CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Properties of Mercury and Mercury Compounds

The physical properties of elemental mercury are shown in Table 2.1. Normally, elemental mercury is a liquid at ambient conditions. It is quite dense and its density is 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 (Wilhelm, 2001)

Atomic number	80
Atomic weight	200.59 atomic mass units
Boiling point	357 °C (675 °F)
Boiling point/rise in pressure	0.0746 °C/torr
Density	13.546 g/cm^3 at 20 °C (0.489 lb/in^3 at 68 °F)
Diffusivity (in air)	0.112 cm^2/sec
Heat capacity	0.0332 cal/g at 20 °C (0.060 Btu/lb at 68 °F)
Henry's law constant	0.0114 atm m^2/mol
Interfacial tension (Hg/H$_2$O)	375 dyne/cm at 20 °C (68 °F)
Melting point	-38.87 °C (-37.97 °F)
Saturation vapor pressure	0.16 N/m^3 (pascal) at 20 °C (68 °F)
Surface tension (in air)	436 dyne/cm at 20 °C (68 °F)
Vaporization rate (still air)	0.007 mg/cm^{2}hr for 10.5 cm^2 droplet at 20 °C

Mercury naturally occurs in the zero, +1, or +2 valence states. The zero is the elemental form of mercury whereas +1 is mercury[I] or mercurous and +2 is mercury [II] or mercuric. Mercurous compounds usually involve Hg-Hg bonds and are generally unstable and rare in nature.

Mercury has been found most extensively in the elemental form or in the inorganic mercuric form. Normal mercuric compounds include mercuric oxide, mercuric chloride, mercuric sulfide and mercuric hydroxide. Organic mercury forms also exist and consist of two main groups which are R-Hg-X compounds and R-Hg-R compounds, where R is organic species, of which methyl (-CH3) is prominent, and X is inorganic anions, such as chloride, nitrate or hydroxide. The R-Hg-X group includes monomethylmercury compounds. The most prominent R-Hg-R compound is dimethylmercury. It is difficult to oxidize mercury in the natural environment and spilled mercury, such as in soil, retains the elemental form indefinitely absent moisture and bacteria until evaporation. Mercury can be oxidized by the stronger oxidants including halogens, hydrogen peroxide, nitric acid and concentrated sulfuric acid. Moreover, mercury is oxidized and methylated in sediments by sulfate-reducing bacteria. Table 2.2 shows the selected solubility and volatility data for elemental mercury and some mercury compounds in water. It is important to note that sulfides of mercury are largely insoluble in water (and oil) and, as pollutants are less available to receptors.

Table 2.2 Solubilities and volatilities of mercury compounds (Wilhelm, 2001)

Formula	State	Volatility	Hg solubility in H_2O; 25°C	Name
Hg^0	Liquid	Boiling Point 357 °C	50 ppb	Elemental
$HgCl_2$	Solid	Boiling Point 302 °C	70 g/L	Mercuric chloride
$HgSO_4$	Solid	decomposes 300 °C	0.03 g/L	Mercuric sulfate
HgO	Solid	decomposes 500 °C	0.05 g/L	Mercuric oxide
HgS	Solid	Sublimes under vacuum; decomposes 560 °C	$-\log K_{sp}^{(1)} = 52$	Mercuric sulfide
$HgSe$	Solid	Sublimes under vacuum; decomposes 800 °C	$-\log K_{sp} \sim 100$	Mercuric selenide
$(CH_3)_2Hg$	Liquid	Boiling Point 96 °C	< 1 ppm	Dimethylmercury
$(C_2H_5)_2Hg$	Liquid	Boiling Point 170 °C	< 1 ppm	Diethylmercury

(1) K_{sp} = solubility product

Silver, gold, copper, zinc, and aluminum rapidly form amalgams with elemental mercury at ambient conditions. The solubility of these metals in elemental mercury is relatively low. The solubility of zinc in mercury is approximately 2 g Zn/100 g Hg, while gold solubility in mercury is only 0.13 g Au/100 g Hg. Silver, copper, and aluminum have even lower solubilities than gold. The affinity of mercury for gold is important in analytical procedures that trap vapor phase mercury on gold collectors.

2.2 Mercury in Hydrocarbon

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. Furthermore, Tao *et al.*, (1998) claimed that the amount of dialkylmercury in natural gas would be less than 1 percent of the total, so organic mercury compounds in produced gas would be expected to partition to separate hydrocarbon liquids as the gas is cooled. Therefore, if dialkylmercury is present in the reservoir and hydrocarbon liquids separate due to natural cooling, dialkylmercury would be found mostly in condensate. Likewise in gas processing, little organic mercury would be expected in sales gas due its partition to liquid streams.

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^0) – 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 such as pipes and vessels, suspended wax, sand and other 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 anion) – 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^0. This category includes dialkylmercury such as dimethylmercury, diethylmercury, etc. 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 that is about 10 times more than elemental mercury. Ionic salts also may be physically suspended in oil or may be attached (adsorbed) to suspended particles.

