

## CHAPTER II



### LITERATURE REVIEWS

This chapter is concerned with the literature reviews of arsenic and mercury. The literature are divided into two sections, mercury section and arsenic section, each section is arranged in to four parts. Part I deals with the chemistry of arsenic or mercury. Part II covers the characterization and identification of arsenic or mercury in petroleum. Part III deals with the problems when arsenic or mercury is found in petroleum. Finally Part IV deals with the study of removal of arsenic and mercury from hydrocarbons. And at the end of this chapter, literature summary is also defined.

#### 2.1 Mercury

Mercury is the third member of the II B group of element which all of the elements in this group loses two electrons to form dipositive ions. The Oxidation State of mercury is 1 and 2. Atomic number of mercury is 80 while atomic weight is 200.59. Mercury is capable of forming hundreds of compounds which its own properties. Mercury has a relatively high vapor pressure at ordinary temperature.

#### Mercury in Petroleum

Mercury is found in wide range of petroleum such as natural gas and crude oil. Mercury compounds are found in various forms: elemental, ionic and organometallic forms. Quantities and types of mercury compounds depend on the source and type of petroleum. For example, amounts of mercury in natural gas condensate were generally 10-3000 ppb (Sarrazin) and 0.5-10 ppb in crude oil (Yan 1990). Distribution of mercury for South East Asian condensate is

shown in Fig.2.1. Amounts of mercury in natural gas condensate of each boiling range of condensate fraction found in South-East Asian are different. For this particular condensate, the majority of mercury is found in the naphtha and kerosene fraction.

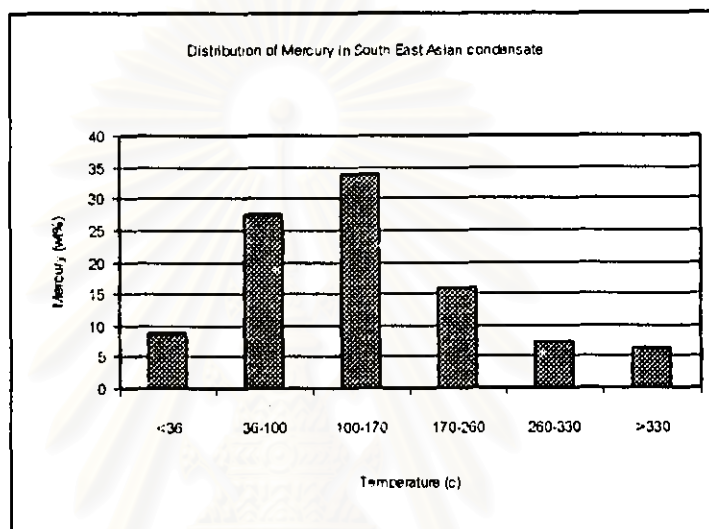


Figure 2.1 Distribution of mercury in natural gas condensate found in South East Asian.

### Catalyst Deactivation by Mercury Compounds

Catalyst used in catalytic processes such as catalytic hydrogenation is susceptible to mercury poisoning. Many investigators studied an effect of mercury on catalysts. For example

Perepelitsa et al. (1979) studied the effect of mercury on hydrogen adsorption on Pd. They found that mercury 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 cyclone on platinum alumna catalyst. The result showed that  $Hg^{2+}$  changed the reaction rate and adsorption properties of Pt.

### Mercury Corrosion

Trace quantity of metallic mercury in natural gas can be a potential cause of problems in Liquefied Natural Gas (LNG) plant. The problems often occurred with aluminum constructed equipment. Mercury can form an amalgam with aluminum component causing stress fractures. Equipment corrosion by mercury has resulted in plan shutdown, which required costly replacements and loss the production. From above mention, it is necessary to remove mercury before processing.

### Removal of Mercury

The method removal of mercury has been investigated for many years. Many processes for removal of mercury compound from hydrocarbon have been purposed. It can be classified into two methods

1. Chemical Treatment
2. Adsorption

### Chemical Treatment

Chemical treatment is a method that uses chemicals such as alkalipolysulfide to converts mercury compounds in petroleum to the form which easy to remove from petroleum. The reaction between mercury and sulfur compounds is shown below



Mercuric sulfide ( $HgS$ ) occurred is a solid material that cannot dissolve in hydrocarbon and is easy to remove from feed stream.

Yan (1990) proposed a method for removing mercury from natural gas condensate by contacting them with 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 shows 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.

Yan (1991) proposed the reaction of trace mercury in natural gas with polysulfide solution in a packed column. The residual mercury in the gas phase can be removed from about 0.1 to below 0.01 ppb. Polysulfide reacts with mercury in the gas phase to form insoluble mercuric sulfide,  $\text{HgS}$ , and thus remove mercury from gas.

