

CHAPTER II



LITERATURE REVIEWS

Mercury occurs naturally in the environment in the form of mineral deposits and also from industrial and agricultural wastes. It can also be found in petroleum too.

The presence of mercury in natural gas has been detected in numerous fields for many years. It is generally in elemental form. In natural gas condensate, mercury is found in various forms: elemental, ionic and organometallic. Quantities and types of mercury depend on the source of the condensate. For example, concentrations and types of mercury containing in various natural gas condensates are shown in Table 2.1. The

Table 2.1 Concentration and types mercury (Yamada).

Sample	A	B	C	D	E
Hg Conc. (ppb)	100-400	20-40	5-15	2	1500-2000
Type of Mercury					
Elementary	○	○	△	×	○
Ionic	⊙	○	○	×	⊙
Organometallic	○	×	×	○	○
Hg concentration order:	⊙ > ○ > △ >> ×				

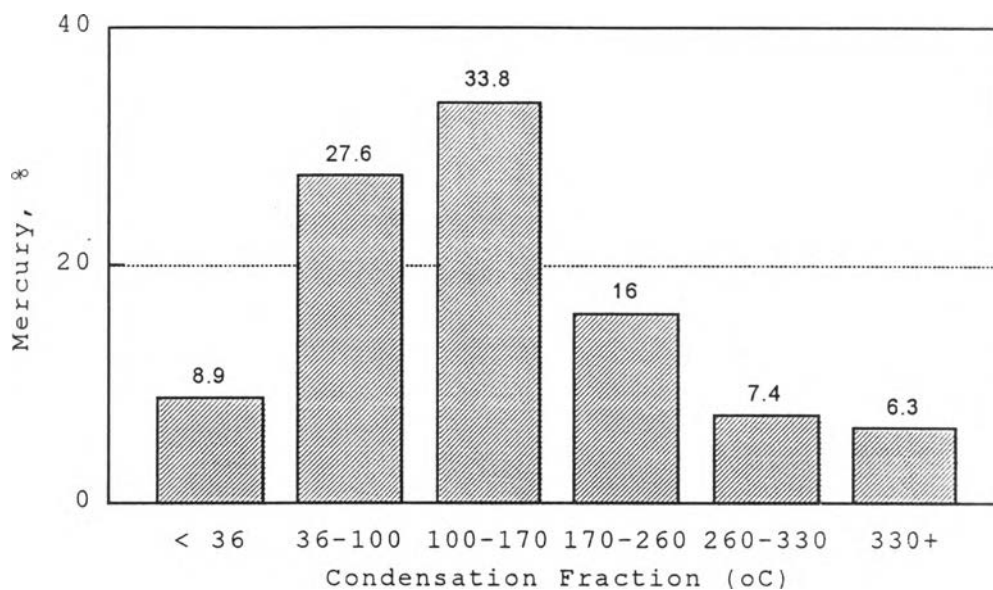


Figure 2.1 Distribution of Mercury in Indonesian Condensate

distribution of mercury for a Indonesian condensate is shown in Figure 2.1. For this condensate, the majority of mercury is found in the naphtha and kerosine fraction.

#### Catalyst Deactivation

Most catalysts used in catalytic processes may lose their activity or their selectivity when it is used for a long time. It is known in the term of "deactivation". The causes of catalyst deactivation may be divided into four groups: poisoning, fouling, sintering and loss of active species. Catalyst poisoning may result from an impurity containing in the feed. The impurity adsorbs on active sites of catalyst and reduces catalyst activities. Fouling is generally used to describe a physical block such as the deposit of dust or

coke. Sintering is an irreversible physical process leading to a reduction of catalyst activity. Finally, the active species may be converted to another form which is less active or selective. Deactivation of catalyst which is caused by mercury is grouped into the chemical poisoning.