4. Complexed mercury (HgK or HgK_2) – Mercury can be present in hydrocarbons as a complex, where K is a ligand such as an 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 feeds to the plant by physical separation techniques such as filtration or centrifugation.

2.3 Effects of Mercury on Processing

Wilhelm and Bloom, (2000) summarized the various detrimental impacts of mercury on gas processing operations.

1. Mercury deposits in cryogenic equipment, sometimes cause cracking of welded aluminum heat exchangers. Numerous cases of cold box failure are recorded in older gas processing plants and steam cracking ethylene plants, however, the introduction of cold box designs that are resistant to mercury and mercury removal systems have served to reduce the incidence of failure.

2. Mercury in gas plant products 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 the cited equipment problems and due to catalyst poisoning.

3. Mercury contaminates treatment processes such as molecular sieve and glycol dehydration units, and amine acid gas removal systems. Contaminated treatment liquids and spent molecular sieve adsorbents are difficult to dispose of and to regenerate.

4. Mercury adsorbent materials used for gas or liquid treatment, when spent, constitute a generated hazardous waste that plant operators must store or process for disposal

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

6. 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.

7. 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.

2.4 Analytical Methods for Mercury

Analytical methods for mercury and mercury compounds in hydrocarbon matrices are differentiated by collection or sampling, species conversion/separation (digestion, extraction, filtration, vaporization) and detection methods. The methods used to determine total mercury in liquid and gaseous hydrocarbons are reasonably well-established and accurate. The methods to identify quantity of species of mercury compounds in liquid hydrocarbons are more recent and less verified. The speciation methodologies now practiced are categorized as either operational or species-specific.

1. Sampling

Sampling of hydrocarbons containing mercury is difficult to accomplish because of partitioning of mercury compounds among phases, species inter-conversion in some sample containers, loss of non-polar compounds in plastic containers and due to adsorption of mercury on sample container surfaces. In samples derived from hot streams or pressurized streams, the volatile mercury compounds (Hg^0 and $Hg(CH_3)_2$) separate between the vapor and liquid phases in sample containers. Therefore analysis of both the liquid and gas phases and a mass balance is required if the concentration of mercury in the produced phase need to be investigated.

The amounts of Hg^0 and $RHgR$ that partition to water are usually a small percentage of the total mercury concentration in coexisting phases because their solubilities is low in water. Besides, if ionic mercury compounds is also present, it will partition to the water phase but the hydrocarbon/water partition ratios depend on pH, salinity, temperature and other factors. Acidic water can encourage formation of a particle rich layer at the water/oil interface that can be very high in mercury concentration. Sampling and analysis protocols should be designed to take these factors into account.

2. Elemental Mercury in Gas

The concentration of Hg^0 in a hydrocarbon gas matrix is difficult to measure directly by spectroscopic methods because of interference by the hydrocarbon. Trapping the mercury in a known gas volume on a collector facilitates analysis by enrichment of mercury in the matrix that is analyzed. A common wet collection method traps mercury in gas in permanganate solution which oxidizes Hg^0 to Hg^{2+}. Then, Hg^{2+} is reduced using stannous chloride to Hg^0 and separated by sparging into an inert gas stream for detection. This method is accurate and reasonably sensitive if sufficient volumes of gas are used, but the apparatus required to collect the samples is somewhat cumbersome and the required sample volumes are large.

Dry collection methods include several that involve amalgamation of Hg^0 on Ag, Au or Au/Pt (sputtered on quartz). The gas containing Hg^0 must contact the metal collector at a very low flow rate for quantitative trapping. The amalgam is heated in an inert (Ar) gas stream to volatilize mercury for detection. Amalgam

trapping is very effective for light, dry gas. If the stream to be sampled contains heavier components, heating the traps (50°C to 150°C) minimizes hydrocarbon condensation without compromise of collection efficiency. The efficiency of amalgamation traps for $Hg(CH_3)_2$ depends on the composition of the gas matrix since the heavier molecules tend to adsorb on the traps and interfere with amalgamation of $Hg(CH_3)_2$. This obstacle has been overcome by using Au/Pt (90/10) traps that are heated slightly about 80°C.

Activated carbon impregnated with iodide is also used to scavenge mercury from gas matrices. After Hg is collected from a known volume, the carbon/KI traps are subjected to routine digestive analysis to determine total Hg. Iodated carbon traps are less sensitive to some contaminants than gold traps and have a higher capture capacity, thus allowing large sample volumes. The iodated carbon traps are suitable for moist gas if they are maintained above the condensation temperature for water. Water condensation dissolves the iodide. The trapping efficiency for dimethyl-mercury is near 100%.

