Three-Tier Inherent Safety Quantification (3-TISQ) for Toxic Release at Preliminary Design Stage

by

Nabila Syahira binti Azizuddin

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A Project Dissertation submitted in partial fulfilment of
the requirements for the
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(Chemical)
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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

THREE-TIER INHERENT SAFETY QUANTIFICATION (3-TISQ) FOR TOXIC RELEASE AT PRELIMINARY DESIGN STAGE

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2014

Approved by,

_____

(Dr. Dzulkarnain Zaini)

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Nabila Syahira Azizuddin

ABSTRACT

Inherent safety is an approach that is aim to minimize or eliminate the main causes of the hazards by adjusting the design of the chemical process plant instead of depending on the existing safety systems of the equipment and procedure of the process. Even though the present facilities and operating procedures has provided the safety engineered system and cost performance, the actual implementation of inherent safety in process design stage has not been commonly implemented in the industries. Current research and development are mainly specifically for explosion and fire cases only. None of these methods were developed to reduce or prevent the major accidents due to toxic release accidents. Therefore, this paper proposes a new technique to evaluate the level of inherent safety of process plant during the preliminary design stage by using the combined assessment of process routes, streams and inherent risk for toxic release accidents. This technique is known as 3-Tier Inherent Safety quantification (3-TISQ). The 3-TISQ technique is able to quantify and prioritize the level of inherent safety of the process route and stream, determine the inherent risk and modify the design up to acceptable level during the preliminary design stage.

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Table of Contents

List of Figures

List of Tables

CHAPTER 1: INTRODUCTION

1.1 Background of Study

The chemical process industry evolution can be related with the advances of technology. This can be proven by looking at the chemical industry itself, where it is now moving on to more complex processes and requires more complex safety technology to prevent major accidents in chemical plants. Major accident have been defined as *'an unexpected, sudden occurrence such as major emission, fire or explosion resulting from uncontrolled developments in the course of the operation of any establishment and leading to serious danger to human health and/or the environment, immediate or delayed, inside or outside the establishment and involving one or more dangerous substance'* [1]. A survey of the type of hardware that caused massive accidents of chemical plants is shown in Figure 1. Piping system failure represents the bulk of accidents, followed by storage tanks and reactors. From the survey, it is clearly presented that the most complicated mechanical components such as pumps and compressors are minimally responsible for large losses [1].

