CHAPTER II

Literature Reviews

2.1 Mercury Compounds

2.1.1 Forms and compounds (Lenihan and Fletcher, 1977)

Mercury compounds are found in various forms. From a toxicological and environmental point of view, the most useful and commonly accepted classification is

1. Metallic mercury, liquid and vapor

2. Inorganic salts, such as sulfides, chlorides, nitrates, and oxides

3. Alkyl compounds, such as those containing an ethyl or methyl radical

4. Alkoxyalkyl compounds, usually of complex nature

5. Aryl compounds particularly the phenylmercurials

2.1.2 Chemistry (Lenihan and Fletcher, 1977)

Mercury is the only metallic element in that it is liquid at ordinary temperatures. Its atomic number is 80 and its atomic weight is usually given as 200.59. Its valences are of 1 and 2. Mercury is capable of forming hundreds of compounds, each with its own chemical properties. Mercury readily forms alloys known as amalgams with practically all metals except iron. Dental fillings are essentially amalgams of mercury and silver. And the importance is that all mercury compounds are volatile usually decomposed to mercury. Mercury has a relatively high vapor pressure at ordinary temperatures. The rate of vaporization increases with increasing in temperature.

2.2 Mercury in Petroleum

Mercury is a metal compound found in wide range of petroleum such as natural gas, condensate and crude oils. Forms and quantities of mercury depend on the source and type of petroleum feedstock (Sarrazin, 1993). Mercury found

in natural gas is generally in metallic form and its concentration varies from 1 to 75 µg/normal m³ (Sarrazin, 1993). On the other hands, natural gas associated condensate is different from natural gas. The mercury which is found in the condensate is presented in various chemical states; elemental, ionic and organometallic (Yamada et al., 1995). The concentration ranges of mercury in natural gas condensate are generally 10-3,000 ppb (Sarrazin, 1993), 15-450 ppb (Yan, 1987). When natural gas condensate from the Gulf of Thailand was determined for the mercury content in the laboratory, it was found that it contained 300 ppb of mercury.

The distribution of mercury for South East Asian condensate is shown in Fig. 2.1. For this particular condensate, the large majority of mercury is found in the naphtha and kerosene fractions. The presence of mercury in natural gas condensates or crude oils can cause major problems such as corrosion and reduced catalyst life.
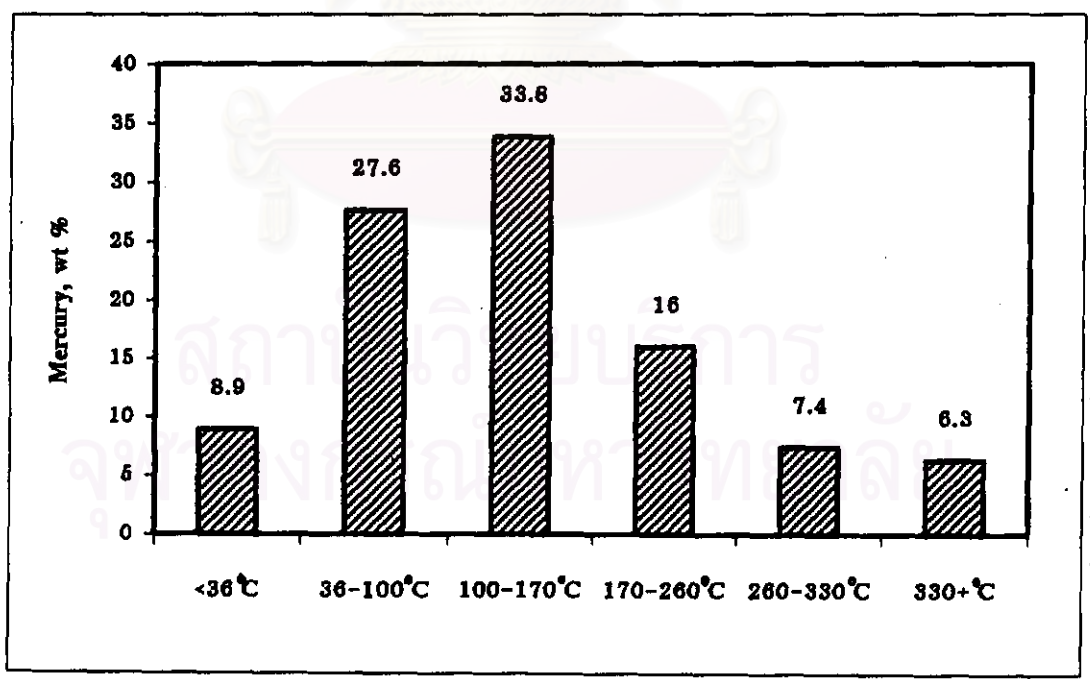

Figure 2.1 Distribution of mercury for South East Asian condensates (Sarrazin, 1993).

