# FUGITIVE EMISSION ESTIMATION FROM STORAGE TANK AND WASTEWATER TREATMENT UNITS

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# FUGITIVE EMISSION ESTIMATION FROM STORAGE TANK AND WASTEWATER TREATMENT UNITS

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#### ABSTRACT

The objective of this study is to develop a systematic method for estimating fugitive emission from storage tank and wastewater treatment (WWT) units. Fugitive emission is the unintentional release of chemical vapors or gases that occur whenever there are discontinuities in the solid barrier maintaining the containment. While the amount released is very small, continuous exposure to chemical substances due to emission may adversely affect workers' health. To achieve the objectives, a comprehensive review is conducted on currently available fugitive emission estimation methods. A combination of emission factor, equation and software techniques is chosen as the methodology to study fugitive emission from storage tank and WWT units. A total of eleven horizontal and vertical tanks as well as nine WWT units are selected in this study. The results are presented as precalculated fugitive emission database for storage tank and WWT units. Dimensions data for storage tank and WWT units are also compiled from various sources for estimating chemical concentration. Three examples are given to demonstrate the application of the precalculated fugitive emission database in estimating fugitive emission and concentration from storage tank and WWT units. To calculate the other losses (e.g. working loss and evaporation loss), TANKS 4.09d software and evaporation loss equation are used. The typical range of fugitive emission individual stream value for both storage tank and WWT units are found to be within 0.01-0.20 kg/h. Calculation using the EPA emission factor leads to higher emission estimates compared to using the controlled emission value. Evaporation loss is found to be the largest source of emission loss from storage tank and WWT compared to fugitive emission, working and breathing losses.

#### ABSTRAK

Objektif kajian ini adalah untuk membangunkan satu metodologi bagi menganggar pelepasan fugitif dari tangki simpanan dan unit rawatan kumbahan (WWT). Pengeluaran fugitif ialah pembebasan wap atau gas kimia secara tidak sengaja yang berlaku bila-bila masa apabila terdapat ketidaksinambungan dalam pembendungan. Walaupun jumlah pelepasan adalah kecil, pendedahan secara berterusan kepada bahan kimia disebabkan pengeluaran fugitif akan mengakibatkan kesan buruk terhadap kesihatan pekerja. Bagi mencapai objektif ini, satu kajian literatur telah dijalankan dengan mendalam untuk memahami kaedah penganggaran pelepasan fugitif yang sedia ada. Kombinasi faktor pancaran, persamaan dan perisian telah digunakan sebagai kaedah untuk mengkaji pelepasan fugitif dari tangki simpanan dan unit rawatan kumbahan. Sejumlah sebelas tangki simpanan serta sembilan unit WWT telah dipilih sebagai kajian. Keputusan kajian dipersembahkan sebagai 'precalculated emission database'. Data dimensi telah dikumpul daripada pelbagai sumber dan disenaraikan. Tiga contoh diberi untuk mendemonstrasikan penggunaan 'precalculated emission database' dalam menganggarkan pelepasan fugitif. Bagi mengira kehilangan sejatan dan kehilangan lain, TANKS 4.09d and persamaan sejatan telah digunakan. Secara umum, nilai aliran individu pengeluaran fugitif bagi tangki and unit WWT didapati berada di dalam lingkungan 0.01-0.20 kg/h. Penggunaan faktor pelepasan EPA didapati menghasilkan nilai jangkaan pelepasan fugitif yang lebih besar berbanding penggunaan nilai perlepasan terkawal. Didapati kehilangan sejatan merupakan sumber pengeluaran terbesar dalam tangki simpanan dan unit WWT berbanding punca kehilangan lain dan pengeluaran fugitif.

