CHAPTER II

LITERATURE SURVEY

2.1 Properties of Mercury and Mercury Compounds

The common physical properties of elemental mercury are listed in Table 2.1. Elemental mercury is a liquid at ambient conditions. Its melting point and boiling point are -38.87 °C and of 357 °C, respectively. Elemental mercury is quite dense (13.5 times more than liquid water under ambient conditions). The high density, the low saturation vapor pressure and high surface tension control the behavior of elemental mercury in solid, liquid and gaseous matrices.

Table 2.1 Physical properties of elemental mercury (Wilhem and Bloom, 2000)

Atomic number	80
Atomic weight	200.59 atomic mass units
Boiling point	367 °C
Boiling point/rise in pressure	0.0746 °C·torr^{-1}
Density	13.546 g·cm^{-3} at 20 °C
Diffusivity (in air)	0.112 cm^2·sec^{-1}
Heat capacity	0.0332 cal·g^{-1} at 20 °C
Henry's law constant	0.0114 atm m^2·mol^{-1}
Interfacial tension (Hg/H$_2$O)	375 dyne·cm^{-1} at 20 °C
Melting point	-38.87 °C
Saturation vapor pressure	0.16 N·m^{-3} at 20 °C
Surface tension (in air)	436 dyne·cm^{-1} at 20 °C
Vaporization rate (in air)	0.007 mg·cm^{-2}·hr^{-1} for 10.5 cm^2 droplet at 20 °C

Mercury occurs in nature as the zero (elemental), +1(mercury[I] or mercurous), and the +2 (mercury[II] or mercuric) valence states. Mercurous compounds usually involve Hg-Hg bonds and generally unstable and rare in nature.

Mercury occurs most prevalently in the elemental form. Common mercuric compounds include mercuric oxide, mercuric chloride, mercuric sulfide and mercuric hydroxide. Organic mercury forms also exist and consist of two main groups: R-Hg-X compounds and R-Hg-R compounds, where R = organic species, of which methyl

(-CH₃) is prominent, and X = inorganic anions, such as chloride, nitrate or hydroxide. The R-Hg-X groups includes monomethylmercury compounds. The most prominent R-Hg-R compound is dimethylmercury.

Mercury is difficult to oxidise in natural environment and spilled mercury (in soil for instance) retains the elemental form. Mercury can be oxidised by the stronger oxidants including hydrogen peroxide and nitric acid. Mercury can be oxidized and methylated in sediments by sulfate-reducing bacteria.

2.2 Mercury in Hydrocarbons (Wilhelm, 2001b)

Elemental mercury and mercury compounds occur naturally in geologic hydrocarbons including coal, natural gas, gas condensates and crude oil. Table 2.2 provides a listing of the mercury species that have been detected and their relative abundance in hydrocarbon matrices (Wilhelm and Bloom, 2000), since analytical speciation techniques do not exist for all of the matrice (especially coal), considerable uncertainty exists for the relative abundance of some species.

The term gas condensate refers to liquids that originate at several locations in a gas processing scheme. An unprocessed condensate (the condensate that directly obtained at the gas well) is the hydrocarbon liquid that separates in the primary separator, either at the wellhead or at the entering of the gas plant. Processed condensate (fractionated condensate) is the C5+ fraction that is a product from a gas separation plant. Naphthas typically originate from the primary distillation of oil in the range of 50 to 150°C. The distribution of hydrocarbon compounds in both condensates and naphtha are similar and mostly in the range C5 to C10. Processed condensate and naphthas typically do not contain suspended mercury compounds while unprocessed condensate can contain some amount.