2.3 Disadvantages of Mercury Compounds in Petroleum

2.3.1 Mercury Corrosion

Equipment may be damaged because mercury accumulates in equipment constructed of various metals, especially aluminum, by forming an amalgam with the metal, for example, in the production of ethylene (Audeh, 1991). A natural gas condensate is commonly passed through a heat exchanger constructed of aluminum. It has been found that mercury tends to amalgamate with the aluminum and creates the risk of corrosion cracking. Recently, failures occur, at the LNG plant at Skikda, Algeria, from tube corrosion in the spiral wound exchangers. Corroded tubes contained white deposits: aluminum oxide, aluminum hydroxide and aluminum carbonates, with trace of elemental mercury (Leeper, 1980).

2.3.2 Catalyst deactivation

Catalytic process such as selective hydrogenation can be deactivated by mercury poisoning (Sarazin, 1993). Poisoning is catalyst deactivation due to the adsorption of some of the impurities in the feed stream, such as nitrogen, sulfur, oxygen, and metal. The poisoning deactivation by metal impurities can permanently deposit on the active sites of the catalyst and causes a loss of catalytic activity. Several researchers studied an effect of mercury on catalyst deactivation. Perepelitsa et al. (1979) studied the effect of mercury on hydrogen adsorption on Pd. 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. Grichina et al. (1991) studied the effect of Hg poisoning on Rh, Ru catalysts. They found that Hg poisoning decreased the amount of adsorbed hydrogen on catalyst and the heat of adsorption was also decreased. They suggested that the Hg poisoning occurred by chemisorption and blockage of the surface of catalyst. In addition, the poisoning of mercury on Pd catalyst in the liquid phase was studied by Sokolskii et al. (1982). They found that mercury had no appreciable effect on the selectivity but it decreased the activation

energy. Morales et al. (1979) studied the poisoning effect on the hydrogenolysis of cyclopentane in which Pt alumina was used as the catalyst. The result showed that Hg^{2+} changed the reaction rate constant and adsorption properties of Pt.

In addition, mercury compounds are extremely toxic with man and animals, especially organic compounds. They damage nervous system on inhalation or ingestion.

2.4 Study of Removal of Mercury Compounds from Petroleum

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

2.4.1 Chemical treatment

This method, mercury reacts with some chemical substance and converts to a mercuric compound such as mercuric sulfide that is insoluble in hydrocarbon and easy to remove from hydrocarbon feedstock. The chemical substance used is usually a sulfur compounds, such as alkali polysulfide. Polysulfide ions react with mercury to give HgS, according to

$$Hg + S_x^{2-} \rightarrow HgS + S_{x-1} \quad : \text{Where } X = 3\text{-}6$$

Several researchers proposed this method. Yan (1990) proposed a method to remove mercury from liquid hydrocarbons, such as natural gas condensate and crude oil, by contacting the hydrocarbon with dilute aqueous alkali solution of alkali metal sulfide salt, Na_2S_x and aqueous NaOH solution. Volume ratios of aqueous solution to hydrocarbon liquid preferably range from 0.1 to 10. Mixing and settling temperatures can be ranged from 50°F to 300°F. The residence time for the mixture react is 0.001 to 100 seconds depending upon the temperature and type of sulfur compound used. The result showed that 80% to 90% of mercury presented in heavy condensate could be removed.

In addition, Yan (1991) studied the removal of trace mercury in natural gas by scrubbing with dilute polysulfide solution. The residual mercury in the gas can be removed from about 0.1 to below 0.01 ppb, a reduction of 90%. In the system, the gas was contacted with stainless steel packing wetted with a solution containing about 3 ppm of polysulfide salt. The mercury in the gas reacts with the polysulfide to form insoluble mercuric sulfide and then it is removed from the gas. In addition, unexpectedly, the stainless steel packing alone, wetted with water, was found to be effective for removing mercury from gases.

Audeh (1989) proposed a process by firstly contacting the liquid condensate with a solution of an alkalipolysulfide and subsequently recovering a liquid hydrocarbon by separating into a hydrocarbon phase and aqueous phase. Then the two phases were separated. After treating, the mercury content decreased from 13 ppb to 0.01 ppb.

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 and may be supported on porous adsorbent such as activated clay, silica gel, zeolite, alumina etc.

2.4.2 Adsorption

The adsorption method comprises contacting the hydrocarbon with an adsorbent at various conditions, depending on type of adsorbent used. Many researchers proposed adsorbents for removal mercury from hydrocarbon.

