

CHAPTER 2

LITERATURE REVIEW



2.1 General

The Bangkok metropolitan area, like many other megacities in the world, has serious air pollution problems. The Pollution Control Department, Thailand's (2000) report on "Pollution Situation in Decade, 1990-2000" indicated that dust (both total dust and respiratory dust) is a major air pollutant. However, the severity of this problem is intending to decrease. While the secondary air pollutant, ozone is shown increasing trend. Other air pollutants such as carbon monoxide, nitrogen dioxide, sulfur dioxide and lead are still under the limit standard.

The Thai government has tried to reduce VOCs emission, the considering control VOCs by implementation of the vapor recovery systems. Gasoline vapors are generally of concern since it was the source of ozone formation or photochemical smog and hazardous and toxicity. The major compounds in gasoline vapor produced ozone at defferent rates as shown in Table 2.1.

2.2 Major sources of VOCs

Sources of hydrocarbons include natural sources and anthropogenic sources. The most serious threat comes from pollutants released into the air as a result of human activities. Major sources of air pollution including VOC's sources were shown in Table 2.2.

Natural sources are biological processes such as respiration and transpiration of trees and grasses, microorganisms in soil, biodegradation of plants and animal wastes and organisms in the ocean. Major anthropogenic sources of hydrocarbons are vehicle fuel such as the exhaust gas and vapor of gasoline. The exhaust gas in both urban and burned gasoline.

Table 2.1 The reaction rate coefficient of various hydrocarbon compounds and its concentration to form ozone

Hydrocarbon Species	Rate Coefficient ($k_{OH} \times 10^{12}$)	Mean Concentration (ppb)	Ozone Production (ppb/h)
Isobutane	51.4	0.21	0.39
Propylene	26.3	0.27	0.26
Ethylene	8.52	0.67	0.21
1,2,4-trimethylbenzene	32.5	0.15	0.18
(m+p)-xylene	19.0	0.21	0.14
1,3,5-trimethylbenzene	57.5	0.06	0.13
Trans-but-2-ene	64.0	0.05	0.12
Toluene	5.96	0.46	0.10
Acetylene	0.82	1.38	0.04
Isobutane	2.33	0.23	0.02
Ethane	0.26	1.85	0.02
1,2-dimethyl-4	32.5	0.01	0.02
Ethylbenzene	1.32	0.24	0.01
Benzene	101	0.05	0.18
Isoprene	53.7	0.01	0.01
α -pinene			

Source: R.G.Derwent, 1999; cited in Pollution Control Department, August 2001

Table 2.2 Air Pollution Emissions by Pollutant and Source, 1993

In thousands of tons.

Source	Particu- Lates ¹	Sulfur Dioxide	Nitrogen Dioxide	VOCs	Carbon Monoxide	Lead
Total	45,489	21,888	23,402	23,312	97,208	4,885
Fuel combustion,	1,212	19,266	11,690	648	5,433	497
Stationary sources						
Electric utilities	270	15,869	7,782	36	322	62
Industrial	219	2,830	3,176	271	667	18
Other fuel combustion	723	600	732	341	4,444	417
Residential	674	178	(NA)	310	4,310	9
Industrial processes	533	1,852	905	3,901	5,219	2,281
Chemical and allied	75	450	414	1,811	1,998	109
Product manufacturing						
Metals processing	141	580	82	74	2,091	2,118

Table 2.2 Air Pollution Emissions by Pollutant and Source, 1993 (Con't)

Source	Particu- Lates ¹	Sulfur Dioxide	Nitrogen Dioxide	VOCs	Carbon Monoxide	Lead
Petroleum and related Industries	26	409	95	720	398	(NA)
Other	311	413	314	486	732	54
Solvent utilization	2	1	3	6,249	2	(NA)
Storage and transport	55	5	3	1,861	56	(NA)
Waste disposal and recycling	248	37	84	2,271	1,732	518
Highway vehicles	197	438	7,437	6,094	59,989	1,383
Light-duty gas vehicles And motorcycles	(NA)	(NA)	3,685	3,584	39,452	1,033
Ligh-duty trucks	(NA)	(NA)	1,3871	612	14,879	(NA)
Heavy-duty gas vehicles	(NA)	(NA)	304	314	4,292	(NA)
Diesels	(NA)	(NA)	2,061	315	1,366	(NA)
Off highway ²	395	278	2,986	2,207	15,272	206
Miscellaneous ³	42,828	11	296	893	9,506	(NA)

NA Not available

¹ Represents both PM-10 fugitive dust

² Includes emissions from farm tractors and their farm machinery, construction equipment, industrial machinery, recreational marine vessels, and small general utility engines such as lawn mowers

³ Includes emissions such as from forest fires and various agricultural activities, fugitive dust from paved and unpaved roads, and other construction and mining activities, and natural sources

Source: Source of tables 374 and 375: US Environmental Protection Agency, National Air Pollutant Emission Trends, 1900-1933. U.S. Bureau of the Census, Statistical Abstract of the United States 1995, 155th ed (Washington, D.C. : US. Government Printing Office, 1995). P.233 – principles of Environmental Management

The latest emission database from the Pollution Control Department (PCD) in 1997 shown in Table 2.3. The emission sources were all in Bangkok and its vicinity :Nonthaburi, Pathum Thani, Samut Prakarn and Nakorn Pathom. Gasoline vapor emission that has known as VOC emission seems to be a major source of VOC of area source.