In natural gas, mercury exists almost exclusively in its elemental form and at concentrations far below saturation suggesting that no liquid mercury phase exists in most reservoirs. The prevalence of dialkylmercury in natural gas is largely unknown but thought to be low (less than 1 percent of total) based on the limited speciation data reported in the literature for gas condensates. Organic mercury

compounds in produced gas would be expected to partition to separated hydrocarbon liquids as the gas is cooled. Therefore, if dialkylmercury is present in the reservoir, it would be found mostly in condensate, less so in gas, in those situations where hydrocarbon liquids separate due to natural cooling. Likewise in gas processing, little organic mercury would be expected in sales gas due its partition to liquid streams.

Table 2.2 Approximate natural abundance of mercury compounds in hydrocarbons (Wilhem and Bloom, 2000)

	Coal	Natural gas	Gas condensate	Crude oil
Hg°	trace	dominant	dominant	dominant
$(CH_3)_2Hg$	not reported	trace	trace, (some)	trace, (some)
$HgCl_2$	some	not reported	some	some
HgS	dominant	not reported	suspended	suspended
HgO	trace	not reported	not reported	not reported
CH_3HgCl	not reported	not reported	trace	trace

Crude oil and gas condensate can contain several chemical forms of mercury, which differ in their chemical and physical properties.

1. Dissolved elemental mercury (Hg°) – Elemental mercury is soluble in crude oil and hydrocarbon liquids in atomic form to a few ppm. Elemental mercury is adsorptive and adsorbs on metallic components (pipes and vessels), suspended wax, sand and another suspended solid materials in liquids. The measured concentration of dissolved elemental mercury typically decreases with distance from the wellhead due to adsorption, reaction with iron, conversion to other forms and loss of the suspended fraction.

2. Dissolved organic mercury (RHgR and RHgX, where R = CH_3, C_2H_5, etc. and X = Cl^- or other inorganic anions) – Dissolved organic mercury compounds are highly soluble in crude oil and gas condensate. Organic mercury compounds are similar to elemental mercury in adsorptive tendencies but differ in their boiling

points and solubilities and thus they partition to distillation fractions in a different fashion from Hg. This category includes dialkylmercury (i.e., dimethylmercury, diethylmercury) and monomethylmercury halides (or other inorganic ions).

3. Inorganic (ionic) mercury salts ($Hg^{2+}X$ or $Hg^{2+}X_2$, where X is an inorganic ion) – Mercury salts (mostly halides) are soluble in oil and gas condensate but preferentially partition to the water phase in primary separations. Mercuric chlorides have a reasonably high solubility in organic liquids (about 10 times more than elemental mercury). Ionic salts also may physically suspend in oil or may attach (adsorbed) to suspended particles.

4. Complex mercury (HgX of HgK) – Mercury can exist in hydrocarbons as a complex, where K is a ligand such as organic acid, porphyrin or thiol. The existence of such compounds in produced hydrocarbons is a matter of speculation at present depending in large part on the particular chemistry of the hydrocarbon fluid.

5. Suspended mercury compounds – The most common examples are mercuric sulfide (HgS) and selenide (HgSe), which are insoluble in water and oil but may be present as suspended solid particles of very small particle size.

6. Suspended adsorbed mercury - This category includes elemental and organic mercury that is not dissolved but rather adsorbed on inert particles such as sand or wax. Suspended mercury and suspended mercury compounds can be separated from liquid feed to the plant by physical separation techniques such as filtration or centrifugation.

Gas and liquid processing can cause transformation of one chemical form of mercury to another. A common example is the reaction of elemental mercury with sulfur compounds. The mixing of gas and/or condensate from sour and sweet wells allows reaction of elemental mercury with S_8 or ionic mercury with H_2S to form particulate HgS that can settle out in tanks and deposit in equipment.

The partitioning of mercury into product and effluent streams in petroleum processing is largely determined by solubility. Table 2.3 (provides the approximate solubility of the common species in several liquid matrices.

Crude oil and gas condensate, when sampled soon after primary separation of water and gas, can contain significant amounts of suspended mercury compounds and or mercury adsorbed on suspended solids. The suspended compounds usually are

mostly HgS but include other mercury species adsorbed on silicates and other suspended colloidal material. The amount of suspended mercury can be a substantial percentage of the total concentration of mercury in liquid samples of produced hydrocarbons and they must be separated (filtered) prior to any analytical speciation of dissolved forms.