Audeh (1991) proposed a process for removal of mercury from natural gas condensate by contacting natural gas condensate with elemental selenium in a reactor vessel. The operating condition, the pressure could be set from about 1 to 40 atm. The temperature could be ranged from about 15-217°C. The space

velocity kept below about 20. It could reduce the amount of mercury in condensate from above 1,100 ppb to below 20 ppb. Yan (1990) used a molecular sieve comprises 0.001-15% elemental silver or gold in or on zeolite A for removing mercury from hydrocarbon fluid.

Tan et al. (1996) proposed a method for removal of organic mercury compound from hydrocarbon fraction by heat treatment. High-temperature heat treatment was used to convert an organic mercury compound into an inorganic mercury compound or elemental mercury at a temperature about 200°C to 900°C. Then hydrocarbon fraction was contacted with an adsorbent in the form of active carbon having at least one of calcium and a calcium compound supported there on. The adsorbent was efficient to remove mercury and cost low capital on an industrial large scale, achieving an extremely low mercury concentration.

Torihata and Nishimura (1989) proposed the method for removing mercury from hydrocarbon. The process was heating hydrocarbon oil containing mercury compounds and then bringing hydrocarbon oil into contact with treating agent. The treating agent was activated carbon itself or activated carbon upon whose surface layer was supported one kind of metal selected from iron, nickel, copper, zinc, tin, aluminum and cadmium.

Ou (1990) used an adsorbent to remove mercury from liquid hydrocarbon. The adsorbent was packed in a column and the mercury-contaminated hydrocarbon was passed through the column at temperatures ranging from about ambient to about 100°C and at pressures from ambient to about 300 psig. The adsorbents used were 1) reduced copper on zinc oxide and alumina, 2) reduced nickel on clay. The hydrocarbon feed was Algerian condensate containing 32 ppb of mercury. The result indicated that Ni adsorbent removed approximately 90% of mercury while Cu adsorbent virtually removed all mercury in the condensate.

In addition, some methods combined between chemical reaction and adsorption. These methods may be known as chemisorption. This method may use the sulfur supported on the adsorbents, such as activated carbon and alumina. Mercury reacts with sulfur supported on the adsorbents and converts to a mercuric sulfide. Mercuric sulfide will deposit on adsorbent. Several methods have been proposed.

Denny et al. (1992) proposed a method for removing mercury from liquid or gaseous feed stream. This method comprises contacting mercury containing feed stream with an adsorbent comprising a metal sulfide. The suitable metals were iron and copper. Forming a precursor comprising a copper or iron compound and then contacting the precursor with gaseous stream containing sulfur compound prepared the presulfided adsorbent. The sulfur compounds were used to sulfide the precursor such as hydrogen sulfide, carbonyl sulfide, mercaptans and polysulfide. The mercury removal process is conducted at a temperature below 100°C and is preferably at temperature at 20°C.

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, inorganic and organic compounds could be adsorbed.

Yan (1996) developed a process for removing mercury compounds from oil by used high-temperature reactive adsorption. The process based on high-temperature chemisorption for selective adsorption of mercury and used a special CuS/C adsorbent, which is effective for removing most type of mercury compounds. In the process, the condensate from the stabilizer at 400-500°F and 220 psi was directly passed over the adsorbent at about 10 LHSV for mercury removal. Laboratory tests showed that the process was capable of

removing up to 99% of mercury. In addition, Yan (1989) proposed a process and compositions for removing elemental mercury vapor from a gas such as natural gas. The mercury-containing gas was contacted with a solid support such as carbon containing elemental sulfur and at least one metals which catalyzes the reaction

$$2Hg + S_2 \rightarrow 2HgS$$
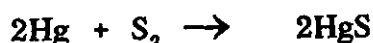
The elemental sulfur was deposited on the solid supported by using of a solvent, which distributes the sulfur in elemental form thereupon. The catalysts of the present invention were selected from the group of Ag, Au, Pd, Pt, Rh, Ir, Mn, Cr, and Mo. Pd and Pt were the most preferred catalysts. The demercuration process was carried out at a temperature below 170°F.

Audeh (1989) proposed a process for remove mercury from gas or liquid hydrocarbon stream. Hydrocarbon stream contaminated with mercury was contacted with a molecular sieve pretreated with an alkali polysulfide. The pretreatment consisted of saturating the sieve with an aqueous solution of the polysulfide and drying the treated molecular sieve to remove the moisture. Furthermore, Chao (1984) proposed a method for preparation of polysulfide containing adsorbent composition and a process for adsorption of mercury from gaseous or liquid stream by using polysulfide-containing adsorbent.