## **TABLE OF CONTENTS**

CHAPTER	TITLE	PAGE
]	DECLARATION	ii
1	ACKNOWLEDGEMENT	111
I	ABSTRACT	iv
1	ABSTRAK	v
r	<b>FABLE OF CONTENTS</b>	vi
l	LIST OF TABLES	ix
l	LIST OF FIGURES	xi
l	LIST OF SYMBOLS	xiv
]	LIST OF ABBREVIATIONS	xvi

1	INT	RODUCTION	1
	1.1	Inherent safety concept	1
	1.2	ISD in process lifecycle	4
	1.3	Research background	6
	1.4	Problem statement	8
	1.5	Significant of study	9
	1.6	Objectives	10
	1.7	Scope of study	10

	1.8	Dissertat	ion outline	11
2	LITE	RATUR	E REVIEW	13
	2.1	Introduct	ion	13
	2.2	Concept	of safety and health	14
	2.3	Occupati	onal injury and illness statistics	16
	2.4	Risk asse	essment	17
	2.5	Route of	exposure	21
	2.6	Health ef	fect of chemical mixtures	23
	2.7	Review o	of fugitive emission estimation methods	25
	2.8	Common	fugitive emission estimation methods	29
		2.8.1	Emission factor based approach	29
		2.8.2	Sampling/Direct measurement	34
		2.8.3	Mass balance/Engineering calculation	38
		2.8.4	Software	40
	2.9	Emission	factor approach justification	42
	2.10	Storage t	ank design	44
		2.10.1	Fixed roof tank	46
		2.10.2	External floating roof tank	47
		2.10.3	Internal floating roof tank	49
		2.10.4	Domed external floating roof tank	50
		2.10.5	Horizontal tank (pressure vessel)	51
		2.10.6	Pressure tank	52
		2.10.7	Variable vapor space tank	53
	2.11	Wastewa	ter treatment units design	54
	2.12	Summary	ý	60
3	MET	HODOL	OGY	61
	3.1	Introduct	ion	61
	3.2	Methodo	logy development	62

vii

	3.2.1	Part 1 – Development of emission factor database	62
	3.2.2	Part 2 - Calculation of fugitive emission using	
		examples	67
	3.2.3	Detailed step by step guideline for examples	73
3.3	Unit geon	netry and dimensions	75
3.4	Summary		81
RES	SULTS AN	D DISCUSSIONS	82
4.1	Introducti	on	82
4.2	Compilat	ion of fugitive emission data for storage tank	83
4.3	Compilat	ion of fugitive emission data for WWT units	91
4.4	Discussio	ns on the fugitive emission data	98
4.5	Overview	of the examples	100
	4.5.1	Example 1: Horizontal tank	100
	4.5.2	Example 2: Equalization tank	103
	4.5.3	Example 3: Collection pit	105
4.6	Common	fugitive emission preventive strategies	107
	4.6.1	Minimization	108
	4.6.2	Substitution	108
	4.6.3	Moderation	109
	4.6.4	Simplification	109
4.7	Summary		110
CON	NCLUSIO	N	111
5.1	Conclusio	on	111
5.2	Recomme	endations for future work	112

4

5

REFERENCES	114
APPENDICES	121-132

## LIST OF TABLES

TABLE NO	. TITLE	PAGE
2.1	Elements within risk assessment (EPA, 1989)	19
2.2	Models of effects of mixtures (Casarett et al., 1986)	24
2.3	Categories of fugitive emission estimation method	26
2.4	Selected emission factor example (Smith et al., 2007)	30
2.5	Air emission factor from wastewater treatment plant (National Pollutant Inventory, 2011)	30
2.6	Screening value range method (EPA, 1995)	32
2.7	Correlation equation emission factor (SBCAPCD, 1997)	33
2.8	Malaysia wastewater standards (Indah Water, 2012)	55
2.9	Common wastewater treatment units list (Atasoy <i>et al.</i> , 2004; EPA, 1994; EPA, 1997; IPIECA, 2010; National Pollutant Inventory, 2011; Tata <i>et al.</i> , 2003; Wu <i>et al.</i> , 2006)	58
3.1	Sample precalculated emission database	66
3.2	Horizontal/Vertical tank dimensions (Couper <i>et al.</i> , 2005)	78
3.3	Active carbon scrubber dimensions (Croll Reynolds, 2011)	78
3.4	Bio trickling filter scrubber dimensions (PRD Tech, 2012)	79
J. T	bio meximo muer seruober unitensions (1 KD 1001, 2012)	1)

