

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Mercury Compounds in Petroleum

Mercury is a common and naturally occurring component of petroleum. It has been known to be trace contaminant in natural gas and condensate for many years. It has been detected in well stream and also in solid waste.

Almost all of the mercury found in natural gas is in elemental form, but in condensate, mercury is almost in the colloidal form and slightly present in other forms: elemental, ionic, and organometallic. The concentration ranges of total mercury in condensate produced from Unocal Thailand's operations in the Gulf of Thailand since 1985 are generally 500 to 800  $\mu\text{g/L}$  (Pongsiri, 1999).

Mercury found in a wide range of petroleum. Types of mercury compounds depend on the source and type of petroleum. For example, distribution of mercury for Southeast Asia condensate is shown in Fig.2.1. The majority of mercury is found in the naphtha and kerosene fraction.

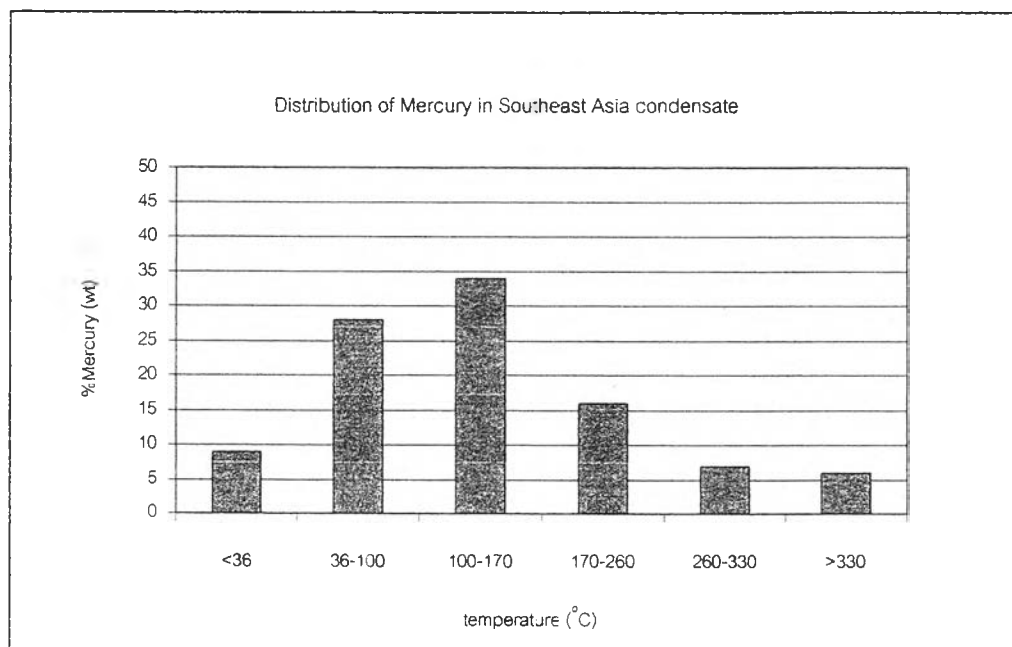


Figure 2.1 Distribution of mercury in Southeast Asia's natural gas condensate

## 2.2 Major effects of mercury on processing

After investigation, mercury has also been found to be the cause of severe catalyst poisoning leading to reduce lifetimes, equipment failure due to forming of an alloy between mercury compound and all metals, and healthy and safety risk concerning as the followings consideration.

### 2.2.1 Catalyst deactivation

One of the major problems related to the operation of heterogeneous catalysis is the catalyst loss of activity with time-on-stream, deactivation. Deactivation is inevitable, but it can be slowed or prevented and some of its consequences can be avoid.

Deactivation can occur by a number of different mechanisms. These are commonly divided into 4 classes, poisoning, coking, sintering, and phase transformation. The mercury compounds have caused the deactivation by poisoning. Poisoning is the loss of activity due to the strong chemisorption on the active site by impurity represent in the feed stream. The study of effect on hydrogenolysis of cyclopentane where Pt alumina was used as catalyst (Morales, 1979). The result showed that mercury as impurities can change the reaction rate constant and adsorption properties of Pt. In addition, Palladium-based catalysts are used for selective hydrogenation of acetylene in steam cracker  $C_2$ ,  $C_3$ ,  $C_4$  and others cuts. The few parts per billion mercury species which can be present in a very wide boiling range in a condensate steam cracker feed are concentrated into the light fractions of the cracker effluent. The catalysts deactivation is accompanied by a greatly reduced catalyst lifetime due to palladium sintering, which occurs when eliminating the mercury during catalyst regeneration (Cameron, 1996).

