# CHAPTER II
# BACKGROUND AND LITERATURE SURVEY


General background on volatile organic compounds emission with the emphasis on hydrocarbon emission, is outlined in this chapter. Starting with overall information, like definition, sources and effects of volatile organic compounds, the focus of this chapter is then shifted to hydrocarbon emission from gasoline storage tanks. This includes mathematical models found in literatures and a proposed model is formulated. Differences in each model are also discussed. Most of materials in the overall information are taken from Environmental Protection Agency of United States (U.S. EPA, 1999a).


## 2.1 Volatile Organic Compounds

### 2.1.1 Definition

VOCs are organic liquids or solids whose room temperature vapor pressure are greater than about 0.01 psia (= 0.0007 atm) and whose atmospheric boiling point are up to about 500°F (= 260°C). It means that most organic compounds with less than about 12 carbon atoms are VOCs. The carbon mentioned here is referred to carbon bonded to carbon, hydrogen, nitrogen, or sulfur, but not carbonate carbon as in $CaCO_3$ nor carbide carbon as in $CaC_2$ or CO or $CO_2$ (Nevers, 1995). Examples of VOCs are benzene and toluene. Generally, VOCs and hydrocarbons are not exactly identical. Unlike hydrocarbons, which contain only hydrogen and carbon, VOCs also have other atoms like oxygen, nitrogen, and sulfur.

### 2.1.2 Effects of VOCs

VOCs affect not only human health but also the environment because VOCs are strongly irritating pollutants and a major component of photochemical smog. At certain concentration levels, they are also very toxic. Moreover, VOCs are also known as a contributor to the formation of ozone (Nevers, 1995).

Ozone is a highly reactive form of oxygen, which is known as the Earth's protective cover (the ozone layer) in the stratosphere. However, in the air at ground level, ozone is the powerful irritating pollutant. The target organs are lungs and eyes. At 0.015 ppm, ozone produces a barely detectable odor. At 1 ppm, it produces a disagreeable sulfur-like odor and may cause headache, irritation of eyes and the upper respiratory tract (Lewis and Sax, 1987). Ozone has also been shown to damage vegetation such as trees and crops.

A mixture of ozone with other pollutants is called smog. In summer, smog can damage vegetation and has adverse effects on human health. It has been shown that photochemical smog strongly affects the growth of certain crops. For example, the Congressional Research Service of the U.S. Library of Congress found that the impacts of photochemical smog are evident in annual crop yield decreases estimated at 1.9-4.3 billion dollar (Panich *et al.*, 1995).

Some VOCs such as benzene have been identified as toxic or mutagenic at high concentration levels, at which are, sometimes, found in urban environments. Benzene is an acute as well as a chronic toxicant. Target organs to acute and chronic poisoning are the blood, bone marrow, central nervous system, respiratory system, and also irritant to eyes, nose and skin. Exposure to benzene for a long time can cause of cancer (Patnaik, 1992). Table 2.1 shows effects of benzene vapor on human beings.

Table 2.1 Effects of benzene vapor on human beings (Thorpe, 1978)

| Concentration | | Duration of Exposure (min) | Effects |
|---|---|---|---|
| ppm | mg/l | | |
| 20,000-19,000 | 65-61 | 5-10 | Fatal |
| 7,500 | 25 | 30 | Dangerous to life |
| 3,000 | 9.6 | 30 | Endurable |
| 1,500 | 4.8 | 60 | Serious symptoms |
| 500 | 1.6 | 60 | Symptoms of illness |
| 150-50 | 0.48-0.16 | 300 | Headache, lassitude, weariness |
| 25 | 0.08 | 480 | None |

Ozone is formed when emissions of nitrogen oxides (NO) and VOCs are combined in hot, stagnant air masses, and in the presence of sunlight. This phenomenon generally occurs in summer time. A general interaction of NO, $NO_2$ and $O_3$ in the atmosphere is described as follows (Nevers, 1995):

$$NO_2 + hv \rightarrow O^* + NO \tag{2.1}$$

where $hv$ represents photon of light, $O^*$ represents oxygen radical, and NO represents nitrogen oxide,

$$O^* + O_2 + M \rightarrow O_3 + M \tag{2.2}$$

where $M$ represents a gas molecule like $N_2$ or $O_2$, and

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2.3}$$

$NO_2$ is decomposed by a light photon to produce NO and the oxygen radical $O^*$. That radical reacts with $O_2$ to form $O_3$. Then $O_3$ reacts with NO to form $NO_2$ and releases $O_2$.