Audeh (1989) studied the removal of residual mercury in liquid hydrocarbon by mixing the hydrocarbon with aqueous polysulfide solution. The process was carried out at temperature of  $70^\circ\text{F}$  and used 0.5 cc 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, inorganic as mercuric chloride and organometallic as diethylmercury. 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.

The disadvantage of chemical treatment method in removal of mercury is the contamination of product with the chemicals used.

### **Adsorption**

Adsorption is a high efficiency method for removing of mercury. The adsorption method comprises contacting the hydrocarbon with an adsorbent at various conditions, depending on type of adsorbent. Mercury is adsorbed and remains in adsorbent. Thus, the treated hydrocarbon is readily free from mercury contamination. There are many studies about removal of Hg by adsorption.

Leeper (1980) proposed corrosion of LNG plant caused by mercury and also method for removal of mercury. For example, natural gas contaminated with mercury is contacted with a fixed bed of metal sulfide on alumina-silica support.

Schnegula et al. (1985) proposed an adsorbent for mercury removal from gas and liquid. The adsorbent comprised a clay support that consists of activated Carbon and sulfur as an active component.

Koyama (1976) used activated clay to remove mercury from waste oil. The oil contaminated with 350 ppm of mercury was stirred with activated clay at temperature of  $80^\circ\text{C}$  for 30 minutes. The mercury content in waste oil was decrease to about 2 ppm.

Mcnamara (1989) studied the used of reactant metal halide such as K, Cu, Fe, and Zn on activated carbon for removal of mercury from liquid hydrocarbons.

Torihata (1988) studied the used of  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  for removal of mercury from heavy condensate. The results show 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.

Duisters et al. (1987) studied a process for removing mercury from 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 that contains active thiol groups. A natural gas condensate containing 35 ppb of mercury was found to have mercury content of less than 1 ppb.

Arakawa (1991) used a fixed bed of cation exchange resins. A fixed bed of cation exchange resin was pretreated with the 5 wt%  $\text{CuCl}_2$  aqueous solution. Hydrocarbon oil containing 200 ppm of  $\text{HgCl}_2$  was treated at temperature of 30 to 75°C. The remaining mercury was found to below 10 ppm.

Arakawa (1991) also used anion exchange resins in a packed column. The anion exchange resins was treated with 5-wt% of  $\text{NH}_2\text{S}$  solution. Hydrocarbon oil containing 400 ppm of mercury was passed through the column at temperature of 50°C. The result found that mercury was decreased to below 10 ppm.

Audeh (1989) used a hydrodesulfurization catalyst such as CoMo catalyst for removing mercury. Natural gas condensate contained 200 ppb of mercury was mixed with  $\text{H}_2\text{S}$  and the mixture was passed through the reactor. Stripping gas used was  $\text{CH}_4$  and the operating conditions was at 125 psig, 200–270°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 by using an adsorbent. 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.

Yan (1989) provided a method for mercury removal by high temperature reactive adsorption. Adsorbent used was Ag or CuS supported on alumina. The temperature used was in the range of 75–400°F. For initial mercury

concentration of 200 ppb the result showed that  $\text{CuS}/\text{Al}_2\text{O}_3$  provided 98.6% mercury removal while  $\text{CuO}/\text{Al}_2\text{O}_3$  and  $\text{Ag}/\text{Al}_2\text{O}_3$  decreased mercury content to below 20 ppb. It was found that high temperature not only improve the adsorption rate but also increase the adsorption capacity.

Noraphol (1995) studied the removal of mercury compounds by adsorption on Cu-Zn adsorbent. His experiments was conducted at  $30^\circ\text{C}$ - $75^\circ\text{C}$  and pressure of 200 psig. Mercuric chloride was used as mercury compounds in ionic form. Phenylmercuric acetate and diphenylmercury used as mercury compounds in organometallic forms. Experimental resulted showed that removal of mercury was significantly dependent on temperature but independent of pressure. In addition, it was also depended on the nature of mercury compounds types.

## 2.2 Arsenic

Arsenic is the third member of the nitrogen family of elements and hence possesses five electrons in the outer shell. Arsenic has atomic number of 33 and atomic weight of 74.9216. Arsenic properties are similar to phosphorus and antimony, with Oxidation State of +3, +5, 0 and -3. The element exists in several allotropic forms prefer a gray crystalline material which low heat and electrical conductivity. Arsenic melts at  $817^\circ\text{C}$  under pressure of 28 atm and sublimate at  $613^\circ\text{C}$  under normal pressure.