3. Total Mercury in Liquids

Analytical methods for total mercury in hydrocarbon liquids include combustion, wet (hot) digestion and wet extraction. Combustion/vaporization techniques vaporize the entire liquid matrix and mercury in the exhaust gas is trapped and analyzed using procedures that are similar to those employed for natural gas. Wet methods oxidize all mercury species in the hydrocarbon liquid matrix to Hg^{2+} that separates to an aqueous phase. Wet digestive methods that use strong acids and heat require pressurized digestion bombs. Extractive methods (BrCl) are preferred for light hydrocarbon liquids. Digestates and extracts are treated with stannous chloride or sodium borohydride to generate Hg^0 and then sparged (Ar). The sparge gas is either sent directly to a detector or collected on a trap amalgamation and then thermally evolved into an inert gas stream for detection. The amalgamation step concentrates the sample and eliminates interference from hydrocarbons.

The most common forms of detection are cold vapor atomic absorbance (CVAA) and cold vapor atomic fluorescence (CVAF). CVAF is a very sensitive method with reported absolute detection limits 100 to 700 pg. The low detection limit allows accurate quantitation of very small samples and dramatically reduces

matrix effects common to other methods by allowing extreme dilution prior to analysis. Moreover, other types of total mercury analysis methods include inductively coupled plasma (ICP) or microwave induced plasma MIP followed by mass spectrometry MS or atomic emission spectrometry (AES) detection. The ICP/MIP techniques avoid digestion of the sample, hence, minimizing some of the potential errors that can occur in multi-step wet chemical processing of liquid samples. Neutron activation analysis (NAA) methods, which also avoid wet processing of samples, also have been used to examine crude oils. NAA, ICP/MIP and MS/AES all report detection limits less than 0.1 ng/g.

4. Speciation of Mercury Compounds

Total mercury concentration typically is determined by oxidative extraction. Suspended mercury is quantitatively determined by measuring total mercury of an agitated sample followed by measuring total mercury of a filtered portion of the agitated sample. Ionic and monoalkyl forms which are HgCl and RHgCl are determined by non-oxidative extraction of filtered samples using dilute acids. Hg^0 is determined by sparging and collecting the volatile component on a trap. The sum of the concentrations of dialkylmercury and complexed mercury often is estimated from the discrepancy in the mass balance.

$$\text{Total Hg} = Hg^0 + (RHgR + HgK) + (HgCl_2 + RHgCl) + \text{suspended Hg} \quad (2.1)$$

2.5 Mercury Removal System

Mercury removal adsorbent beds are used to scavenge mercury from gases or liquid hydrocarbon streams. The adsorbents are a 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. Mercury removal systems for hydrocarbons have been summarized in Table 2.3.

Adsorbents function by reacting mercury or a mercury compound to a chemical compound to a chemical form (HgS, HgI_2 or amalgam) that is insoluble in hydrocarbon liquid and chemically inert to the components of 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, the systems primarily consist of sulfur-impregnated carbon, metal sulfide on carbon or alumina, and regenerative molecular sieve (Ag on zeolite).

Table 2.3 Mercury removal systems for hydrocarbons (Wilhelm and Bloom, 2000)

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
Metal oxide/sulfide	Oxide	HgS	Gas,liquid

In a gas-treatment system that uses a sulfur-impregnated carbon adsorbent, element mercury physically adsorbs on carbon and then reacts to form non-volatile mercury sulfide.

$$Hg^0 + C \rightarrow Hg(C) \tag{2.2}$$

$$Hg(C) + S \rightarrow HgS \tag{2.3}$$

The reaction between Hg^0 and sulfur is a redox reaction in which mercury is oxidized and sulfur is reduced. The resulting mercuric sulfide is nonvolatile, insoluble and is retained on the bed.

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:

$$Hg^0 + CuS \rightarrow HgS + Cu^0 \qquad (2.4)$$

Molecular sieve adsorbents that contain certain metal (silver0 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.

$$Hg^0 + Ag^0 \rightarrow HgAg \qquad (2.5)$$

$$HgAg \rightarrow Hg^0 + Ag^0 \qquad (2.6)$$

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

Metal oxide removal systems for gas are oxide that are partially converted to sulfides by activation with organic sulfide 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 element mercury. The various liquid removal systems have both advantages and disadvantages that depend on feed composition and stream location (Wilhelm et al., 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 mercury 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 that the system is to 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.

$$Hg^0 + C \rightarrow Hg(C) \tag{2.7}$$

$$Hg(C) + 2I^- \rightarrow HgI_2 + 2e^- \tag{2.8}$$

$$XHX + 2I^- \rightarrow HgI_2 + 2X^- \tag{2.9}$$
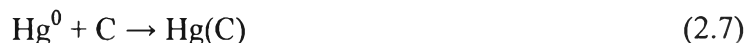
The mercury must be oxidized to react with iodide. In theory, the oxidation step is assisted by carbon, which provides catalysis assistance to the oxidation step. Main advantages of MS systems are that they are relatively insensitive to sulfur, water and aromatics, and they have a high capacity. The 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)

$$XHgX + H_2(Pd) \rightarrow Hg^0 + 2HX \tag{2.10}$$

$$Hg^0 + CuS \rightarrow Cu^0 + HgS \tag{2.11}$$

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 – treatments 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 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.