An effect of mercury on catalysts was studied by many investigators. The study of effect of mercury on hydrogen adsorption on Pd was studied by Perepelitsa et al. (1979). They found that Hg inhibited the adsorption of hydrogen without changing significantly the bond energy and the ionization kinetics of the adsorbed hydrogen. The loss of adsorption capacity depended on structure of Pd. Morales et al. (1979) studied the poisoning effect on the hydrogenolysis of cyclopentane in which Pt alumina was used as catalyst. The result showed that  $\text{Hg}^{2+}$  changed the reaction rate constant and adsorption properties of Pt. The effect of Hg poisoning on Rh, Ru catalysts was studied by Grichina et al. (1991). It was found that the amount of adsorbed hydrogen on catalyst was decreased by Hg poisoning and the heat of adsorption was also decreased. They suggested that the Hg poisoning occurred by chemisorption and blockage of surface of catalyst. The study on Pd catalyst poisoning by Hg in the liquid phase hydrogenation of phenylacetylene was conducted by Sokolskii et al. (1981). The effect of Hg, pyridine and unithiol on the selectivity, reaction order and activation energy of PhCCH hydrogenation to PhEt on Pd/BaSO<sub>4</sub> was conducted at 293-323K and 1.51-8.08 MPa. In

this case, Hg was discussed only. Mercury had no appreciable effect on the selectivity but it decreased the activation energy.

#### Plant Corrosion by Mercury

Trace quantity of metallic mercury in natural gas can be a potential cause of problems in Liquefied Natural Gas (LNG) plant. The problems often take place in the presence of equipment constructed of aluminium. Mercury can form an amalgam with aluminium components causing stress fractures. Failures occurred at the LNG plant at Skikda, Algeria, from tube corrosion in the spiral wound exchangers (Leeper, 1980). Corroded tubes contained white deposits: aluminium oxide, aluminium hydroxide and aluminium carbonates, with traces of elemental mercury.

However, mercury-induced corrosion has resulted in plant shut-downs. For instance, an ethylene plant near Alvin, Texas experienced aluminium alloy piping failed (Hydrocarbon Asia). The presence of mercury in the ethylene plant was first noticed when Algerian condensate was used as a feedstock in early 1985. An inline strainer began to plug where mercury was detected.

#### Removal of Mercury

The removal of mercury has been investigated for many years. It was first studied for removal of elemental mercury from gaseous hydrocarbon. Leeper (1980) proposed corrosion of LNG plant caused by mercury

and also method for Hg removal. For example, natural gas contaminated with mercury is contacted with a fixed bed of metal sulfide on alumina-silica support. Another method comprises passing the gas over activated carbon impregnated with sulfur. However, the latter method is not suitable for treating liquids because solubility of the sulfur in hydrocarbon is rather low. Yan (1991) proposed the reaction of trace mercury in natural gas with polysulfide solution in a packed column. The residual Hg in the gas phase can be removed from about 0.1 to below 0.01 ppb. Polysulfide react with Hg in the gas phase to form insoluble mercuric sulfide, HgS, and thus remove Hg from the gas.

In addition to mercury present in natural gas, mercury is generally present in a wide range liquid hydrocarbon feedstock and in various forms, which contribute to the difficulty of its removal.

Elemental mercury is eliminated by using sulfur supported on solid material. Ionic or inorganic mercury can be removed by ion exchange or reduced to elemental Hg using a reducing reagent such as Sn(II). However, ion-exchange cannot remove elemental mercury. The removal of all Hg species from liquid hydrocarbon is more complicated because of organometallic compounds. Organometallic mercury cannot be removed by ion exchange because of the covalent nature of Hg-C bonds.

From the above reasons, many processes for removal of mercury from liquid hydrocarbon feedstocks

have been proposed. It can be classified into two methods: chemical treatment and adsorption.

### Chemical Treatment

Chemical treatment is a method which converts mercury in petroleum by reacting with some chemicals. The chemical used is usually a sulfur compounds, such as alkali polysulfide. The reaction between sulfur and mercury is shown below



The occurred mercuric sulfide, HgS, is a solid material which cannot dissolve in hydrocarbon and is removed easily from the feed stream. By this method, natural gas condensate is contacted with aqueous solution of sulfide in several different ways, both in batch-wise or continuous processes.

