

CHAPTER I

INTRODUCTION

Natural gas and crude oil that are produced in certain geological area of the world contain mercury in adequate quantities could cause a trouble to refineries or petrochemical plants as undesirable feedstocks. For example, hydrocarbon condensates derived from natural gas produced in region of Indonesia often contain over 1000 parts per billion by weight of mercury, while crude oils from the Austral Basin region of Argentina frequently contain well over 2000 parts per billion by weight of mercury (Frankiewicz *et al.*, 2003). In Thailand, mercury and mercury compound are found in natural gas and condensate as well. From the report of UNOCAL (Thailand), the ranges of mercury concentration in natural gas and condensate are 10 – 25 $\mu\text{g}/\text{m}^3$ and 500 – 800 $\mu\text{g}/\text{l}$ respectively (Chongprasith *et al.*, 2001).

Typically, mercury and its compounds are neurotoxins. Inhalation of mercury vapor, ingestion of ionic mercury or dermal absorption of mercury compounds ultimately results in neurological malfunction (Wilhelm *et al.*, 2000). Besides, in petroleum production aspect, the main reason for removing mercury from natural gas is to protect downstream aluminum heat exchangers, such as those used in cryogenic hydrocarbon recovery natural gas plants and in natural gas liquefaction plants. Mercury has caused numerous aluminum exchanger failures. It amalgamates with aluminum, resulting in a mechanical failure and gas leakage. Moreover, mercury can lead to severe poisoning of catalysts. For example, palladium based catalysts which are used for the selective hydrogenation of acetylenic species in steam cracker C_2 , C_3 , C_4 and other cuts can be deactivated, if there is the few parts per billion of mercury species being present in a condensate steam cracker feed.

Several institutes attempted to improve mercury removal technology. For example, Institut Français du Pétrole (IFP) from France invented the IFP RAM processes which consist of two important steps including the hydrogenation process and mercury removal process using adsorbent CMG 273 to remove mercury. In addition, Universal Oil Product (UOP), USA introduced HgSIV adsorbent which is molecular sieve products containing silver on the surface of zeolite. However,

organic mercury is more prevalent in hydrocarbon liquids. However, a basic understanding of the adsorption mechanism is still lacking, besides, the removal systems for mercury are not suitable for treating unconditioned hydrocarbons due to the fact that raw produced hydrocarbons contain numerous contaminations that interfere with the successful operation of the mercury removal systems. Nonetheless, various researchers has attempted to develop certain promising adsorbents such as activated carbon, wood char, several types of zeolite, etc. in order to increase mercury removal efficiency. In Thailand more recently, Rakrood, (2006) studied diphenylmercury removal by using Beta zeolite, Omega zeolite, L zeolite and commercial adsorbent CMG273 ($\text{CuS}/\text{Al}_2\text{O}_3$) as the adsorbents and n-heptane was chosen to be substituted condensate. From the experiment, Beta zeolite and Omega showed good diphenylmercury removal efficiency at the removal capacities of 90% and 60% for Beta zeolite and Omega zeolite, respectively. Besides, heavy naphtha spiked with diphenylmercury was also tested the diphenylmercury adsorption and the adsorption capacity of Beta zeolite and Omega zeolite decreased to 25% and 40%, respectively, indicating that the complexity of various hydrocarbons in heavy naphtha affects the adsorption capacity.

In this research work, adsorption of mercury and its compounds naturally formed in heavy naphtha, which was the real feed before entering mercury removal unit, was studied. The adsorbents including Beta zeolite with Si/Al ratios of 10, 30, and 100, X zeolite, Y zeolite and ZSM-5 zeolite were examined in batch system. Selected adsorbents were tested in a continuous system for their breakthrough curve. In order to understand the adsorption mechanism, the kinetic of adsorption and adsorption isotherm were also studied at the actual operating temperature, i.e. 50°C.