The characteristic of hydrocarbon found in Bangkok was studied by the Commonwealth Scientific and Industrial Research Organization (CSIRO) with the corporation with the PCD in year 2001. All the major hydrocarbon found were categorized as the hazardous air pollutant as shown in Table 2.4

Table 2.3 Sources of NO_x and HC emission from various activities in Bangkok, 1997.

Activities	NO _x		VOC	
	Ton/year	%	Ton/year	%
Point source	6,552.89	100	381.53	100
Factories	6,544.71	100	380.78	100
Crematoria	2.3312	0	0.2619	0
Incinerator	5.847	0	0.493	0
Area source	6,434.08	100	8,467.86	100
Residential	596.82	8.9	244.49	2.9
Airport	5,864.20	91.1	727.57	8.6
Gas Service Station	-	-	7,495.8	88.5

Source : Pollution Control Department, March 2000

Table 2.4 Characteristics of Bangkok Major Hydrocarbon Sources

Paint	m,p-xylene as a major peak, toluene as a major in one sample
Vehicle Exhaust-Diesel	C3 to C4 alkanes with ethylene as a major peak, aromatics with benzene as a peak, C2 to C10 alkne
Printing	C4 to C10 alkanes with pentane peaks, aromatics with toluene, xylenes, 1,2,4-trimethylbenzene and benzene
Refinery Fugitive	C2 to C10 alkanes with major isopentane peak; aromatics with toluene peak
Fuel-Distribution-Petrol	C3 to C9 alkanes with major isopentane peak; aromatics with toluene peak
Vehicle Exhaust-Petrol	C2 to C10 alkanes with an isopentane peak; aromatics with a major toluene and secondary ethylbenzene peak; alkenes with ethylene peak; alkynes with acetylene peak
Fuel distribution-Diesel	C3 to C10 alkanes with a major isopentane peak; aromatics with a toluene peak
Boiler stack Exhaust	C6 alkanes, a major toluene peak
Vegetation Waste Burning	C2 to C4 alkanes, C2 to C4 alkenes, C2 to C4 alkynes, aromatics including benzenem toluene
Road In-traffic	C2 to C10 alkanes with a major isopentane peak and butane and hexane peaks, C2 to C6 alkenes with an ethylene peak, aromatics particularly toluene, benzene, m,p-xylenes with an acetylene peak
Background Ambient concentration	C2 to C10 alkanes with a isopentane peak; aromatics with a toluene peak; alkenes with a ethylene peak; an isoprene peak; alkynes with an acetylene peak

Source: Pollution Control Department, 2001

2.3 Ozone, VOCs and Hazardous Air Pollutants (HAPs)

2.3.1 Photochemical Reaction and Ozone Formation

The most widespread air pollution problem in areas with temperate climates is ozone, one of the photochemical oxidants, that results from the reaction of nitrogen oxides and hydrocarbons in the presence of sunlight. (U.S. EPA, 1978: cited in Michael P. Walsh, 1995). High ozone concentration depends on the concentration of both VOC and nitrogen oxide. The ratio of both chemicals should be suitable, if the ambient air has low nitrogen oxide “NO_x Limited” or low VOC “VOC Limited”, the ozone concentration would be low. (Kenneth Wark et al.,1998)

In general, hydrocarbons are classed by reactivity into two groups, methane and non-methane hydrocarbons. Methane is relatively stable and low reactivity to any reaction. The reactivity of hydrocarbon on ozone formation is categorized into 5 groups. Each group has 5 times higher reactivity than the previous tier.

Group 1 Methane

Group 2 Ethane

Group 3 Propane, Iso-propane, Ethene, Benzene, Toluene

Group 4 p-xylene, Propene, 1,3-Butadiene, B-Pinene

Group 5 d-Limonene

The coefficient of the reaction rate between hydrocarbon and hydroxyl radical is shown in Table 2.5. Each hydrocarbon produces ozone at a different rate. However, the hydrocarbon that has a low k_{OH} value but at high concentration could produced ozone in the same range as the hydrocarbon that has high k_{OH} value but low concentration. (PCD, 2001)

Table 2.5 The reaction rate coefficient of various hydrocarbons and its concentration to form ozone

Hydrocarbon Species	Rate Coefficient ($k_{OH} \times 10^{12}$)	Mean Concentration (ppb)	Ozone Production (ppb/h)
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Acetylene	0.82	1.38	0.04
Isobutane	2.33	0.23	0.02
Ethane	0.26	1.85	0.02
1,2-dimethyl-4 ethylbenzene	32.5 1.32	0.01 0.24	0.02 0.01
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Source: R.G.Derwent, 1999; cited in Pollution Control Department, August 2001

When inhaled, even at very low levels, ozone could caused an acute respiratory problems, aggravate asthma, caused significant temporary decreases in lung capacity of 15 to over 20 percent in some healthy adults and also inflammation of lung tissue. Moreover, ozone could introduced inflammation of lung tissue besides it made people more susceptible to respiratory illnesses, including bronchitis and pneumonia (US.EPA, Office of Air & Radiation[OAR], 2002)

The OAR also stated that Ground-Level Ozone could harm the environment. It interferes with the ability of plants to produce and store food, so that growth, reproduction and overall plant health are compromised. By weakening sensitive vegetation, ozone makes plants more susceptible to disease, pests, and environmental stresses. The effects of ground-level ozone on long-lived species such as trees are believed to add up over many years so that whole forests or ecosystems can be affected. For example, ozone can adversely impact ecological functions such as water movement, mineral nutrient cycling, and habitats for various animal and plant species. This affect has also been demonstrated in numerous studies that photochemical

pollutants seriously impair the growth of certain crops. For example, the Congressional Research Service of the U.S. Library of Congress found that “the short-run or immediate impacts of ozone are evident in annual crop yield decreases estimated at \$1.9 to \$4.3 billion”. (Congressional Research Service, May 1982; cited in Michael P. Walsh, 1995)