In addition, two famous commercial mercury removal technologies which can separate mercury effectively are introduced by Universal Oil Product (UOP), USA and Institut Français du Pétrole (IFP) from France. UOP created HgSIV adsorbents which are molecular sieve products that contain silver on the outside surface of the molecular sieve pellet or bead. Mercury from the process fluid (either gas or liquid) amalgamates with the silver, and a mercuryfree 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. Physically, HgSIV adsorbents have a similar appearance to conventional molecular sieves. They are available in a beaded or in a palletized form. These HgSIV adsorbents are loaded into an adsorption vessel in the same way as are conventional molecular sieves. There is no need for special care, such as the use of nitrogen blanketing during the installation. But the main drawback of this technology is the emission of mercury to the atmosphere via the dryer regeneration gas. Moreover, Institut Français du Pétrole (IFP) introduced the IFP RAM processes which are designed to convert all non – metallic forms of mercury into metallic mercury before the feedstock enters the process side of the plant for upgrading to fuels and petrochemical intermediates. The IFP RAM processes operate in two stages. The first stage of the RAM II process comprises a reactor loaded with a hydrogenolysis catalyst, MEP841 (Procatalyse), operating under hydrogenolysis condition and in the presence of hydrogen. Both ionic and organomercury species are converted to metallic mercury which is subsequently trapped in the second stage. The first stage also traps arsenic and lead impurities in the feed. The second stage operates at temperature which is generally below 100 °C in the presence of the mercury trapping material, CMG273 (Procatalyse). The CMG273 material is able to trap small amounts of organomercury species without

any prior treatment of the feedstock. Small pilot plant studies carried out using Algerian condensate showed that all of the mercury was adsorbed for a short period of time. The mercury trapping efficiency then falls off and stabilizes at 40%. The addition of the hydrogenolysis pre – treatment step which converts the mercury compounds to elemental mercury before mercury removal, enables the efficiency to remain above 94% throughout the operation. The RAM III process combines aromatics feedstock hydrotreating and mercury removal before entering the aromatics complex. The first stage reactor operates under hydrotreating conditions with the catalysts HR306C (Procatalyse) where sulfur, nitrogen, mercury and arsenic containing compounds are hydrotreated to form dihydrogen sulfide, ammonia, elemental mercury, cinnabar and arsine. The arsine is trapped by the HR306C. Under hydrotreating conditions, cinnabar is decomposed to elemental mercury and is eluted out of the reactor with the effluent. After stabilization, the effluent may be passed directly to the second stage, after the removal of excess hydrogen, where mercury is removed by the CMG273.

2.6 Mathematical Model

The mathematical model of the isothermal, dynamic adsorption breakthrough process in a fixed bed is based on transient material balance, gas or liquid phase, intrapellet mass transfer and adsorption equilibrium relationship. The kinetic aspects are also taken into account along with adsorption equilibrium which can be described by Langmuir equation. The mass transfer rate is represented by Linear Driving Force (LDF) model which is a lumped-parameter model for particle adsorption. The estimation of intrapellet mass-transfer coefficient, k, is an important step in the resolution of the simulation problem.

2.6.1 Modeling Approach

The phenomenon of adsorption is an attraction of adsorbate molecules to an adsorbent surface. The phenomenon arises due to the different concentration of adsorbate in the bulk phase and in the adsorbent or solid phase. During an adsorption

process, overall mass transfer adsorbate specie is depend on various kind of mass transfer resistances and the determination of these resistances is the major step in order to understand slowest mechanism.

Figure 2.1 (a cross section of column) shows a general adsorption process, indicates various mass transfer resistances namely;

1. External film resistance (due to the interaction of solid and liquid)
2. Internal (macro and micro) resistance (due to the geometry of adsorbent)
3. Rate of adsorption (due to active sites on surface of adsorbent)
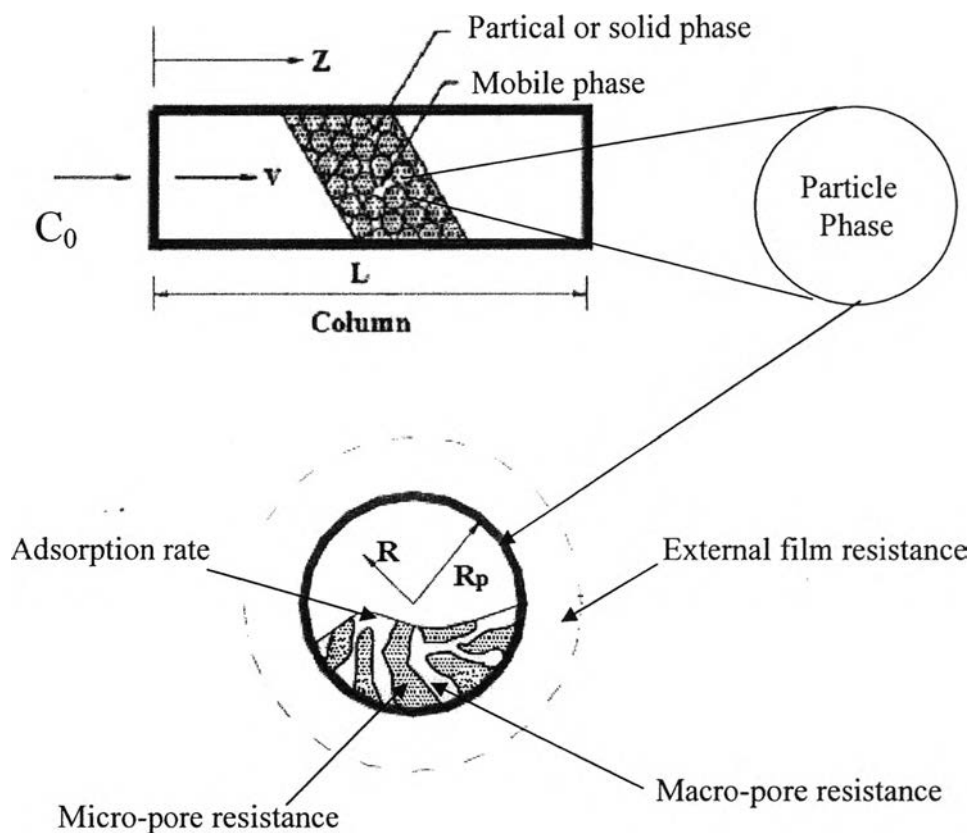
Figure 2.1 Various resistances during adsorption phenomena (Ruthven, 1984).