Table 2.3 Approximate solubility of mercury compounds in liquids; 25 °C (Wilhem, 2001b)

Species	Water (ppm)	Oil (ppm)	Glycol (ppm)
Hg	0.05	2	<1
XHgX	?	miscible	>1
$HgCl_2$	70,000	>10	>50
HgS	0.01	<0.01	<0.01
HgO	50	low	not reported
CH_3HgCl	>10,000	1,000	>1,000

2.3 Mercury in Crude Oil and Condensate

The data for total mercury concentrations in crude oil and gas condensates are compiled in Table 2.4. Condensates can be refined or used as feeds to petrochemical manufacture. The data that appear in the literature reflect the fact that mercury is problematic to petrochemical processes when concentrations exceed a few parts per billion. Thus it is not likely that the data in Table 2.4 are representative of gas field condensates as a whole. One might surmise, however, that condensates may have a higher average THg than crude oils.

Table 2.4 Total Hg in crude oil and gas condensates (Wilhelm, 2001a)

type	no.of samples	range (ppb)	THg mean (ppb)	notes
crude oil	7	0.1-12	3	Libyan
crude oil	2	2.4-5.7	4.3	Middle East
crude oil	7	1.0-3.2	1.7	Africa
crude oil	1	1.9	1.9	Canada
crude oil	4	2.5-9.3	5.0	North Sea
crude oil	6	0.8-12.3	5.2	South America
condensate	4	not reported	15	not reported
condensate	18	not reported	3964	not reported
condensate	8	not reported	20	not reported
condensate	10	not reported	7113	not reported
condensate	5	9-63	30	SE Asia
condensate	7	15-173	40	Asian

As for Thailand, that is also currently producing natural gas and condensate averaging 2,163 MMSCFD of natural gas, and 68,390 BBLD of condensate in 2004 (Ministry of Energy, 2005). The presence of Hg is also reported.

From the offshore platforms in the Gulf of Thailand, mercury has been found in natural gas, condensate, produced water and condensate sludge obtained from tank cleaning in the condensate floating storage unit. The range of mercury concentrations in the gas, condensate and produced water, is presented in Table 2.5 . Some gas is flared off at the central process platforms, which allows some mercury to enter the atmosphere.

Table 2.5 Mercury found in Thailand (Chongprasith *et al.*, 2001)

Source	Range of mercury
natural gas	10-25 $\mu g/m^3$
condensate	500-800 $\mu g/l$
produced water	30-800 $\mu g/l$

2.4 Effects of Mercury on Processing

Wilhelm (1999) has summarized that mercury has several detrimental impacts on gas and liquid processing operations.

2.4.1 Effects of Mercury on Gaseous Processing

- Mercury deposits in cryogenic equipment, sometimes causing cracking of welded aluminum heat exchangers.

- Mercury that distributes in gas plant products – organic mercury partitions to liquid fractions and elemental mercury equilibrates to both liquid and gas – reduces the quality and affects downstream processes. Gas plant products used for chemical manufacture, especially olefins, ethylene, aromatics and MTBE, are at risk to mercury in process feeds due to cited equipment problems and due to catalyst poisoning.

- Mercury contaminates treatment processes such as molecular sieve and glycol dehydration unit, and amine acid gas removal systems.

2.4.2 Effects of Mercury on Liquid Processing

- Contaminated treatment liquids and spent mol-sieve adsorbents from the treatment processes are difficult to dispose off and to regenerate.

- Sludge containing mercury from water treatment systems, separators, desalters, and heat exchangers represents a toxic waste stream that is difficult to store or process for disposal.

- Waste water streams that contain high levels of mercury must be treated to remove mercury prior to discharge thus adding significant costs to plant operational expense.