2.3.2 Hazardous Air Pollutants (HAPs)

Hazardous air pollutants, also known as hazardous and or toxic air pollutants are those pollutants that cause or may cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects. EPA has required to control 188 hazardous air pollutants. Benzene, Toluene, Ethyl benzene, Xylenes and methyl tert-butyl ether which all of these found in gasoline vapor as listed by EPA. (U.S.EPA, 2003)

(a) Benzene

Benzene was characterized as a known human carcinogen for all routes of exposure based upon convincing human evidence as well as supporting evidence from animal studies. (U.S. EPA, Integrated Risk Information System [IRIS], 2000). Many case reports and case series have described the association of leukemia with exposure to benzene, either alone or in combination with other chemicals. Most cases were acute myelogenous leukemia, although some were monocytic, erythroblastic or lymphocytic, and some lymphomas have been noted.

EPA has estimated the benzene emissions from pharmaceutical, plastics, resin, and rubber plants at 495 million tons per year. Its new, far more stringent standards for benzene call for reducing current benzene emissions by 97% at storage tanks and coke by-product recovery plants. EPA proposes that emissions from those sources must cut by 94 tons/year through the use of carbon absorbers and incinerators. The new rules expected to lower total industrial emissions of benzene by 90%. According to EPA, half of the U.S. population were exposed to benzene from industrial sources and gasoline. EPA now estimates that three people died with cancer annually caused

by exposure to benzene emissions (Chem. Mktg. Rep. 1986 cited in U.S department of Labor, Occupational Safety & Health Administration [OSHA],).

(b) Toluene

The main effect of inhale toluene vapour is on the central nervous system (CNS). Symptoms are related to the concentration that exposure. At approximately 50 ppm, slight drowsiness and headache have been reported. Irritation of the nose, throat and respiratory tract has occurred between 50 and 100 ppm. The concentrations up to 100 ppm has caused fatigue and dizziness; over 200 ppm, caused similar symptoms to drunkenness (giddiness), numbness, and mild nausea; over 500 ppm, caused mental confusion and incoordination. At high concentrations (estimated at 10,000 ppm) further depression of the central nervous system can result in unconsciousness and death. Most serious incidences of exposure has occurred when vapours has accumulated in confined spaces. (Canada's National Occupational Health & Safety Resources, 1997)

The International Agency for Research on Cancer (IARC) has determined an inadequate evidence for the carcinogenicity of toluene in humans. OVERALL IARC EVALUATION: Toluene is not classifiable as to its carcinogenicity to humans.

(c) Ethylbenzene

Industrial releases and vehicle emissions are identified as the main sources of human and environmental. A review of data on the environmental behaviour and fate of ethylbenzene concluded that ethylbenzene degraded by photo-oxidation and biodegradation. The principal environmental sink is the atmosphere, where photo-oxidation may contribute to photochemical smog formation.

The most extensive section assesses the toxicity studies results in animals by experimented and *in vitro* test systems. These studies support the conclusion that ethylbenzene has low acute and chronic toxicity and also demonstrated no significant mutagenic properties or teratogenicity in the species tested. Data were judged inadequate to assess carcinogenicity and reproductive toxicity.

An evaluation of the limited data on toxicity to humans notes that inhalation is the major route of exposure, though exposure may also occur via skin absorption or ingestion. Toxic effects observation included prenarctic effects on the central nervous system and limited irritation of the mucous membranes and eyes. As occupational exposure to ethylbenzene alone was rare, the report was unable to reach conclusions concerning the worker's health risks. According to the limited data available, a tentative guidance value for inhaled air was established by using an uncertainty factor (WHO, 1996)

(d) Xylene

A section on environmental levels and human exposure summarized the xylene detected in various environmental media i.e. indoor air, near point sources, and the occupational settings data . An inhalation was the most important route of human exposure to xylene. When concerning kinetics and metabolism in laboratory, shown that xylene was rapidly and efficiently metabolized, more than 90% bio-transformed to methyl hippuric acid and excreted by urine. (WHO, 1997).

A review of numerous studies conducted in laboratory animals and *in vitro* test systems cites evidence of chronic effects on the central nervous system following exposure at moderate concentrations. These findings support the limited data available on humans, where studies suggest that exposure to xylene may have an acute impairing effect on the sensory-motor and information-processing functions of the central nervous system. The report found no evidence that xylene is mutagenic or carcinogenic.

(e) Methyl tert-butyl ether (MTBE)

Concerning environmental levels and human exposure, evaporative emissions from oxygenated gasoline were identified as the main source. The widespread exposure via inhalation occur during a time spent at service stations, while driving cars, in public parking garages, and in homes with attached garages. The report also cites data on exposure levels obtained in numerous studies of urban air, in facilities where MTBE is manufactured or blended, and in such occupational settings as service

stations, garages, and the transportation of neat MTBE and fuel mixtures through pipelines, barges, railroad cars, and trucks.

A review of the kinetics and metabolism of MTBE draws on toxicokinetic data derived from the studies in controlled healthy adult volunteers and in occupationally exposed workers. The data indicated that MTBE was rapidly absorbed into the circulation of inhalation. In rodents, the compound is likewise rapidly absorbed and distributed after exposure by both inhalation and oral routes.