2.6.2 Model Formulation

In an adsorption column, the differential mass balance for an element in bulk fluid phase and in solid phase provides the starting point for developing a

mathematical model in order to describe the dynamic behavior of the system. Figure 2.2 shows a cross section of column, and mass balace for a specie 'i' can be given as:

$$
\begin{bmatrix} \text{Rate of increase} \\ \text{in moles of i} \\ \text{per unit volume} \end{bmatrix} = \begin{bmatrix} \text{Net rate of addition} \\ \text{in moles of i per unit} \\ \text{volume by convection} \end{bmatrix} + \begin{bmatrix} \text{Rate of addition of} \\ \text{moles of i per unit} \\ \text{volume by diffusion} \end{bmatrix} - \begin{bmatrix} \text{Rate of loss of moles} \\ \text{of i per volume by} \\ \text{physical adsorption} \end{bmatrix}
$$

$$
- \begin{bmatrix} \text{Rate of loss of moles} \\ \text{of i per volume by} \\ \text{chemical adsorption} \end{bmatrix} - \begin{bmatrix} \text{Rate of loss of i per volume} \\ \text{due to deactivation by aging} \\ \text{poisoning, cocking} \end{bmatrix}
$$
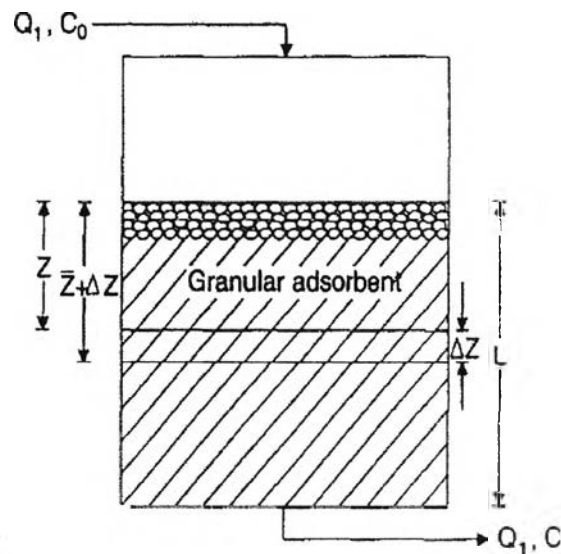
Figure 2.2 Differential mass balance over the packed bed

where C_o, C are the inlet and outlet fluid phase concentrations to adsorber, Q_1 is the volumetric flow rate of fluid, z the distance measured from column inlet, ε the porosity of adsorption bed Under the isothermal conditions and the only concentration gradient in the radial direction, above expression can be written as:

$$
\frac{\partial c}{\partial t} = \left\{ - \frac{\partial (vc)}{\partial z} \right\} + \left\{ D_1 \frac{\partial^2 c}{\partial z^2} \right\} - \left\{ \frac{(1 - \varepsilon)}{\varepsilon} \frac{\partial \overline{q}}{\partial t} \right\} - (-r_i) - A \qquad (2.12)
$$

$$
- D_1 \frac{\partial^2 c}{\partial z^2} + v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \left(\frac{1 - \varepsilon}{\varepsilon} \right) \frac{\partial \overline{q}}{\partial t} + (-r_i) + A = 0 \qquad (2.13)
$$

where D_L is the axial dispersion coefficient and, v the interstitial velocity of fluid, $\bar{q}$ the adsorbate concentration averaged over crystal and pellet, A is representative term for deactivation and $(-r_i)$ is rate of chemical adsorption and for a first order reaction can be given as:

$$(-r_i) = K \, .c \tag{2.14}$$

where K is rate constant for chemical reaction.