Yamada et al. (1995) studied the effect of mercury types and their reactivity to develop a mercury removal process applicable for natural gas condensates. Mercury compounds contained in natural gas condensate were classified in to three types; elementary, ionic, and organic by using the JGC's analysis method. Mercury compounds, especially organic mercury compound, could not be adsorbed on any types of agents. However, the organic mercury compounds could be easily decomposed and converted into elementary mercury by catalytic decomposition method with the catalyst. Therefore, the process for mercury removal composed of catalytic decomposition stage and adsorption stage.

The elementary mercury could be removed to less than 1 ppb with the adsorbent which a main component was metal sulfide. Experimental conditions were shown as follows.

Decomposition Stage

Catalyst	MR-13
Temperature	165-300°C
Pressure	2942 kPa

Adsorption Stage

Adsorbent	MR-3
Temperature	30°C
Pressure	Atmospheric pressure

Courty (1995) proposed a process for removing mercury and arsenic in hydrocarbons. This process used two reactors. In the first reactor, hydrocarbon containing 0.005-3% by weight of sulfur and mercury compound was reacted with hydrogen in the presence of a catalyst to active and convert mercury compound to material which will react with a mercury collection mass in a second reactor. The catalyst contained 0.05-5% by weight of at least one metal selected from the group consisting cobalt and 5-10% by weight of at least one metal selected from the group consisting molybdenum and tungsten. Besides, at least one of metal containing in catalyst was in sulfurized form. The effluent from first reactor was passed to a second reactor containing mercury collection mass that contained a sulfide of at least one metal selected from the group consisting of copper, iron, and silver and an active phase support. The process was conducted with an operating of 1-50 absolute bars, a hydrogen flow of 1-1000 liters of gaseous hydrogen at STP per liter of liquid charged, LHSV 0.1-30, an operating temperature of the catalyst of 180-450°C, and an operating temperature of the mercury collection mass of 0-400°C.

Audeh (1991) proposed the method, which comprise a process for removal of mercury from a natural gas condensate wherein hydrogen sulfide (H_2S) was

mixed into the natural gas condensate. Then this mixture was passed into a reactor containing a catalyst along with a stripping gas such as methane (CH_4). The catalyst may be any hydrodesulfurization (HDS) catalyst, for example, CoMo, NiMo, etc. During the experiment, mercury in the condensate reacts with the hydrogen sulfide according to the following formula

$$H_2S + Hg \rightarrow HgS + H_2$$

Then HgS deposit on the catalyst. This process preferably operates at the pressure of 3-10 atm, the temperature of 210-250°C, and the space velocity below 20. Suitable feed ratios of the condensate-hydrogen sulfide mixture comparing to the stripping gas was 1:600 to 1:750. This process could reduce the amount of mercury in natural gas condensate from above about 200 ppb to below about 20 ppb. In addition, hydrogen sulfide could pass into the reactor by containing in gas stream that gives the similar results. The mercury content in the natural gas condensate could be determined by conventional methods, such as ASTM method D-3223.
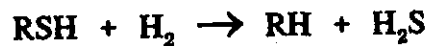
2.5 Hydrotreating

Hydrotreating is employed in industry for one of the following reason: (1) to improve the quality of the downstream product (2) to protect and improve the performance of catalyst used in downstream operations (3) to reduce the sulfur content of feed to meet environmental restriction and (4) to improve the stability of the product.

Hydrotreating consist of several classes of reactions, which occurs simultaneously (Gary and Handwerk, 1994, and Mcketta, 1977).
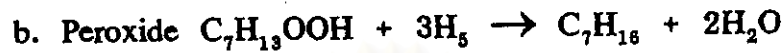
1. Hydrogenation (Saturation)

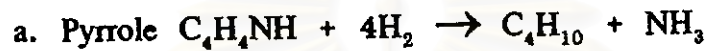$$C_6H_{10} + H_2 \rightarrow C_6H_{12}$$