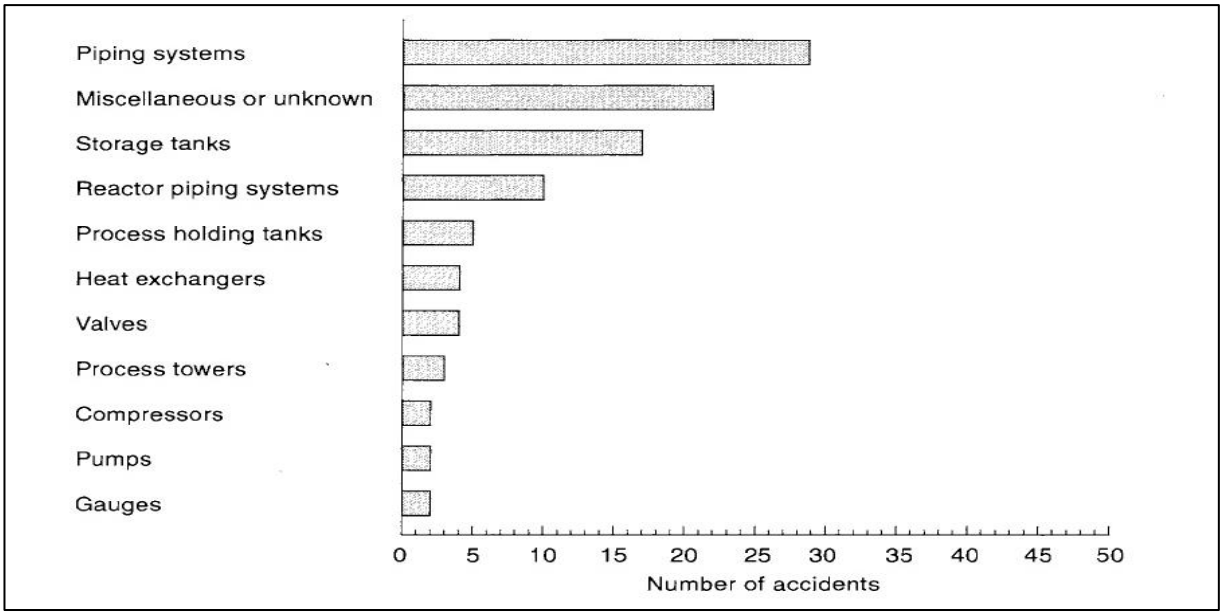

Figure 1: Hardware that associated with massive chemical accidents [1]

The three most cited major accidents (Flixborough, Seveso and Bhopal) are identified here. All these accidents had a momentous impact on public's perception and the chemical engineering profession that added new significance and standards in the safety practice [1].

1) Flixborough, England (June 1974)
   The leakage and explosion of cyclohexane has caused 28 of workers deaths and 36 suffered injuries.

2) Seveso, Italy (July 1976)
   An explosion of TCDD (2,3,7,8-tetrachlorodibenzoparadioxin) was released and over 600 people were evacuated and about 100,000 animals were killed.

3) Bhopal, India (December 1984)
   Estimated 25 tons of extremely toxic methyl isocyanate (MIC) vapor was released killing over 2,000 people and more 20,000 were injured.

Based on the previous major accidents, most of the chemical plants started with minor flaws such as instruments out of order, poor procedure practice, and failure to follow the procedures or good engineering practices. Therefore, to minimize or eliminate (if possible) potential accidents in chemical process plant, any changes such as selecting less hazardous chemical used for the process, can be made earlier before starting any operation. However, according to Kletz [2], history shows that accidents were repeated after a lapse of a few years, and lessons are forgotten as people move on.

1.2 Problem Statement

Previously, the methodologies for inherent safety level (ISL) quantification index based are mainly on process route only. Not only that, mostly earlier work done for index based inherently safer design (ISD) approach focusing on chemical route by using properties of single element. There are also lacking in considering the chemical components as a mixture and developed purposely for toxic release.

Once the best route is selected, the inherently safer design (ISD) can be implemented by improving the inherent safety level (ISL) of the streams. The ISD can be done by ranking the process streams based on ISL within a process route. By using this ISL of the process streams ranking method, the most hazardous streams can be selected. However, this concept has never been addressed for toxic release of the process streams.

After the worst stream has been ranked, the ISD can be done at preliminary design stage by assessing inherent risk of selected stream within a process route. One of the suitable techniques for assessing ISL in process industries is based on Quantitative Risk Assessment (QRA). Although QRA has been widely used in industries, but QRA has not been used at the preliminary design stage yet and to be specific, never been adopted for toxic release.

1.3 Objectives

The main objective of the research is:

1. To develop, an inherently safer design technique for process plant using the following approaches:

    i. Process route index for toxic release
    ii. Process stream index for toxic release
    iii. Inherent risk assessment based on risk matrix for toxic release

1.4 Scope of Study

The scope of study for this project will be covering three main tasks. The first task is to screen the process routes and to select the ‘best’ route that is inherently less dangerous. As for the second task, ISL of the streams within the selected process route will be identified and prioritized. For example, the streams that have low or absent of hazards can be identified and eliminated. After the worst stream is given by the highest level ISL value, the selected streams can be determined using inherent risk assessment which is similar to Quantitative Risk Assessment (QRA) to evaluate the amount of risk as the third task.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Chemical plants comprise varieties of hazards. As the development of chemical, oil and petrochemical industries since 1960s are increasing; the number of major accidents also increases, generally due to loss of containment which containing reactive and hazardous chemicals and this has resulting in the form of fire, explosion or toxic release. During an accident in a process plant, toxic and hazardous materials can be release at a very fast rate and spread in the form of dangerous clouds. Referring to the past accidents that already been discussed in section 1.1, chemical engineers will need a more detailed and deeper understanding of process safety as such it should be evaluated and addressed in the whole lifecycle of a process system or a facility [3]. Therefore, hazard analysis needs to be carried out starting from research and development until decommissioning. In the next section, a few methods of hazards analysis will be reviewed.