3.5	Collection/Equalization tank dimensions* (Expocrete, 2012)	79
3.6	UASB dimensions (Lettinga and Hulshoff Pol, 1991)	80
3.7	Polymer system dimensions (Ovivo, 2012)	80
3.8	Collection/Equalization dimensions* (Abukhari, 2012)	80
4.1	Compilation of precalculated fugitive emission data for storage tank	90
4.2	Compilation of precalculated fugitive emission data for WWT units	97
4.3	Horizontal tank emission calculation	102
4.4	Equalization tank emission calculation	104
4.5	Collection pit emission calculation	106

## LIST OF FIGURES

FIGURE NO	D. TITLE	PAGE
1.1	Cost to fix problem in various stage (Kletz, 1991)	5
1.2	Design paradox and ISD (Hurme and Rahman, 2005)	6
1.3	Simple diagram relating cost with fugitive emission (Szweda, 2000)	7
1.4	Distribution of fugitive emission in oil refinery (Lakhapate, 2010)	8
2.1	Safety and health concept diagram (Hassim and Hurme, 2010)	16
2.2	Risk assessment procedures (Masters, 1997)	19
2.3	Blood level toxic concentration as a function of exposure routes (Crowl and Louvar, 2002)	23
2.4	A valve covered and vacuumed to a analyzer (Onat, 2006)	35
2.5	Portable gas detection/vapor sampling equipment	36
2.6	Portable infrared device – ThermaCAM GasFindIR (S. Plisson-Saune <i>et al.</i> , 2008)	36
2.7	Before and after IR imaging using ThermaCAM GasFindIR (S. Plisson-Saune <i>et al.</i> , 2008)	38
2.8	WATER9 with loaded example	42
2.9	Fixed roof tank configuration (EPA, 2006)	46

2.10	External floating roof tank (pontoon) (EPA, 2006)	48
2.11	External floating roof tank (double deck) (EPA, 2006)	48
2.12	Internal floating roof tank (EPA, 2006)	50
2.13	Domed external floating roof tank (EPA, 2006)	51
2.14	Above ground horizontal storage tank (EPA, 2006)	52
2.15	Pressure tank (GEM Mobile Treatment Service, 2012)	53
2.16	Typical WWTP configuration 1 (Atasoy et al., 2004)	56
2.17	Typical WWTP configuration 2 (Wu et al., 2006)	57
2.18	Typical WWTP configuration 3 (IPIECA, 2010)	57
3.1	Development of precalculated emission database for storage tank and wastewater treatment units	63
3.2	Fugitive emission calculation steps for storage tank and wastewater treatment units	68
3.3	Storage tank simplified diagram	76
3.4	Various WWT units simplified diagram	76
3.5	Scrubber simplified diagram	77
3.6	Upflow anaerobic sludge blanket (UASB) simplified diagram	77
4.1	Tank1 – vertical tank	84
4.2	Tank2 – vertical tank	84
4.3	Tank3 – vertical tank	85
4.4	Tank4 – horizontal tank	85
4.5	Tank4(2) – horizontal tank with backup PRV	86
4.6	Tank5 – vertical tank	86
4.7	Tank5(2) – vertical tank with backup PRV	87
4.8	Tank6 – small vertical tank with backup pump	87

4.9	Tank6(2) – small vertical tank without pump	88
4.10	Tank7 – small vertical tank slight modification	88
4.11	Tank8 – horizontal water tank	89
4.12	Collection tank	92
4.13	Equalization tank	92
4.14	Active carbon scrubber	93
4.15	Bio trickling filter	93
4.16	Acidification tank	94
4.17	Polymer mixing system	94
4.18	Fluoride system – dissolve tank	95
4.19	Fluoride system – makeup tank	95
4.20	UASB	96
4.21	Horizontal tank containing pure acetaldehyde	101
4.22	Horizontal tank emission data	102