2. Hydrodesulfurization (HDS)

$$RSH + H_2 \rightarrow RH + H_2S$$

3. Hydrodeoxygenation (HDO)

a. Phenol $\quad C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$

b. Peroxide $C_7H_{13}OOH + 3H_5 \rightarrow C_7H_{16} + 2H_2O$

4. Hydrodenitrogenation (HDN)

a. Pyrrole $C_4H_4NH + 4H_2 \rightarrow C_4H_{10} + NH_3$

b. Pyridine $C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$

5. Hydrodehalogenation

$$RCl + H_2 \rightarrow RH + HCl$$

6. Hydrocracking

$$C_{10}H_{22} + H_2 \rightarrow C_4H_{10} + C_6H_{14}$$

7. Hydrodemetallation (HDM)

$$R-M + Hydrogen + Catalyst \rightarrow M-Catalyst + RH$$
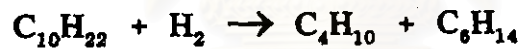
Hydrotreating catalysts consist of metals impregnated on a porous alumina support. The metals are dispersed in a thin layer over the entire alumina surface within the pores. This type of catalyst has a huge catalytic surface for a small weight of catalyst. Cobalt (Co), molybdenum (Mo), and nickel (Ni) are the most commonly used metals for hydrotreating catalysts. Cobalt molybdate catalyst has low activity in the oxide form, and obtains maximum activity when they must is sulfided. The sulfided cobalt molybdate catalysts promote most hydrogenation reactions. Cobalt-molybdenum catalysts are selective for sulfur removal and nickel-molybdenum catalysts are selective for nitrogen removal. However, both catalysts can remove both sulfur and nitrogen (Gary and

Handwerk, 1994). During catalytic hydrotreating, metal-bearing molecules presented in the feed diffuse into the catalyst pellet react at the active sites on the surface of the catalyst and deposit on the surface as coke and metal sulfides. This leads to a buildup of deposit on the surface of the catalyst, and the catalyst pores are filled with deposits. The accumulation of metal sulfide in the pore of catalyst is cause of irreversible deactivation (Pereira, 1989).

Typical ranges of process variables in hydrotreating operations are (Gary and Handwerk, 1994):

Temperature:	316-427°C
Pressure:	100-3,000 psig
Space velocity (LHSV)	1.5-8.0

2.5.1 Hydrodemetallation

Hydrodemetallation is a catalytic process for removing metal from hydrocarbon by using hydrogen contacting with an organometallic compound at the surface of the hydrodemetallation catalyst and producing a metal sulfide and hydrocarbon (Mcketta, 1977).

R-M + Hydrogen + Catalyst $\rightarrow$ M-Catalyst + RH

Different rates of reaction may occur with various types and concentrations of metallic compounds. The two main types of metal compounds in oil are the porphyrins and the asphaltenes. The form of porphyrin is closely related in structure to hemoglobin in mammalian blood and chlorophyll in green plants. The basic porphyrin has four 5 members' pyrole rings and four N atoms. The basic molecule weight of a porphyrin is about 300-600 with a diameter of 12-20 Angstroms. Asphaltene, which may be up to 400,000 in molecular weight, are more polar and aromatic than hydrocarbons and contain much of the heteroatoms S, N, O and metal (Wei, 1991).

The mechanism of hydrodemetallation of porphyrin is proceeds by a consecutive step through one or more hydrogenated intermediates (Agrawal, 1980)

Metal-porphyrin $\rightleftharpoons$ metal-chlorin $\longrightarrow$ metal deposition and ring breakup

The metal-porphyrin is first reversibly hydrogenated to form a metal-chlorin. The second step is irreversible hydrogenolysis of the ring, followed by deposition of metal on the catalyst. Several researchers studied the kinetic and mechanism of hydrodemetallation, as follow;

Reynolds (1991) proposed the model for hydrodemetallation of vanadium and nickel petroporphyrins. Figure 2.2 shows a generalized demetallation sequence for vanadium from many model compounds. In most studies, the hydrogenated intermediate 2 is detected followed by loss of metal. Some studies indicated hydrogenation occurs before demetallation (such as 3 and 4). Clearly in HDM, hydrogenation appears the critical step before metal loss. Hydrodemetallation of non-porphyrins has not been studied because the non-porphyrins have not been unequivocally identified.
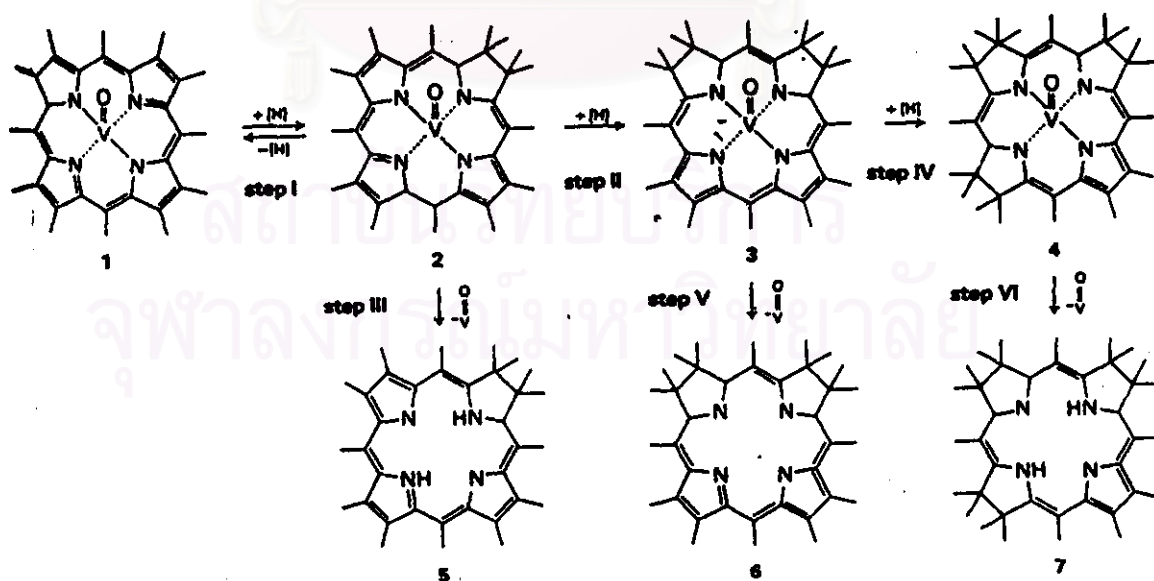