- Mercury deposition in equipment poses a health and safety risk for workers involved in maintenance or inspection activities.

However, the best way to limit the amount of mercury entering the system is by limiting the amount of high mercury condensates being processed. Thus, the preferred location to install mercury removal unit is before the hydrocarbon streams entering the plant.

Presently methods to remove mercury from crude oil are not commercially practiced but technologies are under development, reportedly. For products like naphtha and LPG, fixed-bed sorbents are commercially available and effective. Outlet concentrations less than 1 ppb are possible using a variety of regenerative and non-regenerative technologies. Successful application of sorbents may require analytical speciation in some instances and/or removal of particulates depending where in the refining process mercury removal is attempted. For clean and dry light product streams, applications are straight-forward. Mercury removal is not applied to middle distillates (jet fuel, kerosene and gasoline), mostly because it is not needed

2.5 Mercury Removal Technology (Wilhem, 1999)

Mercury removal sorbent beds are used to scavenge mercury from gas and liquid hydrocarbon stream. The adsorbents are granular or palletized material consisting of a substrate support (zeolite, activated carbon, metal oxide or alumina) and a reactive component (Ag, KI, CuS, metal sulfide, etc.) that is bonded to the support. Strictly speaking, sorbents are more correctly described as chemisorbents because they function by reacting mercury (or a mercury compound) to a chemical form (HgS, HgI_2 or amalgam) that is insoluble in hydrocarbon liquid and chemically inert to a process stream.

Several commercial processes are available for removing mercury and mercury compounds from hydrocarbons. Some commercial mercury removal systems are targeted at gas phase treatment and some are targeted at liquids. In gas phase treatment (Table 2.6), the systems primarily consist of sulfur-impregnated carbon, metal sulfide on carbon or alumina, and regenerative molecular sieve (Ag on zeolite).

In a gas-treatment system that uses a sulfur-impregnated carbon adsorbent, elemental mercury physically adsorbs on carbon and then reacts to form non-volatile mercury sulfide (Wilhelm, 1999):

$$Hg° + C \rightarrow Hg(C) \qquad (2.1)$$

$$Hg(C) + S \rightarrow HgS \qquad (2.2)$$

The reaction between $Hg°$ and sulfur is a redox reaction in which mercury is oxidised and sulfur is reduced. The resulting mercuric sulfide is nonvolatile, insoluble and is retained on the bed.

Table 2.6 Mercury removal systems for hydrocarbons (Wilhem, 1999)

Reactant	Substrate	Complexed form	Application
Sulfur	Carbon, Al_2O_3	HgS	Gas
Metal sulfide	Carbon, Al_2O_3	HgS	Gas, Liquid
Iodide	Carbon	HgI_2	Dry liquid
Pd+ H_2; metal sulfide	Al_2O_3	HgS	Liquid
Ag	Zeolite	Ag/Hg amalgam	Gas, light liquid
Redox/ion exchange	Resin	Hg^{2+}	Gas
Metal oxide/sulfide	Oxide	HgS	Gas, liquid

Metal sulfide (MS, where M = Cu, Mo, Co and others) systems for gas have the advantages that the MS is not soluble in liquid hydrocarbon and it is less sensitive to water. Therefore, metal sulfide systems are more suited to moist, heavy hydrocarbon feeds in which some hydrocarbon condensation is possible. In a MS mercury removal system for gas with an alumina (Al_2O_3) substrate, mercury directly reacts with the metal sulfide. Adsorption on the support is less kinetically favoured than for carbon and is not strictly required for the reaction to occur:

$$Hg^\circ + CuS \rightarrow HgS + Cu^\circ \qquad (2.3)$$

Molecular sieve adsorbents that contain certain metals (silver) selectively capture mercury by an amalgamation process. The system is regenerative in that mercury is released as mercury vapor when heated in the regeneration cycle.

$$Hg^\circ + Ag^\circ \rightarrow HgAg \qquad (2.4)$$

$$HgAg \rightarrow Hg^\circ + Ag^\circ \qquad (2.5)$$

Because of limited capacity, these systems require a regeneration system those cycles frequently and a mercury removal system for the regeneration gas.