The VOCs convert NO to $NO_2$ without using $O_3$, so that there are not enough NO molecules to react with all the $O_3$ molecules, and $O_3$ will accumulates in the atmosphere. This is another cause of ozone formation. A reaction mechanism that explains the reaction between VOCs and NO to form $NO_2$ without using $O_3$ is described below (Nevers, 1995):

$$OH + VOCs \rightarrow RO_2 + H_2 \tag{2.4}$$

$$RO_2 + NO \rightarrow NO_2 + RO \tag{2.5}$$

$$RO + O_2 \rightarrow RCHO + HO_2 \tag{2.6}$$

and
$$HO_2 + NO \rightarrow NO_2 + OH \tag{2.7}$$
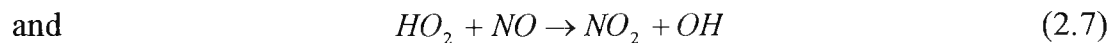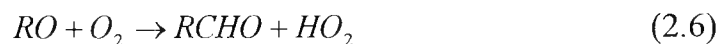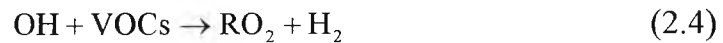
Rearranging equation 2.4 to 2.7 yields

$$VOCs + 2NO + O_2 \rightarrow H_2O + RCHO + 2NO_2 \tag{2.8}$$

One way to reduce the amount of ozone in the atmosphere can be achieved by adding $NO_2$ to the atmosphere because increasing $NO_2$ generates more NO (see Equation 2.1). The large amount of NO thus can react with VOCs as shown in Equation 2.8 and the remaining reacts with ozone as shown in Equation 2.3. And that helps decreasing the amount of ozone in the environment (Nevers, 1995).

### 2.1.3 Sources of VOCs

VOC emission can be found from large sources such as petroleum industries, paper industries, and wastewater treatment. Although some VOCs are emitted from large sources, but most VOCs are considerably

emitted from small sources, such as automobiles, bottles of fingernail polish remover, spray paint cans and solvent usage (Nevers, 1995).

CONCAWE, an oil company in Belgium, estimated that 2% of the man-made hydrocarbons are from evaporation of fuels. Among the fuels, gasoline is one that most easily vaporized, estimated as a loss of 2.78 g/l during transport, storage and refueling. According to Thai National Energy Policy Office, in Bangkok Metropolitan area, where the consumption of gasoline station is about 2 billion litres per year, the estimated emission is 5,560 tons per year (Panich et al., 1995).

Baldarano et al. (1998) presented the data of VOCs emission in urban/suburban of Martorell in Spain as shown in Table 2.2. From this table, gasoline traffic and gas station emit a large amount of VOCs. Gasoline traffic emits VOCs from vehicles on the road while gas stations emit VOCs from vents of gasoline storage tanks. In gas stations, the gasoline storage tanks are located underground and vents are used to control pressure inside the tanks. These vents are the major sources for the VOC emission, especially, when there is a transfer of gasoline from tank trucks to the underground tanks. Furthermore, VOC emission occurs when gasoline is transferred from the underground tanks to customer's vehicles. Environment conditions around gas stations also play an important role to the emission rate.

## 2.2 Literature Surveys

National Energy Policy Office of Thailand (Panich et al.,1995) reported gasoline vapor emitted during refueling of gasoline at 20 gasoline stations in Bangkok and 5 stations in Chon Buri. Five brands of gasoline that used in this research were Bangchak, Esso, Caltex, Shell and PTT. Moreover, the same type of data was also measured when gasoline was transferred from

**Table 2.2** Variance of the data explained by the components identified
(Baldarano *et al.*, 1998)

| Data | Source | %variance | Cumulative variance |
|---|---|---|---|
| 1 | Gasoline traffic and gas stations | 29.4 | 29.4 |
| 2 | Manufacture of aromas and essences Wastewater facility | 20.6 | 50.0 |
| 3 | Manufacture of chlorinated chemicals Biogenic emissions | 7.6 | 57.6 |
| 4 | Use and production of solvents and lacquers | 6.9 | 64.5 |
| 5 | Diesel traffic | 6.2 | 70.7 |
| 6 | Noise | 5.3 | 76.0 |

loading trucks to storage tanks at Shell Oil depot and Esso (Thailand) Oil depot. Gasoline compositions from 5 brands were also analyzed in this study. The results showed that concentrations of non-methane hydrocarbon (NMHC) at the gasoline stations during the non-refueling period were in the range of 0-25 ppm with an average of 15 ppm. During the refueling, the concentration varied in the range of 1-2 ppm up to more than 350 ppm with 25% of measurements in the range of 0-25 ppm and 22% has concentration greater than 350 ppm. PTT, Bangchak and Shell stations showed highest frequency of measurement in the concentration range of 0-25 ppm while Caltex was at 26-50 ppm and Esso was greater than 350 ppm.