Figure 2.2   Mechanisms for HDM of vanadyl petroporphyrin from model substrate and industrial feed studies (Reynolds, 1991).

Bonne et al. (1995) studied the hydrodemetallation kinetics of nickel 5,10,15,20-tetraphenylporphyrin (Ni-TPP) at 613 K in the presence of sulfided Mo/Al_2O_3 catalysts. Hydrodemetallation of Ni-TPP proceeds through a reversible sequential mechanism: the hydrogenated intermediate compounds nickel 5,10,15,20-tetraphenylchlorin (Ni-TPC) and nickel 5,10,15,20-tetraphenylisobacteriochlorin (Ni-TPiB). A scheme for the HDM reaction of Ni-TPP is shown in Fig. 2.3. The mechanism of Ni-TPP HDM is only related to the porphyrin and independent on the catalyst applied or its chemical state. In the kinetic mechanism of Ni-TPP HDM, hydrogenation reactions are approximately first order in H_2 and independent on the H_2S concentration. The hydrogenolysis reaction is approximately second order in H_2 and has an approximately first order dependence with respect to the H_2S concentration. A two-site Langmuir-Hinshelwood model applies with small inhibition by H_2S. Hydrogenation occurs on one type of sites, which are consisted of sulfur vacancies associated with molybdenum. Hydrogenolysis occurs on another type of sites. H_2S promotes the hydrogenolysis step in the HDM of Ni-TPP.
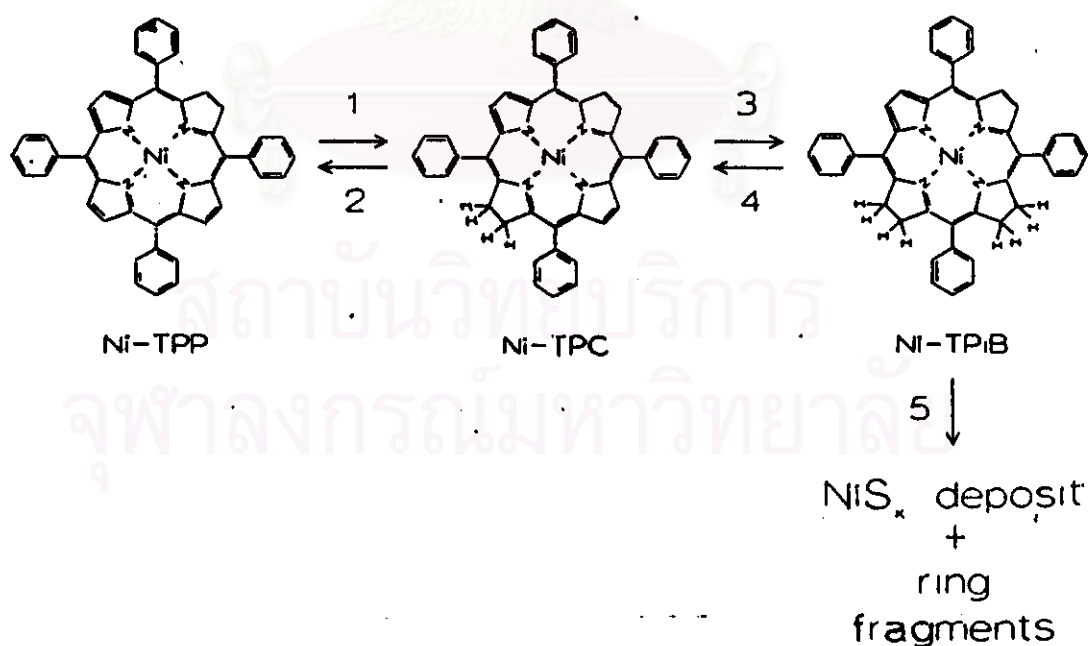

Figure 2.3   A scheme for the HDM reaction of Ni-TPP (Bonne et al., 1995).

