce the amount of mercury in petroleum to protect the catalysts used in any catalytic processes and to meet the environmental limitation.

Several methods have been proposed for mercury removal from both gas and liquid hydrocarbons. It can be classified into two groups: chemical treatment and

adsorption. First method, mercury reacts with some chemical and converts to a mercury compounds such as mercuric sulfide, which is easily removed from the hydrocarbon feedstocks (Audeh, 1989). Adsorption is the most commonly used method for removal of mercury. This method comprises of contacting hydrocarbon containing mercury with an adsorbent (Furuta, 1990). The adsorption is more preferred for high efficiency of mercury removal (Yan, 1987).

Since natural gas has been found to be contaminated with elemental mercury, high efficiency of mercury removal can be attained by using sulfur supported on activated carbon (Leeper, 1980). Elemental mercury contained in naphtha can be adsorbed by using an adsorbent developed by Goto (1992). But it is not always sufficient to take the high efficiency to remove mercury from crude condensate. This problem is believed that it may result from various species of mercury in the condensate. As mentioned above, some condensate contains not only elemental mercury but also ionic and organic mercury compounds. Thus, some study was carried out on the detail of activities of mercury compounds (Furuta, 1990). The result shows that one of the factors which can affect the process for mercury removal from liquid hydrocarbon is the chemical nature of each types of mercury compounds but it is not well established. Thus, this thesis will study on the removal of mercury compounds and the efficiency of adsorbents used.

Adsorbents used for removing of mercury from liquid hydrocarbon usually have a metal as active species

for adsorbing of mercury. From some observations, it is found that copper is frequently used for mercury removal. Copper halide was used for the removal of mercury (Takashi, Torihata, 1989). The CuO-ZnO/Al2O3 was used to adsorb mercury containing in hydrocarbon condensate (Yan, 1990). The role of Cu and Zn in mercury removal process was studied and compared with other metals (Takashi, 1989). However, there is no indication that what forms of mercury can be adsorbed by Cu-Zn/Al2O3. Since these adsorbents was prepared by different technique, its properties are also different. It is very difficult to compare the efficiency of these adsorbents. Good results should be obtained by matching with the adsorbent which is prepared by the same method. From the above reasons, this research concerns with the activity of adsorbents for mercury compounds removal and the composition of adsorbents, which is related to the metal content on support.

Accordingly, this research was conducted on the removal of mercury compounds by adsorption. The adsorbents are prepared by dry impregnation of neutral activated alumina with solution of copper nitrate and zinc nitrate. Mercuric chloride, phenylmercuric acetate and diphenylmercury are selected as model compounds. Toluene is used as liquid carrier because of its solubility.

Liquid feed and product in each experiment are digested with permanganate-persulfate solution in order to convert each type of mercury to ionic form. Quantity of ionic mercury is determined by using cold vapor

technique atomic absorption spectroscopy. Fresh adsorbents are digested according to ASTM D1977-91 in order to determine copper and zinc loaded on each adsorbent. Micromeritics ASAP 2000 is used to analyse total surface area, total pore volume and pore size distribution of each fresh and spent adsorbent.