The hydrocarbon components were mainly $C_4$, $C_5$, $C_6$, $C_7$, benzene and toluene for most of the gasoline brands. The highest frequency of measurement found for $C_4$, $C_5$, $C_6$, $C_7$ and benzene were at 0-1,000 microgram/cubic meter of air while toluene was found mostly in the range of 2,000-3,000 microgram/cubic meter of air (Panich *et al.*,1995).

A similar study was also done by King Mongkut's Institute of Technology, Thonburi (1995). Using a mathematical model to predict the amount of gasoline vapor emission was incorporated in this work. The results showed that total emission rate from the standing loss and filling loss in Thailand was 42,680,000 pounds per year or 19,400,000 kilograms per year.

U.S. Petroleum Committee of the Air Pollution Control Association (1971) prepared the informative report NO.2. This work reported the control of hydrocarbon vapor emissions from petroleum storage tanks. Evaporation loss of liquids, description of emission control equipment, and estimation techniques for the reduction were included in this report.

Nevers (1995) studied controlling of VOCs emission. One of his work that related with this research was emission of gasoline from underground storage tanks and refueling vehicles in gasoline stations. Nevers used mathematical equations to evaluate the fraction of gasoline emitted in vapor per liquid gasoline filled and the results showed that the total emission in the United States was 400,000 gallon per day.

U.S. Environmental Protection Agency (1999b) reported a study of evaporation emission from transportation and storage of petroleum liquid in service stations, motor vehicle tanks and large storage tanks. Furthermore, this report gave a set of equations that can be used to determine the amount of gasoline emitted from the standing loss and filling loss. This model is based on mass balance fundamental also it includes expansion factor and saturation factors in the equations.

Crowl and Louvar (1990) proposed a set of equations that can be used to determine the amount of gasoline emission from standing storage loss and filling loss (refueling loss). A main difference between this model and the U.S. EPA is how mass transfer coefficient terms are defined.

Another similar model to the one proposed by Crowl and Louvar (1990) and U.S. EPA (1995) was presented by Geankoplis (1993). The

concept of this model is to employ mass transfer equations, like Crowl's model, and it also includes a distance that vapor diffuses in the container.

## 2.3 Hydrocarbon Emission in Gasoline Storage Tanks

Generally, hydrocarbon emission in a gasoline storage tank is due to standing loss and filling loss (refueling loss). Major source of gasoline vapor emission is the filling loss that happens when gasoline vapor in the headspace of a storage tank is displaced to the atmosphere by gasoline liquid being loaded into the tank. The quantity of the loss in a storage tank filling depends on several variables. They are methods and rates of filling, tank configurations, and gasoline temperature, vapor pressure and composition of gasoline. The other source of vapor emission from a gasoline storage tank is breathing of the tank. This results from increasing of ambient temperature, which causes liquid gasoline to expand and push gasoline vapor out of the storage tank. Table 2.3 shows several types of hydrocarbon emission from a gasoline storage tank that compiled by U.S. Environment Protection Agency (U.S. EPA, 1999).

## 2.4 Model for VOCs Emission

Models of U.S. EPA and Nevers are discussed in details here. Then, a new model is proposed. Differences between the new model and the previous ones are also mentioned.

### 2.4.1 U.S. EPA Model

The mathematical models developed by the Environmental Protection Agency of United States in 1999 has been used to approximate the amount of organic and petroleum emission from storage tanks. This model is