### Arsenic in Petroleum

Arsenic compounds are distributed throughout the boiling range of petroleum and usually found in crude oil and shale oil. Arsenic is typically found in the range of 0.111-0.236 ppm in petroleum (Fish and Brinckman) and 20-80 ppm for full range shale oil derived from Colorado oil shale. Arsenic compounds are found in various forms: elemental, ionic form and organometallic form.

### Catalyst Deactivation by Mercury Compounds

Many investigators studied an effect of arsenic on catalysts. For example Merryfield et al. (1984) studied the effect of arsenic on Co-Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in hydrodesulfurization. The result showed that 3.6% arsenic on catalyst almost completely deactivates the catalyst.

Hisamitsu et al. (1987) studied the effect of arsenic on hydrodenitrogenation reaction of shale oil on Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The result showed that adding 30 ppm of triphenylarsine significantly accelerated catalyst deactivation.

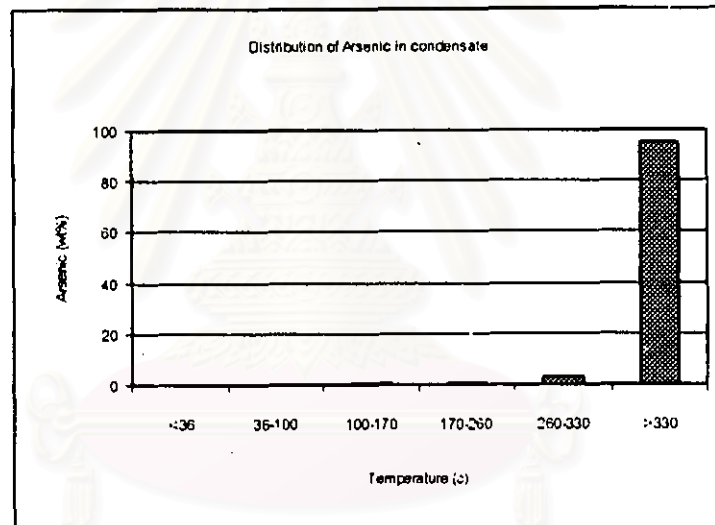


Figure 2.2 Distribution of arsenic compounds found in condensate.

### Removal of Arsenic

Methods of removal of arsenic were classified into three main methods

1. Thermal Treatment
2. Chemical Treatment
3. Adsorption



### Thermal Treatment

Thermal treatment is a method that has been developed initially for arsenic removal. This method is conducted by heating liquid hydrocarbon at the optimum temperature for a time to change the properties of arsenic. Thermal cause arsenic compounds to form solid or tarry material, which can be precipitated from liquid hydrocarbon. The precipitated can be removed buy physical separation.

Curtin (1977) investigated a method of removing arsenic contaminants from hydrocarbonaceous fluid such as synthetic crude oil or shale oil. The method comprised of heating shale oil to a temperature of 801<sup>o</sup>F for 27.7 minutes at pressure of 1,675 psi. Arsenic in shale oil would be convert to solid form and separated from shale oil by filtration or centrifuging. By this method arsenic in shale oil can be reduced to 2 ppm from initial contrition of 17.4 ppm.

Rhodes et al. (1985) purposed a method for removing arsenic from shale oil. This study was similar to Curtin's method except operated at reducing atmosphere. Shale oil was heated to a temperature about 250<sup>o</sup>C in hydrogen environment. After 15 minutes arsenic in shale oil changed to solid form and the concentration of arsenic in product is less than 1 ppm.

The problems of these process are low efficiency, take a long time, costly installing expensive filtration or centrifuging.

### Chemical Treatment

Chemical treatment is a method that convert arsenic in petroleum to the form which more water-extractable by using chemical substance. Water extraction or water leaching then separates the converted arsenic compounds.

Young (1977) used oil-soluble metals such as nickel naphthanate to remove arsenic from shale oil. Nickel naphthanate was blended with crude shale oil containing 50 ppm of arsenic. The mixture solution was pressurized with hydrogen at 110 psig and heated to the temperature of 650<sup>o</sup>F about 2-3 hours. The product had arsenic in water-soluble form of arsenic that existed as an

undissolved solid. The mixture was filtered and then analyzed for arsenic. It was found that the concentration of arsenic in product was decreased from 50 ppm to 15 ppm.

Albertson (1984) used elemental sulfur to removed arsenic from shale oil. The experiments carried out by blended 30 grams of elemental sulfur with 50 ml of raw shale oil and the mixture was hold at temperature of 150°F for 5 minuets. The product hydrocarbon contained 5.5 ppm of arsenic which represent 88.8% removal of arsenic.