From studies in laboratory animals, the reports identified the positive signs of intoxication as depression of the central nervous system, ataxia, and laboured respiration. Most effects on the central nervous system are transient. From a few studies available, the reports concluded that MTBE was moderately irritating to the skin and eyes and induces slight to severe respiratory irritation. Repeated exposure results primarily in increases in organ weights and histopathological effects in the kidney of rats and the liver of mice. The report found no evidence of adverse effects on reproduction, genotoxicity, or mutagenicity. Although limited carcinogenicity studies showed significant increases in tumour incidence, the report judged these findings inconclusive and thus inadequate to support an assessment of carcinogenic risk in humans. (WHO, 1996).

2.4 Gasoline distribution network.

The marketing of petroleum products at wholesale and retail facilities involves and extensive distribution network. Gasoline and other large-volume fuels transportation were distributed primarily by pipeline, ship, and barge to bulk terminals. From bulk terminals, tank trucks generally bring the product to a bulk plant, service station, or commercial customers.

Gasoline and distillate products were produced at the refinery plant and transferred by pipeline, ship, and barge to bulk storage terminals. The products stored in the large tanks before being dispensed into tank trucks for delivery to customers. (Davis, W.T.,ed. 2000). There were an estimated 50 bulk gasoline terminals in

Thailand in year 2000 (Department of Public and Municipal Works, 2000). Some products loaded at bulk gasoline terminals are delivered by truck to bulk plants, which are smaller storage facilities located close to their customers. Tank trucks deliver motor fuels to service stations. The fuels are stored in underground tanks and then pumped directly into motor vehicle fuel tanks using a metering dispenser equipped with a flexible hose and nozzle. The general distribution network in the petroleum-marketing sector is depicted in Figure 2.1. During operations at marketing facilities, emissions of VOCs can occur as a result of product transfer(e.g., loading), during product storage, and from pump, valve, and flange seals and product spillage(Davis, W.T.,ed. 2000))

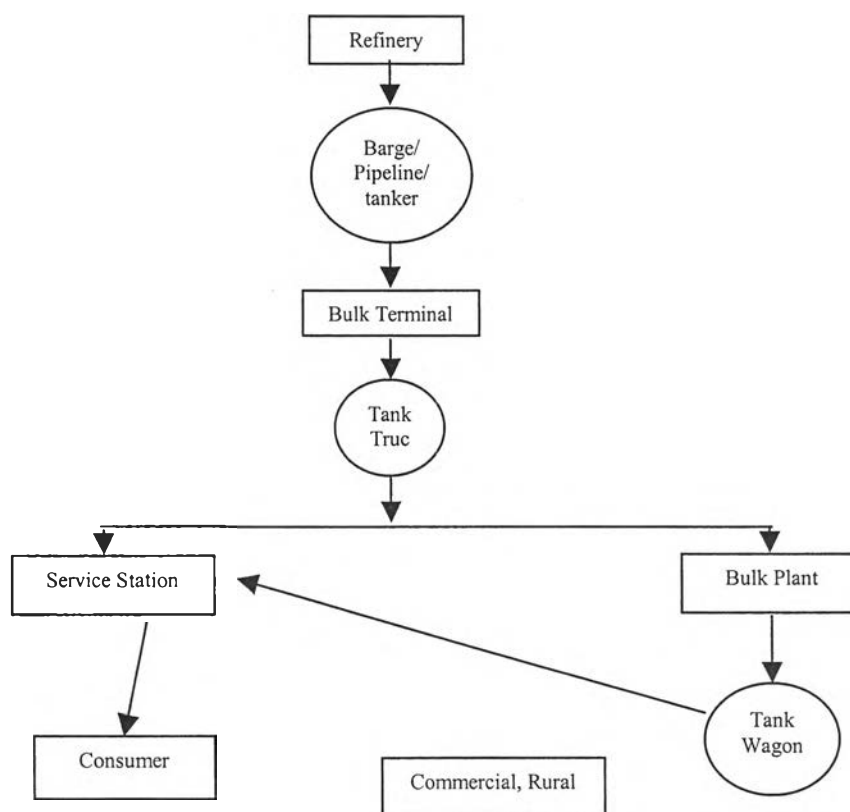


Figure 2.1 Gasoline Distribution Facilities –United State

2.5 Factor influencing gasoline emissions

The pollutants emitted by each of the gasoline distribution facilities are essentially the same. However, the operations that occur at each and the rates of

emissions to the atmosphere differ. The emissions consist of a mixture of VOC vapors and air. The factors influencing emissions, including gasoline composition, temperature, vapor pressure, and methods of loading gasoline. (US.EPA, Office of Air Quality Planning and Standard, 1994)

2.5.1 Hazardous Air Pollutant (HAP) Content of Gasoline Vapor

The vehicles gasoline is a complex hydrocarbon mixture of varying amounts of paraffin, olefins, and aromatics. The report conducted for the EPA by Northeast Corridor in the early 1980's which analyzed gasoline samples in the Northeastern United States. The report has stated that liquid gasoline paraffin contents ranging, 37-67 weight percent, olefins ranging, 0-12 weight percent, and aromatics ranging, 28-52 percent. The average carbon number for gasoline generally falls in the C₅-C₇ range, but gasoline composition could varied widely. The HAP list presented in the Act section 112(b), as amended in 1990, contains additional compounds normally contained in gasoline vapor, including, but not limited to benzene, toluene, hexane, ethylbenzene, naphthalene, cumene, xylenes, n-hexane, 2,2,4-trimethylpentane, and methyl tert-butyl ether (MTBE). (US.EPA, 40 CFR Part 63, February 8, 1994)

The National Institute for petroleum and Energy Research (NIPER) reported that the gasoline composition for the winter of 1991-1992. They found that aromatic volume percentage for unleaded gasoline ranged from 3 percent to almost 65 percent in the samples analyzed, with the averages being 25.9 percent for regular unleaded, 27.9 percent for mid-grade, and 30.3 percent for premium, by approximately. Olefin content ranged from under one to almost 69 percent, with the average reported as 11.6 percent for regular, 9.8 percent for mid-grade, and 6.1 percent for premium.