## LIST OF SYMBOLS

$\Delta T$	-	ambient diurnal temperature change (°C)
$A_f$	-	Land area (m <sup>2</sup> )
$A_n$	-	vertical area (m <sup>2</sup> )
С	-	chemical concentration calculated (kg/m <sup>3</sup> )
D	-	tank diameter (m)
d	-	edge width of area (m)
Ε	-	mass emission rate per time (g/day)
EF	-	uncontrolled emission factor of species i (g/g) or emission factor of equipment/unit (g/source)
f	-	emission control equipment efficiency
$FE_i$	-	emission factor for a particular unit, i (kg/h)
$F_p$	-	paint factor
h	-	height of unit (m)
Hv	-	vapor space height (m)
Кс	-	product factor
LB	-	daily breathing loss (kg/h)
M	-	molecular weight of the chemical calculated
Mv	-	stock vapor molecular weight
$P_A$	-	atmospheric pressure (atm)

- Pv-vapor pressure of stored liquid at bulk liquid condition (atm)Q-influent flow rate (m³) or equipment countQ-air volumetric flow rate calculated (m³)u-average wind speed (m/s)V-volumetric flow rate (m³)
- *x* mass fraction for chemical

## LIST OF ABBREVIATIONS

ACGIH	-	American Conference of Governmental Industrial Hygienists
API	-	American Petroleum Institute
ASSE	-	American Society of Safety Engineers
BASTE	-	Bay Area Sewage Toxics Emissions
BOD	-	Biochemical oxygen demand
CDC	-	Centers for Disease Control and Prevention
COD	-	Chemical oxygen demand
ECHA	-	European Chemicals Agency
EMIS	-	Emission Model of Industrial Sources
EPA	-	U.S. Environmental Protection Agency
EU	-	European Union
HL HAP	-	Heavy liquid Hazardous air pollutant
IMPEL	-	European Union Network for the Implementation and Enforcement of Environmental Law
IOH	-	Inherent occupational health
IOHI	-	Inherent Occupational Health Index
IPCC	-	Intergovernmental Panel on Climate Change
IPPC	-	Integrated Pollution Prevention and Control

IR	-	Infrared			
IR3S	-	Integrated Research System for Sustainability Science			
ISD	-	Inherently safer design			
LL	-	Light liquid			
MIC	-	Methyl iso-cyanate			
MSDS	-	Material safety datasheet			
NMVOC	-	Non-methane volatile organic compounds			
NPI	-	Australia national pollutant inventory			
OECD	-	Organization for Economic Cooperation and Development			
OED	-	Oxford English Dictionary			
OHHI	-	Occupational Health Hazard Index			
OSHA	-	Department of Occupational Safety and Health Administration			
OVA	-	Organic vapor analyzer			
P&ID	-	Piping and instrumental diagram			
PEEP	-	Pooled Emission Estimation Program			
PEL	-	Permissible Exposure Level			
PFD PRV	- -	Process flow diagram Pressure relief valve			
PRHI	-	Process Route Healthiness Index			
R&D	-	Research and development			
REACH	-	Registration, Evaluation, Authorization and Restriction of Chemical substances			
REM	-	Refinery Emission Model			
RWET	-	Refinery wastewater emission tool			
SHE	-	Safety, Health and Environment			
SOCMI	-	Synthetic Organic Chemical Manufacturing Industry			
SV	-	Screening value			
TCE	-	Trichloroethylene			
TLV-STEL	-	Threshold limit value short-term exposure limit (15-mins)			

TLV-TWA	-	Threshold limit value using time weighted average of 8 hours
TSM	-	Trajectory statistical methods
TVA	-	Toxic vapor analyzer
VHAP	-	Volatile hazardous air pollutant
VOC	-	Volatile organic compound
VOL	-	Volatile organic liquid
WCED	-	World Commission on Environment and Development
WWT	-	Wastewater treatment

## LIST OF APPENDICES

APPENDIX	TITLE	PAGE
1	Emission losses calculation	122
2	List of compiled emission factor	124
3	TANKS 4.09d examples emission report	126
4	Evaporation examples calculation sheet	131

### **CHAPTER 1**

### **INTRODUCTION**

## 1.1 Inherent safety concept

Modern chemical process industry is complex due to technological advancement such as the adoption of extreme operating conditions (i.e. higher operating temperature and pressure) which is not possible in the past due to technological restriction (Crowl and Louvar, 2002). The higher the complexity of a process, the more sophisticated safety and health measures are required to safeguard the workers.