2.2 Hazard Analysis in Process Plant Lifecycle Stages

There are few methods that have been practiced in industries for hazard analysis. The methods are:

2.2.1 DOW Fire and Explosion Index (DOW F&EI)

DOW F&EI is first issued by the DOW Chemical Co. in 1964 [4] and currently has become one of the most common hazard identification procedures. The DOW F&EI has a systematic approach to measure the potential risk from a process and calculating estimate potential loss of an accident [5]. This method is designed for rating the relative hazards with the storage, handling and processing of explosive and flammable materials, free from individual judgment factors. It is worthwhile estimating the DOW FEI index at an early stage in the process design, as it will indicate whether alternative, less hazardous process routes should be considered.

The first step of calculating DOW F&EI is to determine the units that would have the highest likelihood of a hazard. Next is to determine the material factor (MF) which it acts as a measure of the intrinsic rate of energy release from the burning, explosion or other chemical reaction of the material. Generally, the more flammable and/or explosive of material have the higher value of MF. Referring to Equation 2.1 is the calculation of The Process Unit Hazards Factor (F_3) where it is the multiplication of General Process Hazard Factor (F_1) and Special Process Hazard Factor (F_2).

$$F_3 = F_1 \times F_2 \qquad \text{Eq. 2.1}$$

Therefore, the DOW F&EI is now can be estimated by multiplying the MF and Process Unit Hazards Factor as shown in Equation 2.2.

$$F\ \&\ EI = MF\ \times\ F_3 \qquad \text{Eq. 2.2}$$

Table 1: Level of hazard and DOW Fire and Explosion Index [1]

DOW F&EI	Degree of Hazard
1 – 60	Light
61 – 96	Moderate
97 – 127	Intermediate
128 – 158	Heavy
159 and above	Severe

2.2.2 Hazard and Operability Studies (HAZOP)

Hazard and Operability Analysis (HAZOP) study has been used for identifying potential hazards and operability problems caused by deviations from design or operating intentions [6]. Basically, HAZOP is a method that assumes that a system or component is safe by having all the operating parameters at acceptable levels. HAZOP is carried out to search hazards in the form of deviations from the norm with possible dangerous consequences. To identify deviations, the study team

is facilitated by using sets of guidewords to determine possible causes and note any prevention ways of the consequences to recommend action. The HAZOP team needs to go through the entire process flow diagrams (PFD) and piping and instrumentation diagrams (PID) to examine and identify deviations. Basically, the parameters studied will include basic process conditions like temperature, pressure and flow. As stated in HSE-UK [7], this approach can be described as a brainstorming technique because it helps stimulate the imagination of team members when determining potential deviations and finding ways to evaluate significances.

2.2.3 Quantitative Risk Assessment (QRA)

Quantitative Risk Assessment (QRA) is most commonly used in the process industries to quantify the risks of 'major hazards'. QRA used in the offshore oil and gas industries, the transport of hazardous materials, the protection of the environment, mass transportation (rail) and the nuclear industry [7]. Typically, QRA acts as a formal and systematic approach of recognizing potentially hazardous events, assessing the likelihood and consequences of those events and expressing the results as risk to people, the environment or the business. However, in order to avoid numerous hazards, to estimate the likelihood of the past accident or incident data, several selections need to be taken care such as, the accident/incident sample, the time period and the statistical method [8]. Shell International Exploration and Production B.V. [9] stated that the application of QRA is not necessarily bounded to huge, complex and costly studies. It can be classify as a quick and cheap technique to assist to figure out the solution to problems for which the solution is not intuitively obvious.

Risk is once proposed as a mathematical function (Equation 2.3) as follows according to Wentz [10]:

$$Risk = f(probability\ or\ frequency, consequences)$$

Eq. 2.3

In addition, risk is frequently defined as a function of the chance that a specified undesired event will occur and the severity of the consequences of the event [9]. As for QRA, chance stated above can be expressed as probability or frequency of an occurrence similar to the Equation 2.3.