In Thailand, Teerawet Titsesang (2000) reported on the BTX concentration in four brands of gasoline sample i.e. regular grade (octane91), and premium grade (octane95). The report has shown that the average of benzene, toluene, and xylene were 11,293.13 ppm, 82,810.64 ppm and 27,247.73 ppm respectively in premium grade's gasoline. While the regular grade's gasoline the benzene, toluene and xylene were 19,270.41ppm, 93,397.65 ppm, and 18,608.93 ppm respectively.

There are three grades of unleaded gasoline in Thailand considered by an octane number, 87, 91 and 95. Benzene and aromatic hydrocarbons contained in those are not more than 3.5% by volume and not more than 35% by volume respectively. While an oxygenated compound content is limited solely for unleaded gasoline octane number 95 do not less than 5.5% by volume. (Notice of The ministry of commerce, 1998)

As all the information's above, the variation in liquid composition causes the composition of the emission's vapor vary in a great deal. Currently, the gasoline that distribute in Thailand are the unleaded gasoline octane number 91 (normal gasoline) and 95 (oxygenated gasoline).

(a) Normal gasoline

The office of Air Quality Planning and Standards of US.EPA conducted a study to locate information on gasoline vapor composition in 1994. They revealed that while a great deal of research was being conducted related to the composition of tailpipe emissions from automobiles, information related to the composition of evaporative emissions from gasoline transfer and storage operations was more limited. However, they obtained a sufficient data for establishing a list of common HAP compounds present in gasoline vapor. These are benzene, toluene, ethylbenzene, naphthalene, cumene, all three orientations of xylene (para, meta, and ortho), n-hexane, 2,2,4-trimethylpentane or iso-octane. They also quantified the HAP content of gasoline vapor by analyzing forty-nine gasoline vapor sources. The summary of the data of HAP weight fractions of normal gasoline is shown as Table 2.6.

(b) Oxygenated gasoline

Oxygenates include a broad range of alcohols and ethers. While there are several alcohol's and ethers that are using in unleaded gasoline, two such components, Methyl Tertiary Butyl Ether (MTBE) and Ethanol that has significant of commercial use. Another ether used is Ethyl Tertiary Butyl Ether (ETBE). The use of oxygenates to reduce exhaust emissions of carbon monoxide. However, the addition of oxygen containing compounds to oxygenated gasoline will significantly increase the HAP

content, all other things being equal. (US.EPA, Office of Air Quality Planning and Standards, 1994)

Table 2.6 Vapor profile of normal gasoline

Hazardous Air Pollutant ^a	Minimum	HAP to VOC ratio (percentage by weight)	
		Arithmetic Average	Maximum
Hexane	0.3	1.6	4.4
Benzene	0.2	0.9	2.2
Toluene	0.4	1.3	4.0
2,2,4-trimethylpentane (iso-octane)	0.03	0.8	2.6
Xylenes	0.05	0.5	1.5
Ethylbenzene	0.03	0.1	0.5
Total HAPs ^b	2.0	4.8	11.0

Source : US.EPA, Office of Air Quality Planning and Standards, 1994

^a Cumene and naphthalene were also identified in some of the data points in small quantities. They are not shown as their addition does not significantly change the analysis

^b The total HAP ratios shown in the table are not simply sums of the individual HAPs were calculated for each individual sample in the data base and the values represented in the table reflect the maximum, minimum, and arithmetic average total HAPs of these samples.

It is expected that MTBE was the most common oxygenate used to meet the oxygen requirement. Traditionally, MTBE also used as an octane booster in unleaded gasolines. The Office of Air Quality Planning and Standards, also reported the results of the normal gasoline analysis showed that MTBE to VOC ratios were 8.8 weight percent for the 11 volume percent liquid and 12 weight percent for the 15 volume percent liquid. Consequently, the expectation of that the inclusion of MTBE in the liquid to meet the oxygen demands will increase the HAP to VOC ratio in gasoline vapor from approximately 5 weightpercent to near 16 percent (with the 15 percent MTBE gasoline).

2.5.2 Methods of Loading Gasoline

The method of loading could affect the emissions generated during the gasoline transfer. There are two basic methods of loading, splash and submerged fill. In the splash loading method, the nozzle is inserted into the top of the tank. Significant turbulence and vapor/liquid contact occur during the splash loading operation, the result was high levels of vapor generation and loss. If the turbulence is great enough, the liquid droplets will enter in the vapor's vent.