In the 19th centuries, there are many notable accidents that occurred in chemical industry leading to significant development of chemical process safety. Several accidents with devastating impacts are often used as educational case studies for teaching safety and health courses e.g. Flixborough, 1974 and Bhopal, 1984 (Crowl and Louvar, 2002).

Basically, there are many existing safety and health measures and among the common ones are such as alarm system, process control, and personal protective equipment. However, these measures are not able to reduce or eliminate the hazard

itself but rather serve to control or manage the existing hazard. Since the hazard is still present within the process, accident will occurs upon failure of any of the measures.

In 1978 a concept to eliminate hazard rather than to contain them was introduced by Trevor Kletz in an article entitled "What You Don't Have, Can't Leak" (Kletz, 1978). The concept is named inherent safety based on a book written by Kletz later on (Kletz, 1984). This book undergoes major revision in later years although the main principles are still basically the same. His work received support from researchers in the same field and was incorporated in many chemical industries. As it is not possible to achieve a perfect safety, the researchers usually called it inherent safer design or simply ISD (Bollinger *et al.*, 1996).

An inherent safer plant relies on fundamental theories, chemistry and physics to prevent accidents rather than control interlocks, control systems, alarms and etc. (Crowl and Louvar, 2002). The plant is tolerant of errors and is often more cost effective due to waste reduction, smaller equipment, energy and raw materials conservation. The plant is also easier to operate as it does not require any sophisticated system thus reducing potential operators' error.

The major approach to an inherent safer design is based on four principles which are:

- Minimize
- Substitute
- Moderate
- Simplify

For minimize, hazard is reduced by decreasing the amount of hazardous chemical used in the process (Crowl and Louvar, 2002). It can also be interpreted as the reduction of transporting and storing hazardous intermediate chemical by producing them "in-situ" which means producing within the process itself.

In most cases, minimization can only be performed until certain extend and the hazard can no longer decrease. The next step would be to substitute the hazardous chemical to a non-hazardous or least hazardous chemical. The concept also applies to replace less safer equipment e.g. flanged pipe to a safer one e.g. welded pipe (Crowl and Louvar, 2002). It is also possible to consider alternatives for the entire process itself.

After performing all possible substitution, next is to consider moderation. Moderation is to employ less hazardous process operating condition (Crowl and Louvar, 2002). Some examples are such as operating process at a temperature and pressure where reactor runaway is not possible and diluting hazardous chemical with inert solution to prevent over-reaction.

Finally the last strategy concerns with reducing the complexity of the plant. A simpler plant is easier to operate than a complex plant since there are fewer devices, systems, equipment to operate and thus less opportunity for errors to occur (Crowl and Louvar, 2002). Some examples given are to design piping system in well-ordered and easy to monitor, delegate manual control to automated control if possible and reduce the amount of buttons on the control panels.

#### **1.2** ISD in process lifecycle

A typical process lifecycle stage starts from research and development, design, construction, operation, retrofitting and maintenance, and finally ends at decommissioning. It is possible to further classify the design stage into preliminary design, basic engineering and detailed engineering (Hassim and Hurme, 2010). Preliminary design deals with the process chemistry, reactions, heat and mass balances and flow sheet while basic engineering covers the process piping and instrumentation diagram. In detailed engineering, detailed documents and drawings for construction and procurement are prepared.

It is logical that inherent safer design should be incorporated starting from process development. The ideal approach would probably be during research and development (R&D) stage where the design is not yet finalized and still a concept. Whatever decision been made within the R&D stage would affects greatly the subsequent development lifecycle. This could be from using alternative process and reaction to modifying an existing process so that it is safer and healthier. Early design stage offers the highest degree of freedom for engineers to fulfill ISD and government policies (Hassim and Hurme, 2010).

Other advantage of applying ISD in earlier stage is due to the cost affiliated. According to Kletz, it is much more economical to fix a problem during conceptual stage as oppose to cleaning up the mess after an accident occurs (Kletz, 1991). A pyramid triangle is shown in Figure 1.1 illustrating this statement. Note that the values shown are only relative values associated with each stage and not the actual cost.