Yan (1988) proposed a method for removing mercury from natural gas condensate. The method comprise contacting the contaminated condensate with dilute aqueous solution of alkali metal sulfide salt,  $\text{Na}_2\text{S}_x$ . 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°C. After homogenization, the mixture was allowed to settle for 1-5 minutes. The result shows that the important variables 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. For example,  $\text{Na}_2\text{S}_x$  solution containing 2,000, 1,000, 500 and 100 ppm of sulfur, each containing 0.8wt% of NaOH were mixed with the condensate. The mercury concentration decreased correspondingly from 220 ppb to 66, 133, 77 and 110 ppm, respectively. The amount of mercury removed increases with an increase in sodium sulfide concentrations but it does not proportionally improve mercury removal. To study the effect of mixing intensity, the blender was set and connected to a power-stat which was varied from 20% to 100%. At 20 and 30% setting, the mercury content in product was decreased to 180 ppb. As the power setting was increased to 50 and 100%, the removal efficiency increased and the mercury concentration in the products decreased to 134 and 71 ppb, corresponding to 33 and 65% mercury removal. These results show the effect of mixing intensity for Hg removal. A residual mercury containing in liquid hydrocarbon was removed by mixing with aqueous polysulfide solution (Audeh, 1987). In this process, pentane containing 13 ppb of mercury was mixed with approximately 0.5 cc of sodium polysulfide which contained 22.2 wt% of sulfur. The process was carried out at ambient or room temperature of 70 °F. After treating, the mercury content in product was less than 0.01 ppb. However, the blank was tested by the same procedure except mixing the hydrocarbon with sulfide solution. It was found that mercury content did not change but remained at 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 represented by a general formula  $MM'S_x$  where M is selected from a group consisting of alkali metal and ammonia 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 three model liquid feeds were prepared by dissolving three types of mercury compounds in light naphtha. The mercury compounds were elemental, inorganic as mercuric chloride and organometallic as diethylmercury. After shaking with 5 wt% of  $Na_2S_4$  solution for 10 minutes, each liquid feed was detected for mercury content. It was found that only elemental and mercuric chloride were removed from liquid feed. Moreover, a model liquid containing 200 ppb of elemental Hg, 200 ppb of mercuric chloride and 200 ppb of diethylmercury was mixed with the  $Na_2S_4$  solution for 10 minutes. Then, 0.5 wt% of  $MoS/\gamma-Al_2O_3$  containing 7% of Mo was added and shaken for 60 minutes at temperature below  $200^\circ C$ . After treating, the liquid hydrocarbon phase was found to have Hg content of 6 ppb. It was found that  $MoS/\gamma-Al_2O_3$  can remove organometallic mercury from the liquid feed.

In addition to the use of  $MoS$ ,  $CoMo$  sulfide was used for Hg removal (Nakayama et al., 1989). Hg and Hg compounds in natural gas condensate were removed by treating the hydrocarbon with SH-contained organic compound such as Cysein and then extracting Hg with the sulfide solution,  $MM'S_x$  (Furuta, 1990).



There is an evidence that organic solvent can be used to extract mercury from hydrocarbon feedstock. The hydrocarbon oil was mixed with an organic peroxide and then the oil mixture was contacted with acidic inorganic substances or mixing with an aqueous solution of organic solvent. After that, the aqueous phase was extracted with activated carbon. (Arakawa, 1991).

### Adsorption

The removal of mercury by adsorption is an extractive method. It provides a high efficiency of Hg removal and does not contaminate with other chemical as described in previous method. The adsorption method comprises contacting the hydrocarbon with an adsorbent at various conditions, depending on type of adsorbent used. Mercury is adsorbed and remains in the adsorbent. Thus, the treated hydrocarbon is readily free from mercury contamination.