The second method of loading is submerged fill. This category is further broken down into the submerged fill pipe method, the fill pipe extends almost to the bottom of the tank. In the bottom loading method, a permanent fill pipe method always using bottom loading, the fill pipe is below the liquid surface level. Liquid turbulence was controlled significantly during submerged loading, the vapor generation was much lower than encountered during splash loading. The schematics of closed compartment top loading and bottom loading shown in Figure 2.2. (Institute of Petroleum, 1994)

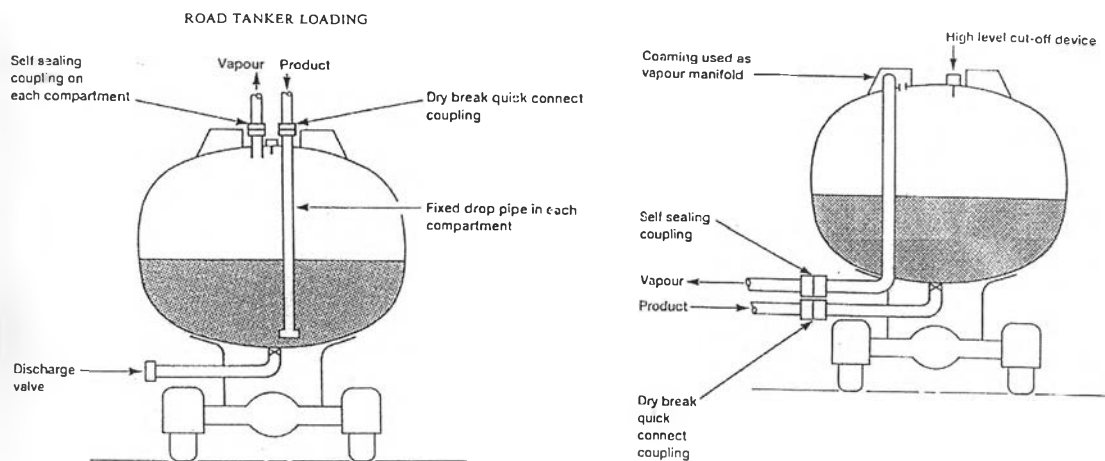


Figure 2.2 Closed compartment top loading and bottom loading

Cargo carriers are sometimes designated to transport only one product, and in such cases are practicing “dedicated service”. Dedicated gasoline cargo carrier return to a loading terminal containing fully or partially air saturated with vapor from the previous load. Cargo tanks may also be “switch loaded” with various products, such as diesel fuel, so that a nonvolatile product being loaded could expelled the remaining

vapors from a previous load of volatile product such as gasoline. These circumstances vary with the type of cargo tank and with the ownership of the carrier, the petroleum liquids being transported, geographic location, and season of the year.

One control measure for gasoline tank trucks is called “vapor balance service”, the cargo tank truck retrieves the vapors displaced during product unloading at bulk plants or service stations and transports the vapors back to the loading terminal. A truck that cargo tank is normally in vapor balance service was saturated with the organic vapors. Therefore the presence of these vapors at the start of submerged loading results in greater loading losses than encountered during non-vapor balance, or “normal”, service. (US.EPA, Office of Air Quality Planning and Standards, 1994)

2.5.3 Temperature and Vapor Pressure

Volatility and temperature are two major impacts of emissions from the gasoline evaporation. The rate of evaporation increases with the increasing temperature, as this increased temperature provides more kinetic energy to the liquid, caused more molecules to vaporize.

Reid vapor pressure (RVP) is a standard industry measure of fuel volatility and represents the vapor pressure of the fuel at 100 °F. The RVP of gasoline is adjusted through blending at the refinery and take account for temperature and pressure differences across the United States. In the summer when warm temperatures enhance volatilization, gasoline can be blended with a lower RVP and still provide ample vaporization for combustion in the vehicle engine. Reducing RVP in the summer, therefore, reduces emissions from gasoline transfer without reducing vehicle performance. Too high an RVP causes vapor lock. During the winter period when cold temperatures inhibit the volatilization, gasoline could be blended with a higher RVP to ensure sufficient volatilization for engine start-up and operation. This increase in RVP when temperatures decrease, and decrease in RVP when temperatures increases, is an attempt to provide a uniform fuel volatility for smooth engine performance all year. (US.EPA, Office of Air Quality Planning and Standards, 1994)

2.6 Vapor recovery system

The emission control of gasoline distribution and market has been addressed in many developed countries, including Thailand. In Europe, two further Directives have been prepared to control VOC emissions – one aimed at reducing vapor emission during gasoline distribution and the other during the refuelling of automobiles.

The reduction of emission during the storage, loading, and off-loading of gasoline is known as “Stage I” vapor control. The control of emission generated during automobile refuelling can be undertaken either by using a system on-board the automobile or modifying the gasoline dispenser and feeding the vapor back to the service station storage tank. The latter is known as “Stage II” vapor control. (Institute of Petroleum, 1992)

Both Stage 1 and 2 comprise of “closed” systems. Uncontrolled emissions occur when any of the “open” tanks in the distribution and marketing chain are filled, eg., the compartment of a road tanker; a rail tank car; the hold of a marine vessel; the underground tank at a service station; or the fuel tank on an automobile. In a closed system vapor is prevented from being emitted to the atmosphere by being captured and collected for subsequent processing, for example in a vapor recovery unit (VRU).

2.6.1 Type of Vapor Recovery Unit

Currently there are four major types of basic process for recovering vapor. Vapor recovery systems however can employ a combination of processes in one unit. Most involve the separation of the hydrocarbons from the air in the vapor stream and their subsequent absorption into a liquid gasoline stream. (The Institute of Petroleum, 1992)

(a) Carbon Adsorption : This type of vapor recovery systems, the incoming vapor was passed through a bed of granular carbon. The hydrocarbons in the stream adsorbed onto the surface of carbon, from which they are subsequently removed by a combination of drawing air in the reverse direction through the bed. The enriched

hydrocarbons are then recovered by passing them counter-current to a gasoline stream from main storage in a re-absorber column.