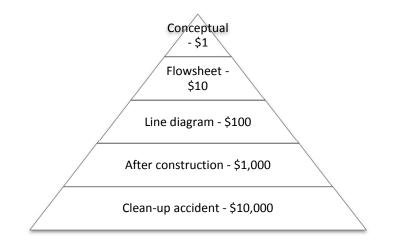


Figure 1.1: Cost to fix problem in various stage (Kletz, 1991)

Although R&D stage seems to be the best stage to apply ISD concept, it is known that R&D stage is also the one with the least amount of information available. Many engineers would argue that without much information, it would be difficult to assess their plant potential hazard and to reduce them using ISD. This concept is known as "design paradox" (Hassim and Hurme, 2010).

A summary of design stages involved, cost associated to incorporate safety feature and the amount of information available can be seen in the graph below. Based on Figure 1.2, an intersection point at pre-engineering stage (also known as preliminary design stage) provide a good starting point to conduct ISD as the amount of information available is enough to provide opportunity for installing inherently safer features as early as possible. The earlier the design incorporate ISD the lesser the cost needed and safer plant.

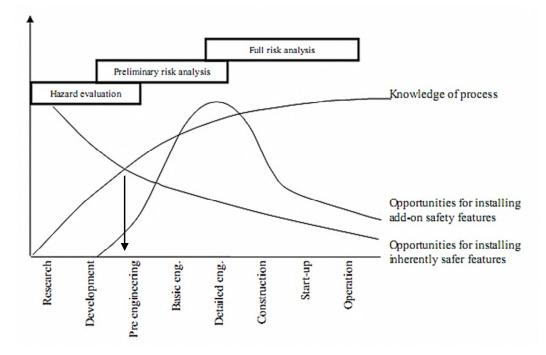


Figure 1.2: Design paradox and ISD (Hurme and Rahman, 2005)

### 1.3 Research background

In process development and design stage, engineers usually need to identify all the emissions from their process based on studies, literatures and simulations. Steps and measures are then taken to reduce the emissions or eliminating them through process simplification, optimization or integration. Many of the emissions are the results of actual process streams from daily operations and can be controlled using various equipment such as scrubber or special recovery system. However, there is often significant amount of not anticipated, spurious leak which is referred to as fugitive emission (Onat, 2006).

Fugitive emission, as defined by various authors, can be summarized as the unintentional release of individual chemical or chemical mixtures, in any physical form (liquid, gas, and solid) in industrial plant (Ellis, 1997; ESA / FSA, 1998; Onat,

2006). Fugitive emission can occurs whenever there are discontinuities in the solid barrier that maintains containment e.g. pump seals, valves, flanges and etc. (Hassim *et al.*, 2010). The amount of fugitive emission released at individual leak points is often very small. Nevertheless, considering the entire plant summing up every leak sources available, fugitive emission can cause a significant impact towards environment and human health (Smith *et al.*, 2007). In the UK, it is estimated that there are over 7,000 deaths associated to work-related carcinogens exposure which accounts for 4.9% of total cancer death (Cherrie, 2009).

Yet, fugitive emission impact is not only limited to environment and health issues but also includes economy. Fugitive emission denotes a major financial burden on the industry due to plant inefficiency, substantial loss of potential products and raw materials and many other invisible costs (Szweda, 2000). Figure 1.3 below shows a graphical representation of the cost associated with fugitive emission. Based on the figure alone, it is clear that the effect of invisible cost is much significant compared to visible cost as it is hard to predict how much economy damage the invisible cost can caused.

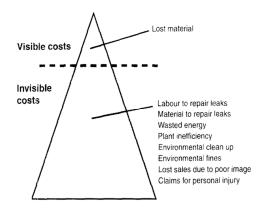


Figure 1.3: Simple diagram relating cost with fugitive emission (Szweda, 2000)

Figure 1.4 shows an example distribution of fugitive emission in an oil refinery. According to Lakhapate (2010), the main sources of fugitive emission are valves (75%) followed by tanks (10%), rotary equipment (10%) and flanges (5%).

Based on this data, we can assume that majority of fugitive emission originated from piping components but there is also significant emission from storage tank which should also be considered. The author did mentioned that fugitive emission in the U.S. had been estimated to be around 300,000 tons per year accounting for around one third of total organic emission from chemical plants and the same situation is occurring in Europe (Lakhapate, 2010).