2.3 Inherent Safety Application in Plant Design

The application of inherent safety in process design has been recognized as a better method to have a safe process plant, without or with minimum damage to the environment and health. Literally, inherent safety purposes to minimize or eliminate the main causes of the hazards by modifying the design during preliminary stage such as the hardware, controls and the operating conditions of the process instead of depending on additional and available engineered safety systems. According to Ashford et al. [11], inherent safety sometimes also referred as "primary prevention" which depends on the development and formation of inherently safe technologies that avoid any possibilities of an accident. Secondary prevention is to reduce probability of an accident. As to compare between primary and secondary prevention [12], "secondary prevention" pursue mitigation and emergency responses to decrease the seriousness of injuries, property and environmental damage due to chemical accidents. Ashford and Zwetsloot [12] have proven that inherently safer options are also economically and technically feasible for plant operations. Although inherent safety is a flexible concept that can be applied at any design or operating stage, its involvement at the earliest stage of designing a process especially during the process route and selecting equipment will produces the best results with respect to time, production, quality and cost. In addition, inherent safety also should considered to be applied to operating existing plant as an alternative to provide significant improvement.

2.4 Previous Methodologies for Quantification of Inherent Safety Level (ISL)

A number of researchers have proposed numerous methodologies for inherent safety level quantification. Most of the methodologies developed emphasis on the

indexing technique for process route evaluation, which is mainly based on the reaction parameters. Lawrence [13] has first published his work which entitled "Quantifying inherent safety of chemical process route" as his doctoral thesis. In this thesis, a prototype index was presented to rank alternative chemical routes based on inherent safety characteristics of the alternatives. The prototype index is inclusive seven parameters which concerns on the physical properties of chemicals and condition of reaction steps. Every route is assessed against the process score using a scoring table, which evaluates the temperature, pressure, reaction yield, inventory, toxicity, explosiveness and flammability. In this prototype index, it has been tested using a number of routes to produce methyl methacrylate (MMA). The prototype index also was verified and improved by a panel of experts who ranked the alternative routes. According to Lawrence [13], the experts' judgment and experience of inherent safety were needed in order to help to make comments and also for improvement of the index. Questionnaires were given to the experts and were asked to rank the process route accordingly among themselves. The rankings resulted from the experts corresponding closely to the ranking from the calculated prototype index.

There is also another methodology for quantification of inherent safety level proposed by Heikkilä [14] which introduced weighting factors such as pressure, temperature, composition, etc. of the chemical process route and can be adjusted based on the indices scores as shown in Table 2.

Table 2: Inherent safety sub-indices (ISI) [14]

Chemical inherent safety index, I_{CI}	**Symbol**	**Score**
Heat of main reaction	I_{RM}	0 to 4
Heat of side reaction, max	I_{RS}	0 to 4
Chemical interaction	I_{INT}	0 to 4
Flammability	I_{FL}	0 to 4
Explosiveness	I_{EX}	0 to 4
Toxic exposure	I_{TOX}	0 to 6
Corrosiveness	I_{COR}	0 to 2
Process inherent safety index, I_{PI}		
Inventory	I_{I}	0 to 5
Process temperature	I_{T}	0 to 4
Process pressure	I_{P}	0 to 4
Equipment safety	I_{EQ}	
ISBL – Inside Battery Limits		0 to 4
OSBL – Outside Battery Limits		0 to 3
Safety of process structure	I_{ST}	0 to 5

Based on the score ranges resulted from the experts' evaluation in Table 2, it can be related with the expected impact of the parameter to the plant safety. Heikkilä [14] concluded that a wider score range for instance, 0 to 6 for toxicity and 0 to 5 for inventory which 6 and 5 are the maximum scores means that it has the most significant to the inherent safety. The scores for each parameter are mainly obtained from the previous researches and/or organizations. Referring to the Table 3, the flammability classifications are based on European Union Directive [14], whereas for explosiveness in Table 4, it is already specific to be subjectively assigned based on the previous researches.