In order to provide continuous availability of the system, units are usually designed with two carbon beds so that while one is operational the other is being regenerated by removal of the hydrocarbons. A control system is needed to ensure correct sequencing of the carbon bed operation and availability of the absorption stream.

(b) Lean Oil Absorption : The hydrocarbons in the incoming gasoline vapor stream are absorbed into a liquid of low vapor pressure, eg. Chilled kerosine or other suitable solvent. The combined product can then be held in storage for subsequent processing. In the second phase of the process the two elements, the absorbed gasoline and the absorbing medium, are separated by distillation. The gasoline vapor is passed to a reabsorber vessel served by a gasoline stream and the solvent is returned to low temperature storage for reuse via a chilling system.

A control system is provided to ensure optimum operation of the separate phase and the availability of utilities. A heating system is required for the distillation process and a refrigeration system for chilling the absorption medium.

(c) Refrigeration/Condensation: The hydrocarbons in the vapor stream are condensed by using a cold heat exchange medium. This medium could use a refrigeration process or a liquefied gas such as nitrogen. Very large refrigeration compressors may be needed to handle maximum vapor flows. An alternative is to store cooling capacity during off-peak periods using a medium such as kerosine. This permits the use of smaller compressors. A control system is provided to ensure that refrigeration output or the availability of the prechilled medium matches the demand presented by the incoming vapor.

(d) Membrane : A hydrocarbon selective membrane can be used to separate the hydrocarbons in the incoming vapor from the air. The main factors determining the separation efficiency are the type of membrane, the surface area of the membrane, and the pressure differential across the membrane.

The incoming vapors to the membrane module are pressurized using a compressor or blower. The majority of the hydrocarbons pass to the permeable side of the membrane upon which maintained by a vacuum. These hydrocarbons rich vapor stream can then be passed to a reabsorber vessel served by a gasoline stream from storage in which the hydrocarbons are recovered. Those unrecovered pass back to the inlet of the unit. Some recovery also occurs due to the compression of the vapors at the inlet compressor.

However, there is only carbon absorption technique being used in Thailand. There are approximately 7 units across the country (Petroleum Institute of Thailand, Memorandum, February 10, 2000).

2.6.2 Effectiveness of Vapor Recovery Unit

The US.EPA gathered test data of vapor recovery unit from various stated agencies including the California Air Resources Board and the American Petroleum Institute. The vapor control systems tested are carbon adsorber, thermal oxidizer, refrigeration unit, compression unit. The data indicated that control systems of all three types easily meet the appropriate emission limitations and that emission rates less than 10 mg/liter could achieved (US.EPA, Office of Air Quality Planning and Standards, 1994). The report was focus on the control of HAPs. They stated that the vapor recovery processors could possible controlled HAPs with reduction the percentage of than total VOC.

The Pacific Environmental Service, Inc has conducted the test for determination of the control device efficiency of HAPs for US.EPA in 1989. The results showed that a carbon adsorption and refrigeration system were significantly reduced VOC and benzene in the vapor stream.

In a report entitled "Determining the Benzene Emission Factor of Existing Marketing Terminal Vapor Recovery Units" in June, 1990, AmTest, Inc. (for API) described an emissions testing in the Pacific Northwest. The intent of this test program was to make a rapid determination of the ability of existing vapor recovery units at bulk terminals to meet the EPA proposed benzene emission standard (1989)

of 0.2 mg/liter. One control system was a refrigeration system designed to meet the 80 mg/liter VOC standard and the other four were carbon adsorption systems designed for the adsorption systems ranged from 0.7 to 2.1 mg/liter. While emissions from the refrigeration system were 69.9 mg/liter, the average benzene concentration in super grade averaged 2.5 percent. The benzene emissions averaged less than 0.01 mg/liter, and the concentration in the system outlet vapors was less than 3 ppm.

The report also summarized the test results from an independent study conducted by an API member company in southeastern Pennsylvania. This testing was conducted November 14-17, 1989, on four systems described in the reports as charcoal, refrigeration, lean oil charcoal, and compression. Hydrocarbon emission rates were 11 to 14 mg/liter for the refrigeration and compression systems. Control efficiency for benzene was well over 99 percent for all systems except the compression type, which controlled benzene at 72 percent.

Inlet and outlet vapor samples also analyzed for toluene and xylene content. Toluene control efficiencies were approximately 99 percent for all systems except the compression system, which controlled toluene at about 75 percent. Xylene was controlled at 85 to 98 percent for the three systems and at about 76 percent by the compression system.

Another study on vapor recovery units efficiency was done under the title 'Hazardous Air Pollutant Emissions from Gasoline Loading Operations at Bulk Gasoline Terminals' by Pacific Environmental Services, Inc. under The American Petroleum Institute (API) in 1998. Control efficiencies of eight HAP compounds were derived for carbon adsorption units and thermal oxidizers. The results from the carbon adsorption units indicated that the average control efficiencies for HAPs was over 99% and insensitive to the total VOC control efficiencies of the treatment unit. The thermal oxidizer emission tests indicated that the control efficiencies for HAPs were similar to the control efficiencies for total VOCs. The Table 2.7 summarizes the average control efficiency found in the reports.

2.7 Concerned legislation

Since there are increasing worldwide concerns on the environmental and health effects of emission of volatile organic compounds (VOCs) which has led to legislation in a number of countries.

The control of gasoline evaporative emission is most advanced in the United States, since it introduced in 1971. Control of evaporative emission from gasoline storing and transporting, include delivery to and storage in a service station underground storage tank, are commonly called “Stage I” operations. “Stage II” control involves recovering fuel vapor during refuelling.