Metal oxide removal systems for gas are oxides that are partially converted to sulfides by activation with organic sulfides or H_2S. The resulting adsorbent has adsorptive characteristics of the oxides and reactive characteristics of a metal sulfide. Metal oxide systems have the advantage that they are not harmed by sour gas.

Mercury removal processes for liquid hydrocarbons consist of iodide-impregnated carbon, metal sulfide on carbon or alumina, a mol-sieve amalgam system and a two-step process consisting of a hydrogenation conversion catalyst followed by MS reaction with elemental mercury. The various liquid removal systems have both advantages and disadvantages that depend on feed composition and stream location (Wilhelm and Bloom, 2000). Their function reacts primarily with elemental mercury and with some mercury compounds to form insoluble chemical form. Removal systems are ineffective in reacting with suspended mercurymercury such as HgS. If HgS is present in a liquid feed, the feed liquid must be filtered (or otherwise treated) to remove suspended solids in order to make the system function effectively. Most mercury removal systems for liquids are chemically specific to one form of mercury, usually elemental. If the feed contains substantial amounts of ionic,

dialkyl or complexed mercury, then the removal system may not achieve designed criteria for removal efficiency.

The carbon/iodide system consists of potassium iodide impregnated carbon with a large pore diameter. The carbon/iodide adsorbent will scavenge elemental and organic mercury.

$$Hg^\circ + C \rightarrow Hg(C) \tag{2.6}$$

$$Hg(C) + 2I^- \rightarrow HgI_2 + 2e^- \tag{2.7}$$

$$XHX + 2I^- \rightarrow HgI_2 + 2X^- \tag{2.8}$$
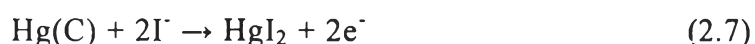
The mercury must be oxidised to react with iodide. In theory, the oxidation step is assisted by carbon, which provides catalytic assistance to the oxidation step. Main advantages of MS systems are that they are relatively insensitive to sulfur, water and aromatics, and they have a high capacity. The large capacity translates into smaller bed size and longer bed life.

Reportedly, metal sulfides on alumina do not react efficiently with liquid-phase organic mercury. For feeds that contain a significant amount of organic mercury, one system uses an initial hydrogenation step in which organic mercury is converted to elemental mercury on a catalyst. Elemental mercury is then captured by a metal-sulfide (CuS or other metal sulfides) impregnated alumina (Al_2O_3).

$$XHgX + H_2(Pd) \rightarrow Hg^\circ + 2HX \tag{2.9}$$

$$Hg^\circ + CuS \rightarrow Cu^\circ + HgS \tag{2.10}$$

However, this process has the advantage that it is relatively insensitive to moisture and high molecular weight compounds—it will withstand plant inlet conditions in some cases. But the major drawback is that the hydrogenation step requires hydrogen and high temperature.

The liquid-phase regenerable molecular sieve (zeolite) system is analogous to the gas-phase system using silver to amalgamate with mercury.

Amalgamative systems require regeneration and a separate mercury-treatment system for the regeneration of gas. But water condensed from these systems also will contain mercury.

Metal oxide mercury removal systems for liquid-phase treatment are similar to the metal oxide systems for gas and consist of metal oxides that are activated by reaction with H_2S. They function in generally the same manner as metal sulfide systems. Metal oxide systems are less affected by contaminants (sulfur compounds, aromatic, olefinic and heavy hydrocarbons) than carbon-based adsorbents.