Yakovleva (1987) used sodium hydroxide solution for leaching of arsenic from antimony dusts, which arsenic concentration about 5-10 ppm. After leaching with sodium hydroxide at temperature of 90°C for 30 minutes arsenic was removed more than 98%.

Arakawa (1988) studied the method of removing arsenic from petroleum fraction by contacting with iron ion. The petroleum fraction in this study preferred 4°C or lower hydrocarbon. Petroleum was contacted with 5% ferric nitrate solution at 25-100°C for 5-200 minutes. The arsenic content was decreased to below 10 ppm.

Chemical treatment can achieve high percentage of arsenic but the remaining concentration of arsenic is in the part per million (ppm) levels. Other disadvantage of this method is that chemicals used for removal of arsenic may contaminate or cause equipment corrosion.

### **Adsorption**

Adsorption is a high efficiency method for removing of arsenic. The adsorption method comprises contacting the hydrocarbon with an adsorbent at various conditions, depending on type of adsorbent used. Arsenic is adsorbed and remained in adsorbent. Thus, the treated hydrocarbon is readily free from arsenic contamination. There are many studies about removal of arsenic by adsorption.

Young (1977) used NiO-MoO/Al<sub>2</sub>O<sub>3</sub> as the catalytic adsorbent to remove arsenic in shale oil. The adsorbent was presulfided before operation. During the first 4 days of adsorption, which occurred at pressure of 200 psi and temperature of 650<sup>o</sup>F. Colorado crude shale oil containing 720 ppm of arsenic had arsenic concentration in product did not exceed 2.0 ppm.

Showa Electric Wire and Cable Co., Ltd. (1982) suggested that activated carbon could be used for removing arsenic from naphtha. Naphtha containing 206 ppb of arsenic was mixed with powder activated carbon at a 5 volume percent dosage. Thus, the arsenic content was decreased to 10 ppb.

Silverman (1985) studied the method for removal of arsenic from petroleum by contacting with quadrolobe alumina with or without hydrogen or nitrogen at temperature 500-800<sup>o</sup>F and at pressure of 250-750 psi. The results showed that the efficiencies of arsenic removal were in the range of 92.9-97.9%.

Child et al. (1986) suggested that the presence of nickel is the key to high dearsenation activity. The dearsenation reaction mechanism is not well understood, but the effectiveness of nickel containing catalysts in removing arsenic compounds presumably arises from the formation of stable nickel arsenide compounds such as NiAs<sub>2</sub>.

Ichikawa et al. (1988) used the catalyst to remove arsenic from heavy crude oil. The catalyst consisted of copper on alumina support and had 41wt% of copper. The pore volume and pore diameter was 0.141 ml/g and 40-300 Å, respectively. A naphtha containing 1000 ppb of arsenic (tributylarsine or hydrogen arsenide) was contacted with this catalyst in order to decrease arsenic content. Percent removed of arsenic was 98% comparing with initial concentration.

Nattawut (1995) studied the removal of arsenic compounds by adsorption on Ni-Mo adsorbent. The experiments were conducted at temperature of 30<sup>o</sup>C-75<sup>o</sup>C and pressure range of 200 psig to 600 psig. Phenylarsine oxide and arsenic oxide were used as representatives for typical organic and inorganic

compounds in petroleum. Results showed that the removal of arsenic compounds was independent of pressure but strongly dependent on temperature. Arsenic compounds was adsorbed on nickel phase and formed nickel arsenide ( $\text{NiAs}_2$ ) while the formation of molybdenum and arsenic could not be identified.

#### Literature summary

1. Arsenic in petroleum is in ionic and organometallic forms while mercury in petroleum is in elemental, ionic and organometallic forms.
2. Arsenic and mercury in petroleum leads to catalysts poisoning, especially hydrogenation catalysts.
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. Methods for arsenic removal are classified into three methods: thermal treatment, chemical treatment and adsorption. Adsorption is the most widely used method because it provides high efficiency on arsenic removal.
5. Both arsenic and mercury removal in the gas phase provide higher efficiency than in liquid phase. One of the factors concerns with different forms of arsenic in gas and liquid phase.
6. The study of effect of forms of arsenic and mercury compounds on the adsorption of arsenic and mercury is not clearly known.
7. There are many adsorbents used for removing both arsenic and mercury such as Mo, Ni, Cu, Zn, Pb or Fe. The Ni-Cu/ $\text{Al}_2\text{O}_3$  adsorbent is preferred.
8. The operating conditions for removing arsenic and mercury by adsorption in liquid phase depends on the adsorbent used. In general, the pressure range from 10-1000 psig, and the temperature interval  $30^\circ\text{C}$ - $200^\circ\text{C}$ .