Permissible emission from vapor recovery units in the United States was varied depending on their location, the date of installation, or potential to emit hazardous air pollutants. The current Control Techniques Guideline (CTG) level of compliance limit for ozone nonattainment areas is 80 mg VOC/liter (mg/l) of gasoline loaded. The current NSPS compliance limit is 35 mg/l (40 CFR 60, Subpart XX). Finally, the Gasoline Distribution (Stage I) NESHAP (40 CFR 63, Subpart R) requires a compliance limit of 10 g/l. (API, Health and Environmental Affairs Department :5-6, 1998)

Almost similarly, in Europe, The European Commission has been prepared two directions to control VOC emissions. One aimed to reduce vapor emission during gasoline distribution and refueling of automobiles. The reduction of emissions during the storage, loading and off-loading of gasoline is known as “Stage 1” vapor control. It is subdivided into:

Stage 1a: the control of emission during the storage and loading of gasoline at terminals,

Stage 1b: the control of emissions during off-loading at service stations.

Table 2.7 Control efficiencies(CE) of vapor control unit for HAP at gasoline loading rack

HAP Compound	Carbon Adsorber			Thermal Oxidizer		
	Average CE%	Min CE%	Max CE%	Average CE%	Min CE%	Max CE%
MTBE	99.65	98.49	100.0	99.79	99.63	99.96
Benzene	99.97	99.86	100.0	99.83	99.16	100.0
Toluene	99.93	99.62	100.0	98.86	96.42	100.0
Ethybenzene	99.66	98.54	100.0	100.0	100.0	100.0
'm,p-Xylene	99.55	97.98	100.0	99.21	96.06	100.0
o-Xylene	99.61	97.69	100.0	100.0	100.0	100.0
Xylene Average	99.58	Na	Na	99.60	Na	Na
Hexane	99.88	99.0	100.0	99.48	98.29	100.0
Isooctane	99.62	97.51	100.0	99.76	99.39	100.0
Total HAP	99.74	98.77	100.0	99.56	99.42	99.97
Total HAP w/o MTBE	99.82	99.02	100.0	99.52	99.32	100.0
Average HAP CE%	99.73	98.59	100.0	99.61	98.62	100.0
Total VOC	97.30	87.44	99.94	99.47	99.0	99.77

Source : The American Petroleum Institute, Health and Environmental Affairs Department , October 1998

The control of emissions generated during automobile refueling could undertaken either by using a system on-board the automobile or by modifying the gasoline dispenser and feeding the vapor back to the service station storage tank. The latter is known as “Stage 2” vapor control. (Institute of Petroleum, 1992) The Figure 2.3 shows the location of the stage diagrammatically.

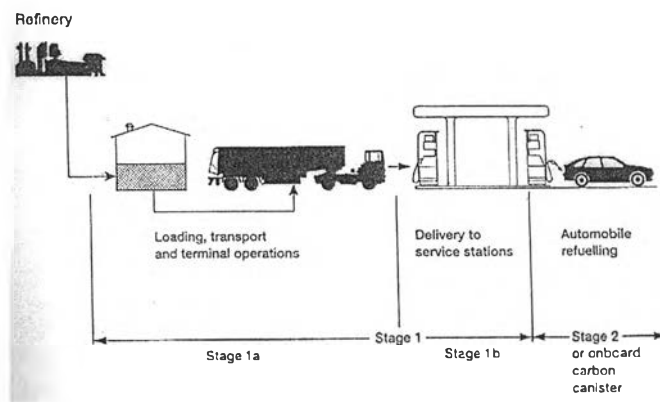


Figure 2.3 The “stages” of vapor emission control

In European region they states that the mean concentration of vapor in the exhaust from the vapor recovery unit corrected for dilution during treatment must not exceed 35 g/normal cubic meter (Nm³) for any one hour. (EUROPEAN PARLIAMENT AND COUNCIL DIRECTIVE 94/63/EC, 1994)

To accommodate the problem of gasoline emission during transfer in Thailand, the Science, Technology and Environmental Department has notified the business that gasoline emissions at gasoline terminals should not over 17 milligram of total volatile organic compounds per one liter in emitted vapor per hour. This notice was promulgated in July 1, 2002. (Notice of Science, Technology and Environmental Department, 2001)

2.8 Test method for hazardous air pollutant and non hazardous air pollutant from vapor recovery unit

The report titled 'Hazardous Air Pollutant Emissions from Gasoline Loading Operations at Bulk Gasoline Terminals' was conducted by the American Petroleum Institute (API) in 1998. They developed a test protocol for selected HAPs.

The method is designed to give an indication of eleven volatile organic compounds air pollutants (Benzene, Toluene, 2,2,4-trimethylpentane, Cumene, Ethylbenzene, n-Hexane, Methanol, MTBE, m-Xylene and p-Xylene) in VRU inlet and vent streams. In addition to HAPs and seven non HAPs (Methane, Propane, I-Butane, n- Pentane and n-Hexane) also including.

The sampling technique in the report was performed by gas samples were extracted from both inlet and vent streams of VRU at three intervals throughout a standard six hour compliance test. Inlet and vent stream was trapped over two hour periods into tedlar gas sample bags. The EPA Method 18, section 7.1 sampling procedures was followed. After the initial sampling, all Tedlar bag gas samples were sub-sampled on site into SUMMA polished canisters following the general guidelines of EPA-600/4-89-017 Method TO-14. Then the sample aliquots from the SUMMA polished canisters were analysed on a gas chromatography (GC) with a photo ionization detector (PID) and a flame ionization detector (FID) in series.