### 2.2.2 Equipment failure

Mercury can cause this problem by forming amalgams with a variety of metals, including aluminum, copper, brass, zinc, chromium, iron, and nickel. When these amalgams form with metal components of processing equipment, corrosion of the equipment results, because the amalgam is weaker than the mercury-free metal

(Leeper, 1980). In the past, mercury has been found to be responsible for the catalytic corrosion of cryogenic equipment at several sites. Amalgamation with aluminum tube of the low temperature heat exchangers greatly accelerates the attack of aluminum by trace amounts of liquid feed.

Many plants that process the petroleum without eliminating trace amounts of mercury have to early shutdown for process line maintenance. For example, aluminum alloys heat exchanger in cold box unit failed since the mercury compounds are adsorbed and formed the complex composition on the surface. The unit has been detected for removal of its surface so that the plant might have to shut down for maintenance. The first notice has been reported when Algerian condensate was used as a feedstock in Liquefied Natural Gas (LNG) Plant in 1985.

### 2.2.3 Health and safety risk

The considerations for health and safety of workers in petroleum processing involve exposure of workers to dermal absorption of mercury compounds. Mercury and its compounds have very high toxicity. Ingestion of ionic mercury or dermal absorption of mercury compounds results in neurological dysfunction. The period of time between exposure and exhibition of symptoms varies depending upon the type of mercury species and content of exposure.

Estimation of the potential risk to oil-field workers due to mercury compounds in petroleum liquids is uncertain because of the lack of data on protecting from those compounds.

## 2.3 Removal of Mercury

The removal of mercury has been investigated for many years. Many processes for removal of mercury compounds from petroleum have been developed. There are two methods currently used at present as the followings.

1. Chemical Treatment and
2. Adsorption

### 2.3.1 Chemical Treatment

Chemical treatment is a method that converts mercury compounds in petroleum to the form that is easy for elimination. The method uses chemical compounds such as alkali polysulfide to react with those mercury compounds. The reaction between mercury and sulfur compounds is shown below.



Mercuric sulfide (HgS) occurred is a solid material that cannot dissolve in liquid hydrocarbon and is easy to remove from feed stream by method of solid-liquid separation.

Yan (1990) proposed a method for removing mercury from natural gas condensate by contacting with a dilute aqueous solution of alkali metal sulfide salt and recovering the treated liquid hydrocarbon. The alkali metal sulfide salt used was  $\text{Na}_2\text{S}_x$ . The mercury content in the condensate was 220 ppb. The study was carried out by mixing the condensate with  $\text{Na}_2\text{S}_x$  and aqueous NaOH solution of varied concentration at temperature of  $75^\circ\text{C}$ . The result showed that the important factors in removing mercury from the condensate are intensity of mixing, concentration of  $\text{Na}_2\text{S}_x$ , volume ratio of caustic solution of  $\text{Na}_2\text{S}_x$  and efficiency of phase separation.

Audeh (1989) studied the removal of residual mercury in liquid hydrocarbon by mixing with aqueous polysulfide solution. The process was carried out at temperature of  $70^\circ\text{F}$  and used 0.5 ml of sodium polysulfide which contained 22.2 wt% of sulfur. The mercury in product was decreased to less than 0.01 ppb from initial concentration of 13 ppb.

Furuta et al. (1988) studied the effect of mercury compounds on mercury removal by using aqueous solution of sulfur compound. The sulfur compound was represent by a general formula  $\text{MM}'\text{S}_x$  where M is selected from a group consisting of alkali metal, ammonium radical, M' is selected from a group consisting of alkali metal, ammonium radical and hydrogen, and x is a number of at least 1. The mercury

compounds were elemental, mercuric chloride as inorganic and diethylmercury as organometallic. After shaking with 5 wt% of  $\text{Na}_2\text{S}_4$  solution for 10 minutes, it was found that only elemental and mercuric chloride were removed from liquid feed. Furthermore, after mixed with  $\text{Na}_2\text{S}_4$  solution, then, 0.5 wt% of  $\text{MoS}/\gamma\text{-Al}_2\text{O}_3$  containing 7% of Mo was added at temperature below  $200^\circ\text{C}$ . After treating, the liquid hydrocarbon phase was found to have mercury content of 6 ppb from initial concentration of 200 ppb. It was found that  $\text{MoS}/\gamma\text{-Al}_2\text{O}_3$  could also remove organometallic mercury from the liquid feed too.

Torihata and Kawashima (1989) used a cupric compound or stannous compound or both to remove mercury from hydrocarbon oils by contacting the cupric compound and/or stannous compound with the oil. The cupric compound and/or stannous compound used in this method may be in any suitable form such as a powder, an aqueous solution or an alcoholic solution.

### 2.3.2 Adsorption

Adsorption is an alternative method for removing of mercury. The adsorption method comprises contacting the liquid hydrocarbon with an adsorbent at various conditions, depending on type of adsorbent used. Mercury compounds are adsorbed and remain on surface of adsorbent. The treated liquid hydrocarbon is then readily free from mercury contamination. There are many studies about removal of mercury compounds by adsorption.