**Table 2.3** Evaporative emissions from gasoline storage tanks operations
( U.S. EPA, 1999b)

| Emission Source | Emission Rate | |
|---|---|---|
| | mg/l | lb/10$^3$ gal |
| -Filling underground tank (Stage I) | | |
|   Submerged filling | 880 | 7.3 |
|   Splash filling | 1,380 | 11.5 |
|   Balanced submerged filling | 40 | 0.3 |
| -Underground tank breathing and emptying | 120 | 1.0 |
| -Vehicle refueling operations (Stage II) | | |
|   Displacement losses (uncontrolled) | 1,320 | 11.0 |
|   Displacement losses (controlled) | 132 | 1.1 |
|   Spillage | 80 | 0.7 |

based on mass balance inside a storage tank. The amount of gasoline loss is equal to gasoline vapor that accumulates in the vapor space of the storage tank. Moreover, expansion factor and saturation factor are included in this model for more accuracy. The main equation of the model is

$$L_S = V_V W_V K_E K_S \qquad (2.9)$$

where

$L_S$   = standing storage loss, lb/yr

$V_V$   = vapor space volume, ft$^3$

$W_V$   = vapor density, lb/ft$^3$

$K_E$   = vapor space expansion factor, dimensionless and

$K_S$   = vented vapor saturation factor, dimensionless

The tank vapor space volume ($V_V$) can be calculated as follows

$$V_V = \frac{\pi}{4} D^2 H_{VO} \qquad (2.10)$$

where

$V_V$   = vapor space volume, ft$^3$

$D$   = tank diameter, ft and

$H_{VO}$   = vapor space outage, ft

Vapor density ($W_V$) is estimated by

$$W_V = \frac{M_V P_{VA}}{R T_{LA}} \qquad (2.11)$$

where

$W_V$     = vapor density, lb/ft$^3$

$M_V$     = molecular weight of VOC, lb/lb-mole (See Appendix A)

$P_{VA}$     = true vapor pressure, psia (See Appendix A)

$R$     = the ideal gas constant, 10.731 psia.ft$^3$/lb-mole.R, and

$T_{LA}$     = daily average liquid surface temperature, R (See Appendix A)

Vapor space expansion factor ($K_E$) is calculated with the following equations:

$$K_E = \frac{\Delta T_V}{T_{LA}} + \frac{\Delta P_V - \Delta P_B}{P_A - P_{VA}} \qquad (2.12)$$

where

$K_E$     = vapor space expansion factor, dimensionless

$\Delta T_V$     = daily temperature range, R (See Appendix A), and

$\Delta P_V$     = daily vapor pressure range, psi

$P_A$     = atmospheric pressure, psia

$$\Delta P_V = P_{VX} - P_{VN} \quad \text{or} \qquad (2.13)$$

$$\Delta P_V = \frac{0.5BP_{VA}\Delta T_V}{T_{LA}^2}$$ (2.14)

$P_{VX}$ = vapor pressure at maximum liquid temperature, psi

$P_{VN}$ = vapor pressure at minimum liquid temperature, psi, and

$\Delta P_B$ = breather vent pressure setting range, psi

$$\Delta P_B = P_{BP} - P_{BV}$$ (2.15)

$P_{BP}$ = breather vent pressure setting, psig, and

$P_{BV}$ = breather vent vacuum setting, psig and

Vented vapor saturation factor ($K_S$) is calculated by

$$K_S = \frac{1}{1+0.053P_{VA}H_{VO}}$$ (2.16)

where

$K_s$ = vented vapor saturation pressure, dimensionless, and

$H_{VO}$ = vapor space outage, ft

Generally, these equations are applied to above ground storage tanks. All of solar parameters have not effect on system because this work focus only on underground storage tank. Therefore, the present work will neglect some parameters such as tank paint solar absorption ($\alpha$) and daily total solar insulation factor (I) before applying this model.

### 2.4.2 Nevers Model

The Nevers model was developed based on two fundamentals (Nevers, 1995). First, it is the vapor emit resulting from the simple thermal expansions of vapor and liquid in a storage tank. Second, it is the vapor emit resulting from the vaporization of gasoline as the temperature is raised.

The volume of vapor emitted due to simple thermal expansion is

$$\begin{pmatrix} \text{Volume of} \\ \text{vapor emitted} \end{pmatrix} = \begin{pmatrix} \text{increase in} \\ \text{vapor volume} \end{pmatrix} + \begin{pmatrix} \text{incrase in} \\ \text{liquid volume} \end{pmatrix} - \begin{pmatrix} \text{increase in} \\ \text{tank volume} \end{pmatrix} \qquad (2.17)$$

The fractional change in volume caused by heating is normally expressed as

$$\frac{dV}{V} = \alpha dT \qquad (2.18)$$

where

T    = system temperature

α    = thermal expansion coefficient

Substituting Equation (2.18) in Equation (2.17), yields

$$\left( \frac{\Delta V}{V} \right)_{\text{expelled}} = \left( \frac{V_{\text{vapor}}}{V_{\text{tank}}} \alpha_{\text{vapor}} + \frac{V_{\text{liquid}}}{V_{\text{tank}}} \alpha_{\text{liquid}} - V_{\text{tank}} \right) \qquad (2.19)$$