Literature survey was conducted to screen the removal of mercury by adsorption method. Koyama (1976) used an activated clay to remove Hg from waste oils. The oils contaminated with 350 ppm of mercury were stirred with activated clay at temperature of 80°C for 30 minutes. The mercury content was decreased to 2 ppm. Schnegula et al. (1985) proposed an adsorbent for Hg removal from gases and liquids. The adsorbent comprised a clay support which consists of activated C and sulfur as an active components. The 40wt% of activated C was mixed with 30wt% of clay and sulfur. Then the mixture of

activated C was kneaded with 20-30wt% of water. Alternatively, the clay was ground to 90% particles at below 0.04 mm. and then swelled in water to specific surface area of 500-700 m<sup>2</sup>/g (1985). During swelling, the clay undergoes cation exchange. In addition, an activated C adsorbent is used for removal of Hg from liquid hydrocarbons, i.e., naphtha (McNamara, 1989). The activated C was impregnated with a reactant metal halide such as K, Cu, Fe, and Zn or other reducing halides. The use of Cu<sup>2+</sup> and Sn<sup>2+</sup> was studied by Torihata (1988). The process comprises contacting hydrocarbon oil with a Cu<sup>2+</sup> and/or Sn<sup>2+</sup> in 3 ways:

- 1) liquid-liquid contact with a solution of Cu<sup>2+</sup> or Sn<sup>2+</sup> compound.
- 2) contact with a powder of Cu<sup>2+</sup> or Sn<sup>2+</sup> compound
- 3) contact with Cu<sup>2+</sup> or Sn<sup>2+</sup> supported on porous material such as alumina, silica-alumina.

The preferable metal compound was in a halide form, e.g., CuCl<sub>2</sub>, CuI<sub>2</sub>, SnCl<sub>3</sub> and SnI<sub>2</sub>. Heavy condensate was filtrated to remove sludge and a filtrate containing approximately 130 ppb of Hg. A powder of SnI<sub>2</sub> 1.0 g was added to the filtrate and the mixture was stirred for 1 hr. The Hg concentration of treated filtrate was 2.7 ppb, corresponding to 97.9% Hg removal. When 10 mL of 1% SnCl<sub>4</sub> solution was added, the Hg content was decreased to 79 ppb with 39.2% Hg removal. A 10 wt% of CuCl<sub>2</sub> supported

on activated carbon was used, mercury content was 2.9 ppb with 97.8% Hg removal.

Duisters et al. (1987) studied a process for removing mercury from organic media, e.g., natural gas condensate. The process comprises contacting the condensate with an ion exchange resin. The ion exchange resin used is a macroporous copolymer of styrene and divinylbenzene which contains active thiol groups, for example, IMAC TMR of Rohm & Hass Company. A natural gas condensate containing 35 ppb of mercury was passed in upflow direction through a glass column, which is packed with IMAC TMR ion exchange resin, at temperature of 25°C and a pressure of 1 bar. The condensate was passed through the column at flow rate of 500 g/hr. The effluent condensate was found to have mercury content of less than 1 ppb.

Stuewe et al. (1989) suggest a process for removing trace element, e.g., Hg, As and Pb, from hydrocarbons at temperature of -20 to 70°C. The adsorbent used was a polymer containing thioureido group, e.g., Lewatit TP 214, and polyaminomethyl styrene. The polymer had an average grain size of 0.3-1.3 mm. and available capacity of 1.3-2.0 equivalent/L. This polymer was treated with Na<sub>2</sub>S. A filter bed of the polymer was used to treat the hydrocarbon mixture at 1-25 bar, 10-40°C and LHSV of 1-10 hr<sup>-1</sup>. Arakawa (1991) used a fixed bed of cation exchange resins. A fixed bed of cation exchange resin was pretreated with the 5 wt% CuCl<sub>2</sub> aqueous solution at flow rate of 1 mL/min. Hydrocarbon oil containing 200

ppm  $\text{HgCl}_2$  was then passed through the treated resin at 3 to 5 mL/min and a temperature of 30 to 75°C.  $\text{HgCl}_2$  concentration decreased to below 10 ppm. Anion exchange resins loaded with sulfur ion were also used to remove mercury and its compounds (Arakawa, 1991). The anion exchange resins were packed in a column and treated with 5 wt% of  $\text{NH}_3\text{S}$  solution at flow rate of 1 mL/min. Hydrocarbon oil containing 400 ppm of Hg was passed through the S loaded column at temperature of 50°C and 3-5 mL/min. The Hg content was decreased to below 10 ppm.