Chao (1984) proposed an adsorbent for mercury removal from toluene. The adsorbent comprised of metal sulfide such as iron, nickel, copper and cobalt on zeolite support. The results shown the comparison that adsorbent supported with iron sulfide had the better efficiency after treated the feed by stirred at  $110^\circ\text{C}$  for 3 hours.

Torihata (1988) studied the used of  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  for removal of mercury from a heavy condensate. The result shown that  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  supported on porous material such as activated carbon can remove mercury to concentration about 2.7 ppb from initial concentration of 130 ppb, corresponding to 97.9% Hg removal.

Torihata (1989) provided a study of mercury removal from LNG feed. The mercury compound in feed stream consisted of elemental, ionic and organometallic. The adsorbent used were in-group of iron, nickel and copper; by the form of metallic, metal oxide and metal sulfide, on alumina support. The treated feed had the final concentration depending on the higher temperature, the lower concentration.

Audeh (1989) used a hydrodesulfurization catalyst such as CoMo catalyst for removing mercury. Natural gas condensate contained 200 ppb of mercury was mixed with  $H_2S$  and the mixture was passed through the reactor. Stripping gas used was  $CH_4$  and the operating conditions was at 125 psig, 200-270 $^{\circ}C$ , flow rate 10 ml/hr. The treated condensate had mercury content below 10 ppb with 95% mercury removal.

Ou (1990) studied a method for removal of mercury from liquid hydrocarbon by using an adsorbent. The adsorbent was packed in a column and the mercury-contaminated hydrocarbon was passed through the column at temperatures ranging from about ambient to 100  $^{\circ}C$  and at pressures from ambient to about 300 psig. This method was directed to an effective way of removing elemental and ionic mercury from liquid hydrocarbon. The adsorbent used was reduced copper on zinc oxide and alumina that performed virtually removed all mercury in condensate feed. Another adsorbent used was reduced nickel on clay, which reduced 90% mercury of Algerian condensate containing 32 ppb of mercury.

Furuta (1990) proposed a method for removing mercury from a liquid hydrocarbon. The method comprised contacting the liquid hydrocarbon with adsorbent composing of multi-component metal sulfide supported on a carrier. The first metal component was molybdenum and second metal was selected from the group consisting of cobalt and nickel. It was found that the mercury in the form of elemental, ionic and organometallic could be adsorbed.

McNamara (1994) studied the use of reactant metal halide such as potassium, copper, iron, zinc, titanium, tin, gold, silver and chromium on activated carbon for removing mercury from liquid hydrocarbon. The results shown that there were two groups classified. One group called Reducing agent such as tin, titanium and copper, and the other called Amalgamating agent such as silver, zinc, tin, gold, copper and chromium. The latter caused bond between mercury compounds with them. The former can cause mercury compounds transforming into easier adsorbed compounds.

Courty (1995) provided an experiment for removing elemental mercury from condensate of liquefied gas. The adsorbent used composed with nickel polysulfide 1.96 wt% and molybdenum polysulfide 8 wt%. It was reported that the experiment could decrease concentration of mercury compounds from 1000 ppb to 10 ppb at condition temperature 40°C and pressure 30 bars.

Tantichaipakorn (1998) studied the removal of mercury compounds by adsorption on Ni-Cu adsorbent. His experiments were conducted at 30°C to 70°C and ambient pressure. Mercuric chloride was used as mercury compounds in ionic form. Diphenylmercury used as mercury compounds in organometallic forms. The results showed that removal of mercury was significantly dependent of temperature. In addition, it was also depended on the nature of mercury compounds types.

Furthermore, there were found some problems while operate the adsorption process. They were reported that mercury compounds could be adsorbed on a reactor wall produced with stainless-steel type 316. Yan (1991) reported that the stainless-steel reactor could adsorb mercury compounds to below 98%. Soontaranurak (1998) found that mercury compounds could be adsorbed on a reactor wall produced with stainless-steel type 316 while operated a hydrometallation reaction. It is found that stainless-steel type 316 composes with chromium, iron, nickel, molybdenum and manganese as major component.

## Literature summary

1. Mercury compounds in petroleum is in form of elemental, ionic and organometallic.
2. Mercury compounds in petroleum lead to several problems such as catalyst poisoning, equipment failure and healthy risk.
3. Methods for mercury removal are classified into two methods: chemical treatment and adsorption. Adsorption is the most widely used because of its high efficiency and convenient.
4. There are many adsorbents provided for removing of mercury such as molybdenum, iron, chromium, nickel and manganese.
5. From 4, said metal are found as composition in stainless steel 316 that can adsorb some mercury compounds on its surface.
6. In general, the operating conditions for mercury removal by adsorption depends on the adsorbent use, temperature and natural of each mercury compound.