The volume of vapor emitted due to vaporization is

$$\left( \frac{\Delta V_{\text{emitted}}}{V_{\text{tank}}} \right) = \left( \frac{V_{\text{vapor}}}{V_{\text{tank}}} \right) \left( y_{\text{gasoline final}} - y_{\text{gasoline initial}} \right) \qquad (2.20)$$

where

$y_{\text{gasoline final}}$    = final vapor mole fraction of gasoline and

$y_{\text{gasoline initial}}$    = initial vapor mole fraction of gasoline

### 2.4.3 Proposed Model

The Nevers model is difference from the U.S. EPA model in the basic fundamental. Thermal expansion and vaporization of materials are employed to formulate the Nevers model while the U.S. EPA model is emphasized on mass balance including expansion and saturation factors.

Compiling these concepts together, it can produce a more efficiency model that will be applied in this work.

In the present work, a proposed model to predict the standing loss from a gasoline storage tank is developed also based on mass balance inside a storage tank. Emission from the tank is due to liquid expansion, vapor expansion and especially diffusion. It has to be pointed out that diffusion influences on the gasoline emission in some extent. Moreover, size of the ventillation tube (vent size) relating to diffusion effect is also incorporated into the present model. Therefore, including diffusion factor in this model should promote more accuracy results than the other models. The expansion of storage tank did not mention in this model because this expansion was very low value compared with liquid expansion and vapor expansion. The model can be written as

$$Standing\ loss(L_S)\ =\ Loss\ from\ gasoline\ diffusion\ +$$
$$Loss\ from\ vapor\ expansion\ +$$
$$Loss\ from\ liquid\ expansion \tag{2.21}$$

Loss from gasoline diffusion ($L_D$) was derived from the Fick's law of molecular diffusion by multiplying molecular weight and cross sectional area of the ventillation tube.

$$L_D = M_V A J_{AZ} \tag{2.22}$$

$$J_{AZ} = \frac{D_G P_{VA}}{RT\Delta z} \tag{2.23}$$

where

$L_D$ = loss from diffusion, g/day

$M_V$ = vapor molecular weight, lb/lb-mole

$A$  = vent area, $cm^2$

$J_{AZ}$  = molar flux of component A in z direction, $mol/m^2 s$

$D_G$  = molar diffusivity of gasoline, $cm^2/s$ (See Appendix B)

and  $\Delta z$  = vent height, cm

Substituting molar flux ($J_{AZ}$) in Equation (2.22), it yields

$$L_D = \frac{D_G A}{\Delta z}\left(\frac{P_{VA}M_V}{RT}\right)$$

(2.24)

and from Equation (2.11)  $W_V = \frac{P_{VA}M_V}{RT}$

Equation (2.24) becomes  $L_D = \frac{D_G A}{\Delta z}W_V$

(2.25)

Loss from vapor expansion ($L_{VE}$) is estimated by

$$L_{VE} = V_V \alpha_V W_V$$

(2.26)

where

$L_{VE}$  = loss from vapor expansion, g/day

$V_V$  = vapor space volume, litre

$\alpha_V$  = vapor expansion coefficient, dimensionless (See Appendix B)

$W_V$  = vapor density, g/litre

Loss from liquid expansion ($L_{LE}$) is increasing of liquid volume by simple thermal expansion. Because gasoline vapor in the headspace was replaced and pushed out of a storage tank in the same volume of expanded liquid, therefore gasoline vapor density can used to evaluate loss from liquid expansion. Loss from liquid expansion, $L_{LE}$, can be calculated from

$$L_{LE} = V_L \alpha_L W_V \tag{2.27}$$

where

$L_{LE}$ = losses from liquid expansion, g/day

$V_L$ = volume of liquid gasoline, litre

$\alpha_L$ = liquid expansion coefficient, dimensionless (See Appendix B)

$W_V$ = vapor density, g/litre

Substituting Equation (2.25), (2.26) and (2.27) into, Equation (2.21), it gives

$$L_S = \frac{D_G A}{\Delta z} W_V + V_V \alpha_V W_V + V_L \alpha_L W_L \tag{2.28}$$

or

$$L_E = \left( \frac{D_G A}{\Delta z} + V_V \alpha_V + V_L \alpha_L \right) W_V \tag{2.29}$$