Extensive research has been undertaken in order to find ways to remove mercury from both gaseous and liquid hydrocarbons streams. In general, there are two types of mercury removal technologies, namely mercury trapping, and mercury displacement. Both involve contacting the gas stream with a mercury removal unit, containing a sulfur-based bed, or equivalent adsorbent. Former method consists of trapping the element until bed becomes spent, and must be replaced. The latter involves trapping the mercury, and regenerating the unit in a cyclic process. The regeneration gas (contaminated with mercury) is diluted with distribution gas and sent to the distribution gas line. There are at least two big competitors of the mercury removal technology: Universal Oil Products (UOP) (mercury displacement) with Hg-SIV^{TM}, and Institut Français du Pétrole (IFP) (mercury trapping) with their CMG$^{®}$273^{TM}. They both claim excellent trapping efficiency for their marketed products.

2.6 Zeolites X and Y

Zeolites are microporous crystals of alkali earth aluminosilicates with the following stoichiometry:

$$M_{x/n} [(AlO_2)_x (SiO_2)_y] \cdot wH_2O$$
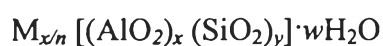
With n being the valence of the cation M, x and y integres with y/x equal to or greater than 1, and w the number of molecules of water per cell.

There are large varieties of natural zeolites (chabazite, mordenite, faujasite, etc., each different in crystallographic structure) and more than 150 have been synthesized. Only zeolites X and Y which are used in this work will be mentioned here. The synthetic zeolites X and Y and the natural zeolite faujasite all have the same framework structure which is shown in Figure 2.1
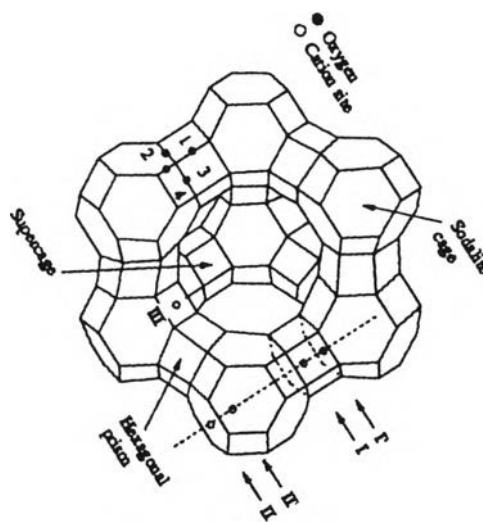

Figure 2.1 Framework of X and Y type zeolites (Fitch, 1986)

The crystallographic unit cell consists of and array of eight cages containing a total of 192 AlO_2 and SiO_2 tetrahedral units. The framework may be thought of as a tetrahedral lattice of sodalite units connected through six-membered oxygen bridges, or equivalently as a tetrahedral arrangement of double six-ring units. The resulting channel structure is very open with each cage connected to four other cages through twelve-membered oxygen rings of free diameter ~ 7.4 Å. The difference between the X and Y sieves lies in the Si /Al ratio which is within the range 1-1.5 for X and 1.5-3.0 for Y. There is a corresponding difference in the number of exchangeable univalent cation (Na in case of NaX and NaY), which varies from about 10-12 per cage for X to as low as 6 for high silica Y.

These zeolites are produced by hydrothermal crystallization between 20 and 175°C from freshly prepared aluminosilicate gels. The crystals, generally from 1 to 5 micrometers, are washed then compacted and shaped with an inorganic bonding

agent (clay) and finally calcinated. The final product is in the form of beads or extrudates. Zeolite with low Al contents are prepared by the process of dealumination, where by a reactant such as SiC_4 extracts Al from the framework. Zeolite Y prepared this way is called ultrastable.