Ware and Wei (1985) proposed a sequential mechanism for the hydrodemetallation of nickel porphyrin. The first process was hydrogenation of peripheral double bonds. The following process was the hydrogenolysis step, which resulted in breaking of the ring and removal of metal. They also concluded that the rate-limiting step was hydrogenolysis and ring opening.

Agrawal and Wei (1984) studied hydrodemetallation of nickel and vanadium etioporphyrin. Experiments were studied in high-pressure liquid-phase flow-reactor over $CoO-MoO_3/Al_2O_3$ catalyst. For both nickel and vanadium hydrodemetallation, the mechanism consists of three major kinetic steps. The first step is hydrogenation of metal porphyrin to the reaction intermediate metal chlorin with a first-order dependence on the metal etioporphyrin concentration in the solution and a first-order dependence on hydrogen pressure. The second reaction is the reversible dehydrogenation of the intermediate back to the metal etioporphyrins, which is first order to the intermediate concentrations in solution and zero order to hydrogen pressure. The third reaction is the irreversible hydrogenolysis of the intermediates concentration and demetallation, which is first order to the intermediate concentrations and second order to hydrogen pressure.

Chen and Massoth (1988) studied the kinetics of hydrodemetallation (HDM) of vanadium porphyrin (VP) and nickel porphyrin (NP) model compounds with sulfided $CoMo/Al_2O_3$ catalyst. These experiments were performed in a batch stirred autoclave at several temperatures, hydrogen pressures, and initial porphyrin conditions. The results showed that the HDM rate of vanadium (VP) and nickel (NP) porphyrin model compounds increases with temperature and hydrogen pressure but the effect of pressure was less pronounced at higher hydrogen pressure, indicating an approach to surface saturation of hydrogen. HDM rate was very low without catalyst or hydrogen. HDM kinetic follow pseudo first order above 350°C and lower order at lower temperature. A hydrogenated intermediate leading to deposit metal was found for both reactants.

Hung and Wei (1980) studied the kinetic of hydrodemetallation (HDM) of nickel ethioporphyrin (NiEtio), nickel tetraphenylporphyrin (Ni-TPP) and vanadyl etioporphyrin (Vo-Etio). These have been studied in batch autoclave experiments, with white oil as solvent and $CoO_3 - MoO_3/Al_2O_3$ as catalyst without presulfiding. The results for Ni-Etio and Ni-TPP showed that the kinetic data could be represented by fractional order kinetic and depended on temperature and pressure. For Vo-Etio the kinetic data can be represented by fractional order kinetic too. In comparison to nickel removal, vanadium removal has a larger activation energy and a smaller hydrogen pressure dependence.

Tamm, Harnsberger, and Bridge (1981) studied the deposition of nickel, vanadium, and iron compounds on and in the catalyst during hydroprocessing of residuum by Electron microprobe techniques. From the distributions of the deposited metal, the effects of process and catalyst variables indicate that removal of nickel and vanadium is diffusion controlled and removal of iron is reaction controlled. Based on these studies, two distinct mechanisms of catalyst deactivation by feed metals are proposed (1) poisoning of the active surface, (2) physical obstruction of the pore structure.

Several experiments suggested the operating condition and catalysts that were suitable for hydrodemetallation.

Kang et al. (1988) studied the effect of catalyst composition on the hydrodemetallation of atmospheric residue oil. The oil to be treated was atmospheric bottom (ATB) of Kuwait crude oil. The HDM activity tests were performed in a stirred one-liter semibatch type autoclave reactor with 20 g of presulfide catalyst and 400 g of ATB oil at 375°C, pressure 1500 psi, hydrogen flow rate 300 cm^3/min and basket spinning rate of 400 rpm. It was found that the NiMo catalysts exhibited a higher HDM activity than the CoMo catalyst.

Partridge et al (1994) proposed a process for treating heavy oil by contacting the oil with hydrogen in a reactor that contained an activated carbon hydrotreating catalyst. The hydrotreating catalyst compositions could also comprise molybdenum or tungsten component, and cobalt or nickel component. The activate carbon having an average pore diameter from about $100A^\circ$ to about $400A^\circ$ could increase demetallation capacity of the catalyst. Processing condition preferably include a temperature range of from about 600°F to about 1000°F, a pressure of from 500 to about 2500 psig, and WHSV of from about 0.2 to about 5 hr^{-1}.

Dai et al. (1994) proposed a process for hydrodemetallation of hydrocarbon feedstock such as residue, vacuum gas oil, etc. The process comprised contacting the feedstock with hydrogen and catalyst comprised about 1.0-6.0 wt% of an oxide of a Group VIII metal such as nickel or cobalt: about 12.0-25.0 wt% of an oxide of molybdenum, and 0-5 wt% of on oxide of phosphorus, base on the support alumina.