The rate of adsorption can be described by linear driving force (LDF) equation as indicated below:

$$\frac{\partial \bar{q}}{\partial t} = k(q^* - \bar{q}) \tag{2.15}$$

where k is the LDF mass transfer coefficient in the unit of s^{-1} and q* represents the equilibrium adsorbed phase concentration which can be determined from the concentration in the mobile phase using the Langmuir equation as indicated below:

$$q^* = \frac{q_{max} b.c}{1 + b.c} \tag{2.16}$$

where q_{max} and b are Langmuir isotherm parameters. The term $\partial \bar{q}/\partial t$ represents the overall rate of mass transfer for adsorbed component average over a particle. Substituting equation (2.14) and equation (2.15) into equation (2.13),

$$-D_l \frac{\partial^2 c}{\partial z^2} + v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + k\left(\frac{1-\varepsilon}{\varepsilon}\right)(q^* - \bar{q}) + K\,.C + A = 0 \tag{2.17}$$

The dynamic response of the column which is concentration profiles in the mobile (c) and adsorbed phase ($\bar{q}$) along the packed bed adsorber can be determined by solving equation (2.17) subject to the following initial and boundary conditions:

Initial conditions: $t = 0, z > 0$, $c = c(0,z)$ and $q = q(0,z)$

Boundary conditions: $z = 0, t > 0$, $c = c_{inlet}$

$$z = L, t > 0, \qquad \frac{\partial c}{\partial z} = 0$$

where c_{inlet} represents the initial feed concentration or concentration of bulk fluid.

The response to a perturbation in the feed composition involves a mass transfer zone or concentration front which propagates through the column with a characteristic velocity determined by the equilibrium isotherm. The location of the front at any time may be found simply from an overall mass balance, but in order to determine the form of the concentration front Equations (2.14) and (2.16) must be solved simultaneously (Ruthven, 1984).

2.6.3 Numerical Algorithm

The method of lines (MOLs) can be applied to discretize partial differential equations presented in Eq. (2.17) into a set of ordinary differential equations (ODEs) by using the central finite difference method. Then, the 4th order Runge-Kutta method available in the MATLAB® programming language can be applied to solve ODE in order to predict the mercury concentration in the fluid phase leaving the adsorber with time.

2.6.3.1 The Method of Lines (MOLs)

This explicit method will convert PDE into a set of first-order ODE's with initial value problem. For 1st order derivative, $\dfrac{\partial c}{\partial z}$ in terms of central finite differences with error of order h^2 can be expressed in terms of their respective definitions:

$$\frac{dc_i}{dz} = \frac{1}{2\Delta z}(c_i - c_{i-1}) + O(\Delta z^2) \qquad (2.18)$$

For 2nd order derivative term, $\dfrac{\partial^2 c}{\partial z^2}$ in terms of central finite differences with the error of order h^2 can be expressed in terms of their respective definitions:

$$\frac{d^2 c_{i,j}}{dz^2} = \frac{1}{\Delta z^2}(c_{i+1,j} - 2c_{i,j} + c_{i-1,j}) + O(\Delta z^2) \qquad (2.19)$$

where i is the step size number of axial direction and j the step size number of time. Finally, MATLAB language is programmed to solve the set of ODEs.

2.7 Kinetic Models

Numerous publications in literature on adsorption kinetic are available. The typical kinetic model normally considers both external and internal mass transfer resistances. A general model involves complicated mathematical computation to obtain the related diffusion coefficients of the model.

Therefore, for the simplicity and practical use of engineering applications, the global kinetic expressions such as Lagergren Pseudo 1st order and 2nd order, and Elovich rate equations, were tested to describe the adsorption kinetic (Chang, *et al.,* 2004).

a) For pseudo 1st order of the Lagergren equation, the kinetic rate can be expressed,

$$\frac{dq_t}{dt} = k_{e1}(q_e - q_t). \qquad (2.20)$$

Integrating Eq. (2.20) with the conditions ($q_t = 0$ at $t = 0$; $q_t = q_t$ at $t = t$)

$$\ln(q_e - q_t) = \ln(q_e) - k_{e1}t \qquad (2.21)$$

where q_t and q_e is the adsorption capacity at time t and at equilibrium, and k_{e1} is the equilibrium rate constant of the pseudo 1st order sorption.

b) For the pseudo 2nd order, the kinetic rate can be written,

$$\frac{dq_t}{dt} = k_{e2}(q_e - q_t)^2.$$

(2.22)

Integrating Eq. (2.22) with the conditions ($q_t = 0$ at $t = 0$; $q_t = q_t$ at $t = t$) yields

$$\frac{t}{q_t} = \frac{1}{k_{e2}q_e^2} + \frac{t}{q_e}$$

(2.23)

where k_{e2} is the equilibrium rate constant of the Pseudo-second-order sorption.

c) The rate expression of Elovich equation can be expressed,

$$\frac{dq_t}{dt} = a\, e^{(-bq_t)}$$

(2.24)

Integrating Eq. (2.24) with the conditions ($q_t = 0$ at $t = 0$; $q_t = q_t$ at $t = t$) and subsequent linearization results,

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t + t_0)$$

(2.25)

where a and b are the parameters of the Elovich rate equation; t_0 is equal to $1/(ab)$. If $abt \gg 1$, Eq. (2.25) can further be simplified as:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t)$$

(2.26)

2.8 Literature Review
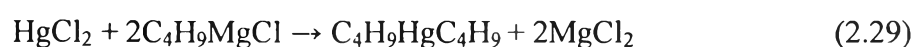
2.8.1 Analysis Technique

The speciation of mercury is very important. If the sorts of mercury existing in condensates or crude oil are completely detected, the mercury removal methods will be chosen properly.