Many research work regarding to removal of mercury are mainly devoted to the adsorption of adsorbate in gas phase on X and Y zeolite. Kinetics is the main difference between adsorption in the liquid phase and in the gas phase. The mass transfers to the adsorption sites are much slower in the liquid phase than in the gas phase, but the adsorption capacities and the selectivities are of the same order of magnitude. It depends only on the nature of the compensation cation, the silica-alumina ratio, and the preadsorbed water amount. The effects of these parameters are related to the acid-base properties of the adsorbent (Bellat *et al.*, 1995)

Furlan *et al.* (1992), have studied the role of water content on the adsorbent selectivity to separate liquid mixtures of *p*-xylene and *o*-xylene by X zeolite. The experiment using the liquid-phase adsorption in fixed beds containing zeolite type X whose cation Na^+ was replaced by Ba^{2+} and K^+. Using adsorpbents with preestablished contents of water. The results shown that an optimum water content in X zeolites with a value around 3.25 wt % occurs for the selectivity in separating *p*-xylenes and *o*-xylenes.

2.7 Literature Review

In U.S. Pat. No. 4,874,525, 1993, UOP HgSIV adsorbents were invented for effective mercury removal in existing molecular sieve adsorption units. Since cryogenic plants need dry inlet streams, molecular sieve dryers already exist in most plants with natural gas liquid recovery. HgSIV adsorbents are molecular sieve products that contain silver (metal), selectively capture mercury by an amalgamation process, on the outside surface of the molecular sieve pellet or bead due to the discovery that the effectiveness of the silver constituent of the zeolite on the outer portion of the adsorbent particle is many times greater than silver values located more deeply into the particle. Thus, for example, the adsorbent particle may comprise crystallites of a zeolite which have been bonded to a non-zeolitic inner core

such as glass bead or other dense phase material and for reasons not fully understood, zeolites having the faujasite, i.e. zeolite X and zeolite Y, are found to be superior sorbents and are particularly preferred. The system is regenerative in that mercury is released as mercury vapor when heated in the regeneration cycle. Mercury (Hg) from the process fluid (either gas or liquid) amalgamates with the silver, and a mercury-free dry process fluid is obtained. Adding a layer of one of the HgSIV adsorbents to an existing dryer results in the removal of both the design water load and the mercury without requiring a larger dryer. Mercury and water are both regenerated from the HgSIV adsorbents using conventional gas dryer techniques.

$$Hg^{\circ} + Ag^{\circ} \rightarrow HgAg \qquad (2.11)$$

$$HgAg \rightarrow Hg^{\circ} + Ag^{\circ} \qquad (2.12)$$

But because of the limited capacity, these systems require a regeneration system that cycles frequently and a mercury removal system for the regeneration gas (Wilhelm, 1999).

The diverse Hg species present in raw condensates, or in crude oil, appear to present a major problem. IFP has been able to avoid this problem by submitting the feedstock to a simple, two-step procedure, permitting the elimination of both As and Hg impurities with very high efficiencies as appeared in the U.S. Pat. No. 4,911,825, 1990. According to the process, a mixture of a charge with hydrogen is contacted with a catalyst containing at least one metal from the group consisting of iron, cobalt, nickel and palladium (nickel or a combination of nickel with palladium are preferably used) followed by-or mixed with-a trapping material including sulfur or a metal sulfide deposited on a support chosen from the group consisting of alumina, silica-aluminas, silica, zeolites, clays, activated carbon and alumina cements.

The first step requires passing the contaminant-containing feed over a fixed bed reactor loaded with hydrogenolysis catalyst where both catalytic hydrogenolysis reaction and As captation occur in a presence of hydrogen required to hydrogenolyse the organomercury compounds based on the following reaction.

$$AsR_3 + M\text{-}H \rightarrow M\text{-}AsR_2 + RH \tag{2.13}$$

And

$$R\text{-}Hg\text{-}R + 2M\text{-}H \rightarrow Hg + 2RH \tag{2.14}$$

The As-free feed is subsequently cooled down and fed to the second stage in the presence of a trapping material. The second step involves the simple chemical bonding of metallic Hg to selective trapping masses.

$$Hg^{\circ} + MS \rightarrow HgS + M^{\cdot} \tag{2.15}$$

The metal sulfide on the support has the advantage that it is relatively insensitive to moisture and high molecular weight compounds. Thus, it will withstand plant inlet conditions in some cases. The major drawback of this system is that the hydrogenolysis step requires hydrogen and elevated temperature (Wilhelm, 1999).