Wei and Zhao (1992) studied the deposition of nickel on hydrodemetallation catalyst $CoMo/Al_2O_3$. Operating conditions for the hydrodemetallation experiment ranged from 588 K to 623 K at hydrogen pressure of 4.8 MPa and hydrogen sulfide partial pressure at about 14 kPa (0.3 vol%). It can be concluded that nickel deposits on hydrodemetallation catalyst are in crystallite form.

Absi-Halabi et al. (1995) studied the relation between catalyst activity, deactivation and pore size distribution in hydroprocessing of vacuum residues. They used four catalysts with different unimodal and bimodal pore size distribution. The performance of the catalyst was examined by using Kuwait vacuum residue as feedstock under the following conditions, pressure 12 MPa, LHSV 2 hr^{-1}, H_2/oil 1000 ml/ml, temperature 440°C. The result showed that the effect of catalyst pore size was significant for different reactions. For HDM

and HDN reaction, large-pore catalysts having a major proportion of the pore volume in 100-300 nm pore were more effective.

Dejonghe et al. (1990) studied the deposition of vanadium on Mo-based HDM catalysts. They found that vanadium deposited in vanadium sulfide form and may replace Ni in the NIMoS phase.

Mohammed et al. (1985) studied the effect of temperature and space velocity by using Bai-Hassan reduced crude, which constitute about 49.5 wt% of the original crude oil. It was carried on a commercial NiMo/alumina catalyst in a trickle-bed reactor. The reaction temperature varied from 320 to 420°C with liquid hourly space velocity (LHSV) ranging from 0.37 to 2.6 h^{-1}. Hydrogen pressure was kept constant throughout the experiments at 6.1 MPa, with hydrogen oil ratio of 300 normal litters/liters feed. Nickel and vanadium levels were determined. It was found that in the low temperature region, (<360°C) the removal of nickel was greater than that of vanadium. However, as the temperature increased (>380°C) and low LHSV, nickel were more difficult to remove than vanadium. And removal of metal decreased when LHSV increased.

Bhan et al. (1986) proposed the method for upgrading the used lubricating oil. They used a high surface alumina (gamma type) in the guard-bed to remove metal contaminant before hydrotreating. At temperature below 275°C, the metal removal activity of the guard beds reduced drastically. Higher operating temperature resulted in higher metal removal activity, but also caused the large molecular weight species to thermal crack. The optimum temperature for operating the guard-bed reactors was in the range 290-300°C. At this temperature, all metal and phosphorus were removed.

In addition, the chemical forms of the metals in the feed are a very important determinant in the metals deposition process and in the potential effects on catalyst activity.

Silbernagel and Riley (1980) proposed the research by determining how the chemical form of the metals in the feed influenced the desulfurization and metal deposition processes. The hydrodesulfurization tests were carried out with three feed stocks: (1) a whole Venezuelar crude (2) its deasphalted oil (DAO) and (3) a whole crude oil after a hydrofluoric acid (HF) treatment. Vanadium in deasphalted component occurs almost exclusively as vanadyl porphyrin. Whole crude oil after a hydrofluoric acid treatment resulted that some vanadium remains in a vanadyl form but not vanadyl porphyrin. Porphyrin species can be removed by this treating. The demetallization process is also different. Under identical operating condition, the metal from the DAO are removed 90%, from the whole crude 60%, and 25% from the HF treated feed. Besides, the metal distributions along the reactor length showed that the chemical form of the metals in the feed is a very important in the metals deposition process. Furthermore, all of the vanadium deposited on the catalyst appears as a Va^{2+} form.

Literature Summary

1. Mercury in petroleum is in elementary, inorganic and organometallic forms.

2. Mercury presenting in petroleum can cause major problems such as catalyst poisoning, corrosion, and pollution of environment.

3. Methods for mercury removal are classified into two groups: chemical reaction and adsorption. In some cases, these methods are not always sufficient to take the high performance to remove mercury from heavy and dirty hydrocarbons such as crude condensate that has the complex organometallic compounds. Thus some methods combined between chemical treatment and adsorption was applied to remove mercury.

4. Hydrodemetallation is the method that has the high efficiency to remove organometallic compounds from liquid hydrocarbon.

5. $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ is commonly used metal as hydrotreating catalysts.

6. Suitable operating conditions for mercury removal by hydrodemetallation are at the temperature range from 120-250°C, at pressure 3-10 atm, LHSV below 20, and the feed ratios of the condensate-hydrogen sulfide mixture comparing to the hydrogen gas is 1:600 to 1:750.