Chromatographic techniques have been applied successfully to hydrocarbon liquids and are also capable to investigate the various mercury species. Both gas chromatography (GC) and high-performance liquid chromatography (HPLC) techniques have been used successfully. Schickling and Broekaert, (1995) used HPLC, matrix destruction dichromate, borohydride reduction and CVAA to examine gas condensates. Detection limits (3σ) of approximately 10 ng were achieved for RHgR (R = phenyl), $HgCl_2$ and RHgCl. The importance in this work were observations of the reaction of ionic and organic mercury. Chromatographic separation of standard mixtures of mercuric chloride and diphenylmercury produced only a peak confirmed to be monophenylmercury chloride.

$$RHgR + HgCl_2 \rightarrow 2RHgCl \tag{2.27}$$

Whether reactions of ionic and other organic mercury compounds occur was not examined and remains uncertain.

Snell et al., (1996) used GC, post-column combustion, amalgamation PtrAu and MIP–AES. MIP–AES achieved a detection limits (3σ) between 0.25 and 5 ng/ml for the various species. Separation of organic, inorganic and monomethylmercury species was accomplished using GC, following derivatization using Grignard reagent (butylmagnesium chloride) :

$$CH_3HgCl + C_4H_9MgCl \rightarrow CH_3HgC_4H_9 + MgCl_2 \tag{2.28}$$

$$HgCl_2 + 2C_4H_9MgCl \rightarrow C_4H_9HgC_4H_9 + 2MgCl_2 \tag{2.29}$$

Zettlitzer et al., (1997) used HPLC, post-column oxidation UV-PCO and CVAA to examine monoalkylmercury and GC–MS to examine dialkylmercury

in German condensates. The speciation scheme included operational steps for Hg^0 and HgCl. The detection limit for the GC–MS procedure was greater than 1 ppm and thus, did not allow quantitative determination of dialkylmercury.

Tao *et al.*, (1998) used GC–ICP–MS to examine a variety of condensates and naphthas. The procedures developed by Tao were rigorously verified as to recovery and sensitivity using spikes, replicates and blanks. Tao optimized injection procedures for the GC and verified recoveries close to 100% for all of the mercury species examined.

2.8.2 Mercury Seperation

Recently, some researchers tried to study the mercury removal capability of zeolite and other adsorbent for improving the effectiveness of existed mercury removal process. Shafawi *et al.*, (1999) evaluated three commercial mercury removal systems including system AA, BB and CC. System AA was a two-stage process involving a species conversion step prior to trapping of mercury on an alumina-adsorbent impregnated with a metal sulphide, whereas systems BB and CC were single-stage trapping processes using sulphide impregnated carbon and molecular sieves, respectively. In addition, both real and substitute condensate sample which is hexane containing dimethylmercury (DMM), diethylmercury (DEM) and dibutylmercury (DBM) species were used in this experiment. The result indicated that system AA was unable to remove all mercury species from the condensate stream. Only elemental mercury could be completely removed from the condensate stream but the hydrogenolysis reactor that was able to convert some of the organomercury to its elemental form can produce the elemental mercury about 30% of the total mercury content. Therefore, there are some types of organomercury that still be present in the condensate stream. Another drawback is the degrading of condensates since some unsaturated hydrocarbons, such as aromatics and olefinic compounds, in condensates could be destroyed by the hydrogenation process. Meanwhile, system BB that is a carbon-based product impregnated with sulfur compound can remove organomercury close to 100%. Three species of organomercury including dimethylmercury, diethylmercury and dibutylmercury were spiked into the n-hexane. There were no peaks detected in the product samples

after the reactor. In the system CC, the overall performance is not good. The capabilities in removing dimethylmercury, diethylmercury and dibutylmercury were 55, 80 and 22% respectively.

Jurng et al., (2002) performed the experiment to investigate various adsorbents for their mercury removal capabilities from incineration flue gas. Four different adsorbents used in this experiment are natural zeolite, Bentonite, activated carbon and wood char. The cylindrical – shaped adsorbent columns with ten layers, 5 cm in diameter and 20 cm in length were used. The carbon – based adsorbents which are wood char and activated carbon showed the excellent results for mercury removal. The cumulative mercury removal efficiency of wood char was already over 80% in the first layer and reached 99% by the fourth layer as well as experiments using AC gave similar results. This result is very encouraging considering the fact that the specific surface area of wood char was just one third of the activated carbon's. Hence, the BET surface area cannot be related to mercury adsorption directly due to the difference in pore size distributions between adsorbents. For natural zeolite and Bentonite, their mercury removal capabilities are poor. It could be seen from the results that the cumulative mercury removal efficiencies of natural zeolite and Bentonite were less than 10% in the first layer and reached only 50% throughout the whole adsorbent layers. The reason is probably due to either a lack of chemical affinities towards mercury, or much stronger affinities towards other major chemical constituents in real incineration off-gases.