Audeh used a hydrodesulfurization catalyst such as CoMo catalyst for removing mercury. There are three alternative ways:

- 1) mix elemental sulfur with the condensate and along with hydrogen stream, the condensate mixture was fed through a reactor containing the CoMo catalyst (Audeh, 1989),
- 2) the natural gas condensate was passed over CoMo catalyst in a reactor vessel and simultaneously the mixture of  $\text{CH}_4$  and  $\text{H}_2\text{S}$  were fed (Audeh, 1989),
- 3)  $\text{H}_2\text{S}$  was mixed with the condensate and the mixture was passed through the reactor, and stripping gas ( $\text{CH}_4$ ) was simultaneously passed over the catalyst (Audeh, 1989)

Natural gas condensate contained 200 ppb of mercury. The condensate or condensate mixtures was fed at a flow rate of 10 mL/hr, 125 psig and 200-270°C. It

was found that the treated condensate had mercury content below 10 ppb with 95% mercury removal.

Yan (1989) provided a method for Hg removal by high temperature reactive adsorption. Adsorbent mass included a reactive adsorbent such as Ag or CuS supported on alumina. First, an effect of temperature was studied by using CuS/Al<sub>2</sub>O<sub>3</sub> and at LHSV of 80 hr<sup>-1</sup>. The result indicated that Hg removal increased with temperature which was varied from 75-400°F. High temperature have been found to not only improve the adsorption rate but also increase the adsorption capacity. The effectiveness of different adsorbents was also studied. It was found that CuS/Al<sub>2</sub>O<sub>3</sub> and feed rate of 10 hr<sup>-1</sup> provided 98.6% mercury removal as initial mercury concentration was 220 ppb. While CuO/Al<sub>2</sub>O<sub>3</sub> and Ag/Al<sub>2</sub>O<sub>3</sub> decreased mercury content to below 20 ppb. Only Fe/Al<sub>2</sub>O<sub>3</sub> demonstrated inadequate adsorption capability.

Ou (1990) investigated a method for removal of mercury by using an adsorbent. This method was directed to an effective way of removing elemental and/or ionic mercury from liquid hydrocarbon. The adsorbents used were 1) reduced copper on zinc oxide and alumina and 2) reduced nickel on clay. The hydrocarbon feed was Algerian condensate containing 32 ppb of mercury. The results indicated that Ni adsorbent removed approximately 90% of mercury while Cu adsorbent virtually removed all mercury in the condensate.

Natural gas condensate was hydrorefined to remove mercury and optionally arsenic by contacting with 2

groups of catalysts (Roussel, 1988). First, catalyst contained Ni, Co, Fe and/or Pd was used at temperature of 130-250°C and pressure of 1-50 bar and H/catalyst volume ratio of (1-500):1. Second one was a Si- or S compound containing solvent was used to removal Hg at 0-175°C and 1-50 bar and space velocity of 1-50 hr<sup>-1</sup>. The refined product was found to have Hg content below 20 ppm and arsenic content below 1 ppm. Boitiaux et al. (1991) studied the removal of mercury and/or arsenic from feedstocks for solvent dearomatization. Feedstocks containing Hg and/or As and amounts of S were mixed with hydrogen and reacted with a mixture of metals selected from Ni, Co, Fe, Pd and Pt, >1 metal selected from Cr, Mo, W and U and a porous material to remove As. The resulting mixture was then contacted with a metal sulfide, i.e., Cu, Fe and Ag, to remove mercury.

### Literature Summary

1. Mercury in petroleum is in elementary, inorganic and organometallic forms
2. Mercury present in petroleum leads to catalyst poisoning, especially hydrogenation catalyst.
3. Methods for mercury removal are classified into two methods: chemical treatment and adsorption. Adsorption is the most widely used method because it provides high efficiency on mercury removal and more convenient.
4. Difference of mercury removal between gas and liquid phase may result from type of mercury in each phase.
5. Adsorbents used for removing mercury usually are transition metals supported on porous inorganic materials.  $\text{Cu/Al}_2\text{O}_3$  is preferred to use as adsorbent.
6. Operating condition for mercury removal in liquid depends on type adsorbent used.