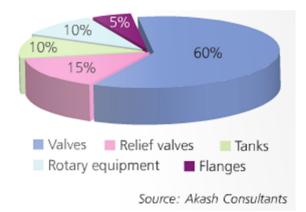


Figure 1.4: Distribution of fugitive emission in oil refinery (Lakhapate, 2010)

#### **1.4 Problem statement**

A complete plant fugitive emission study requires the study of both inside battery limit (ISBL) and outside battery limit (OSBL) units. Hassim *et al.* (2010) introduced a simple yet reliable method to estimate fugitive emission during design stage for various unit operations also known as process module. However, their work focuses only on process units (ISBL) such as reactor, distillation column, absorber, flash column and etc. They did not include a study for OSBL unit such as storage tank and wastewater treatment units which are also major fugitive emission contributors. There are various methods developed by different organization to estimate fugitive emission from storage tank and wastewater treatment units. However, many of these methods suffer from certain weaknesses. Among some of the weaknesses identified are such:

- The methods require many data which are not available during earlier design stage hence the methods can only be used to assess existing plant
- The methods are complicated to use, require specific knowledge or complex calculation thus preventing non-engineer/non-technical end user from using them
- The methods are tedious, time-intensive and costly thus are not feasible for design stage that has very limited resources

Thus, a new or improved methodology to evaluate fugitive emission from storage tank and wastewater treatment units during early design stage is recommended to allow a throughout plant fugitive emission study.

#### 1.5 Significant of study

The outcome of this study will provide process designers and engineers with a systematic method to perform simple fugitive emission estimation from storage tank and WWT units with less effort, time and cost. Not only users are able to quantify the amount of fugitive emission from those units, the data can also expose most hazard associated with fugitive emission during early process design. Based on the identified risk, counter measures can be taken to reduce or eliminate the hazards through the various inherent safer principles. This will create a fundamentally healthier and safer working environment for the workers and also complies with government policies to achieve sustainable development.

### 1.6 Objectives

The objectives of this study are:

- 1. To review existing fugitive emission estimation methods
- 2. To develop a new or improved method for estimating fugitive emission from storage tank and wastewater treatment units
- 3. To create a precalculated emission database for storage tank and wastewater treatment units
- 4. To calculate fugitive emission in mass flow rate and concentration using examples
- 5. To determine health risk of storage tank and WWT units based on examples

## 1.7 Scope of study

This study will involve only few common storage tank and wastewater treatment units used in chemical industry. The study will review both theoretical (e.g., calculations, rule of thumb, guidelines) and instrumental methods to evaluate fugitive emission but the proposed methodology for emissions estimation will be based on theoretical methods, not involving any instrument for measurement. The study is limited to preliminary design stage and long term periodic fugitive emission release. After estimating emission concentration based on examples, a simple estimation of health risk is performed based on the chemicals concentration estimates and their associated exposure limit value.

### **1.8** Dissertation outline

This dissertation comprises of five chapters. Chapter one is the introduction chapter providing a brief introduction on sustainability, SHE, regulations and importance of SHE in process development, inherent safety concept, fugitive emission, hazard of fugitive emission and importance of evaluating fugitive emission in earlier process design stage, problem statement, aim of study, significant of study, objective and scope of study.

Chapter two covers the literature review which includes basic concept of occupational health, risk and risk assessment, exposure route, storage tank and WWT units assessment methods currently available, summary and conclusion of the review on currently available methods, design of storage tank and WWT units.

Chapter three describes the methodology taken in order to evaluate fugitive emission from storage tank and WWT units. This chapter includes a brief introduction, calculations, materials and resources used to complete the study, parameters studied, and procedures to validate the propose method.

Chapter four presents tabulated data and graphical presentation of fugitive emission rates for both storage tank and WWT units. A list of common units dimension is compiled from various sources. Three examples to calculate fugitive emission for storage tank and WWT units are shown. Other losses are calculated using TANKS 4.09d and evaporation loss equation. Chapter five concludes this dissertation with conclusion and recommendations for future work.

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