The use of activated carbon containing metal halides for removal of mercury from liquid hydrocarbons was claimed by McNamara *et al* (1994), particularly even trace levels of mercury, where the metal is selected from the group consisting of K, Ca, Fe and Zn, where halides is selected from the group consisting of Br, Cr and I. With the experimental condition, ambient temperature and pressure, it was found that the adsorbent was quite effective to remove even the trace amount of mercury presented.

In year 2000 (Shafawi *et al.*), have tested three commercially available mercury removal systems. Both real and substitute condensate samples i.e. hexane containing dimethylmercury (DMM), diethylmercury (DEM) and dibutylmercury (DBM) species were used in the test. The systems were designated AA (using hydrogenolysis catalyst to convert organo- and inorganic mercury to elemental mercury and then using a sulfide-containing alumina for removal of elemental

mercury), BB (a carbon based adsorbent which contained sulfur as the active material) and CC (molecular sieve-based adsorbent with undisclosed active material). The tested results shown that all three pilot plants can reduce the mercury content of the final products. For the adsorbent system AA, elemental mercury measured in the liquid product from first reactor was only about 30% of the total mercury content. Incomplete conversion of the organomercury species to mercury metal by this reactor may be due to competition between the organomercury species and the unsaturated compounds in the matrix during the hydrogenolysis reaction. The second reactor, for mercury trapping, was able to adsorb efficiently elemental mercury present in the liquid stream (the product from the first reactor) but was unable to remove the organomercury content from the condensate stream. However, the main types of mercury present in the condensate which are organometallic (>80%) was discussed in this context. For the system BB, the results showed no peaks of three organomercury species in the product samples after the reactor. Therefore, the efficiency in removing spiked DMM, DEM and DBM from the n-hexane hydrocarbon sample was closed to 100%. Finally for CC system, efficiency of removal for different mercury species spiked into the n-hexane was variable. The overall performance of the adsorbent in removing DMM, DEM and DBM species was 55, 80 and 22%, respectively.

Yan *et al.* (2003) presented a systematic study on the capture of trace mercury vapor from simulated coal-fired flue gases, using activated carbons. The experiments were conducted on a bench-scale fixed-bed reactor with focus on the variable flue gas components and compositions to understand the interaction and competitive adsorption of different gas components, O_2, CO_2, SO_2 and moisture, one by one, into the simulated flue gas system which contained only nitrogen and elemental mercury vapor. Performance comparing of five commercially available activated carbons different in quantity of sulfur content and one prepared H_2S-exhausted activated carbon were evaluated.

The studied carbons displayed a wide margin regarding to their ability to adsorb mercury vapor from simulated flue gas with variable gas compositions. The quantity of sulfur component at the carbon surfaces are the key issue relative to the different capacities observed.

Due to the lack of knowledge concerning removal of Hg° from real flue gas of pulverised-coal combustion, recently, Zeng *et al.* (2004) investigated the adsorption of vapor-phase elemental mercury (Hg°) from pulverised-coal combustion flue gas by commercially available granular activated carbons treated with zinc chloride ($ZnCl_2$) impregnation (0-5 %wt). The effects of adsorption temperature and $ZnCl_2$ solution concerning on the mercury removal performance were also studied. The experimental setup was designed to allow pulverised bituminous coal and air flow into ceramic combustion chamber, which was maintained at 1200 °C. The flue gas was sucked into a column packed with activated carbon samples, which operated at various temperatures (200-500 °C). Adsorption results showed that activated carbon impregnated with 5% $ZnCl_2$ impregnation actually decreased BET surface area and normally for physisorption the amount of adsorbed Hg° decreases proportional to surface area. Therefore, this trend displayed the occurrence of chemisorption of elemental mercury onto Cl-impregnated carbon.