2.8.3 Mercury Adsorption

Chojnacki et al., (2004) used the natural zeolite from clinoptilotile group for removing mercury from industrial effluents from copper smelter and refinery. The mechanism of adsorption and kinetic of adsorption are investigated and it was found that natural zeolite could be used for binding of cations in the process of ion exchange that was identified as the dominating mechanism of the process (beside physical adsorption). Due to the mechanism recognized as ion-exchange, heavy metal ions adsorption was found to be strongly pH-dependent. In this process, cations bind to deprotonated groups on zeolite surface. Three functional acidic groups were identified on the zeolite surface with pKa 3.10, 7.26 and 10.7. The

maximum cation exchange capacity of zeolite was evaluated as 1.21 meq/g. Furthermore, mercury adsorption with zeolite was found to be rapid, reversible, first order reaction. Equilibrium was reached after 15 min.

Moreover, kinetic of adsorption and adsorption isotherms of mercury adsorption by several adsorbents were investigated by many researchers. Benhammou *et al.*, (2005) studied the adsorption of mercury(II) and chromium(VI) in aqueous solution onto Moroccan stevensite. The adsorption study of this experiment examined the influence of the pH solution on the mercury(II) adsorption and it was found that the amount adsorbed of mercury(II) increased with increasing pH from 1.5 to 4. This can be explained by the diminution of the competition between H^+ protons and mercury(II) cations towards the adsorption sites. Besides, the kinetic of mercury(II) adsorption was studied by using three concentrations of mercury(II) which are 0.5, 0.25 and 0.125 mmol/l. From the results, the adsorption of mercury(II) is rapid during the first 20 minutes and the equilibrium is then attained within 40 minutes. Several simplified kinetic models such as pseudo-first-order, intra-particle diffusion, external mass transfer and pseudo-second-order can be used to analyze the experimental data of the adsorption kinetic but only pseudo-second-order agrees with the reaction:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

(2.30)

where k (g mmol^{-1}min^{-1}) is the rate constant, $v_0 = kq_e^2$, the initial adsorptionrate (mmol g^{-1}min^{-1}), q_t, q_e (mmol/g) are the adsorbed quantity at time 't' and equilibrium. The initial rate for mercury(II) adsorption is 54.35 mmol kg^{-1}min^{-1}. As the good fitting with pseudo-second-order model ($R^2 > 0.97$) indicated that the adsorption can be controlled by surface complication mechanism.

Kadirvelu *et al.*, (2004) prepared activated carbon from sago industry waste in order to remove mercury(II) especially dispose of sago industry. Sago waste material generated in the preparation process of sago made up of cellulose, hemi-cellulose and lignin. Firstly, effect of agitation time was investigated by using three concentration of mercury(II), 20, 30, 40, 50 ppm and the results showed that the

adsorption of mercury(II) increases with an increase in agitation time and attains equilibrium in 105 min for 20 ppm and 120 min for 30, 40 and 50 ppm mercury(II) respectively. In comparison, the equilibrium time for carbonized waste newsprint fiber which is the research of Aoyama *et al.* is 16 hours for 100 ppm of mercury(II). Hence, this indicated that sago carbon requires lesser contact time for complete removal of mercury(II) compared to activated carbon made from newsprint fiber at optimum conditions. This is due to higher surface area and more functional groups present in the sago waste carbon. Moreover, the first order rate expression given by Lagergren and Svenkar which is

$$\log_{10}(q_e - q) = \log_{10} q_e - K_{ad}t/2.303 \qquad (2.31)$$

were used to investigate kinetic of adsorption of mercury (II) where, q and q_e are the amount of mercury(II) adsorbed by g of carbon at time 't' and at equilibrium time, respectively, and K_{ad} is the rate of adsorption (min^{-1}). The fairly linear plots of $\log_{10}(q_e - q)$ versus time at different initial mercury(II) concentrations confirmed the applicability of the above equation for mercury (II) adsorption onto sago waste carbon. Besides, the Langmuir isotherm model was applied to analyze the adsorption equilibrium of mercury (II) onto sago carbon.

$$C_e/q_e = 1/(Q_o b) + C_e/Q_o \qquad (2.32)$$

Where, C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed (mg/g), and Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The linear plot of C_e/q_e versus C_e showed that the adsorption followed the Langmuir isotherm model for mercury(II) adsorption. The values of Q_o and b were calculated from the slope and intercept of the plot, and the values obtained were $Q_o = 55.6$ mg/g and b = 0.375 l/mg.