Table 3: Flammability sub-index, IFL [14]

Flammability classification	**Score of I_{FL}**
Non-flammable	0
Combustible (flash point > 55°C)	1
Flammable (flash point < 55°C)	2
Easily flammable (flash point < 21°C)	3
Very flammable (flash point < 0°C and boiling point < 35°C)	4

Table 4: Explosiveness sub-index, IEX [14]

Difference in UEL – LEL (%)	**Score of I_{EX}**
Non-explosive	0
0 – 20	1
20 – 45	2
45 – 70	3
70 – 100	4

Palaniappan et al. [15] however improved Heikkilä's index systems by introducing supplementary indices which are worst chemical index (WCI), worst reaction index (WRI) and total chemical index (TCI). These supplementary indices were done with regards to a situation where the chemical route contains a highly toxic chemical and highly flammable chemical and this may causes complication when only one of them is being taken into account. This causes underestimated hazard of the process since both of the chemical may causes severity to the plant and surrounding. Therefore, WCI was proposed as it is the summation of maximum values of flammability, toxicity, reactivity and explosiveness of all materials involved in the reaction step. In the same way, WRI is calculated as the sum of the maximum of the individual indices of temperature, pressure, yield and heat of reaction of all of the reactions involved in the process. The TCI is the amount of hazardous chemicals involved in the route. And so, single route with one highly toxic

chemical is safer compared to route contains several toxic chemicals. TCI is also summation of the ICI of all of the chemicals contributed in the process route. The inherent safety index components (Table 5) involved are the individual and overall chemical index, individual and overall reaction index, hazardous chemical and reaction index, overall safety index and supplementary indices for each process route. The component of inherent safety index was carried out by evaluating four routes to produce acetic acid shown in Table 6.

Table 5: Inherent safety index equations [15]

Component of inherent safety index	**Notation**	**Equations**
Individual reaction index	IRI	$R_t + R_p + R_y + R_h$
Individual chemical index	ICI	$N_r + N_f + N_t + N_e$
Hazardous chemical index	HCI	max(ICI)
Hazardous reaction index	HRI	max(IRI)
Overall chemical index	OCI	max(ICI)
Overall reaction index	ORI	∑IRI
Overall safety index	OSI	∑(OCI + ORI)
Worst chemical index	WCI	$\max(N_r) + \max(N_f) + \max(N_t) + \max(N_e)$
Worst reaction index	WRI	$\max(R_t) + \max(R_p) + \max(R_y) + \max(R_h)$
Total chemical index	TCI	∑ICI

Table 6: Index calculation using Acetic Acid Process Routes [15]

Process	Reactions	IRI	ICI	HCI	HRI	OCI	ORI	OSI	WCI	WRI	TCI
Methane oxidation	step 1: methane + oxygen → methanol + carbon monoxide + water	9	7	10	9	17	14	31	12	9	32
	step 2: methanol + carbon monoxide → acetic acid	5	10								
Halcon vapor-phase oxidation	ethylene + oxygen → acetic acid	11	8	8	11	8	11	19	12	11	16
Acetaldehyde oxidation	acetaldehyde + oxygen → acetic acid	6	12	12	6	12	6	18	13	6	20
Low-pressure carbonylation	methanol + carbon monoxide → acetic acid	7	10	10	7	10	7	17	12	7	25

Later, there was another new development has been done by Gupta and Edwards [16] which is a graphical method for measuring inherent safety level. The inherently safer design (ISD) measurement procedure suggested by them can be applied to differentiate between two or more processes for the same end product, which is in their paper focusing on to produce methyl methacrylic acid (MMA) (The details of MMA routes is in Appendix A). The procedure is considering each of the main parameters affecting the safety (e.g., temperature, pressure, toxicity, flammability, etc.) and the possible range values of all the parameters can manage for these process routes that included in the consideration for an end product. Next, these values are plotted for every step in every process route and being compared. Referring to Figure 2 below, the example used is to compare six routes to produce MMA, and based on pressure perspective, the acetone cyanohydrin (ACH) route has a major advantage over the other five routes as this route operates at much lower pressure compared to other routes.

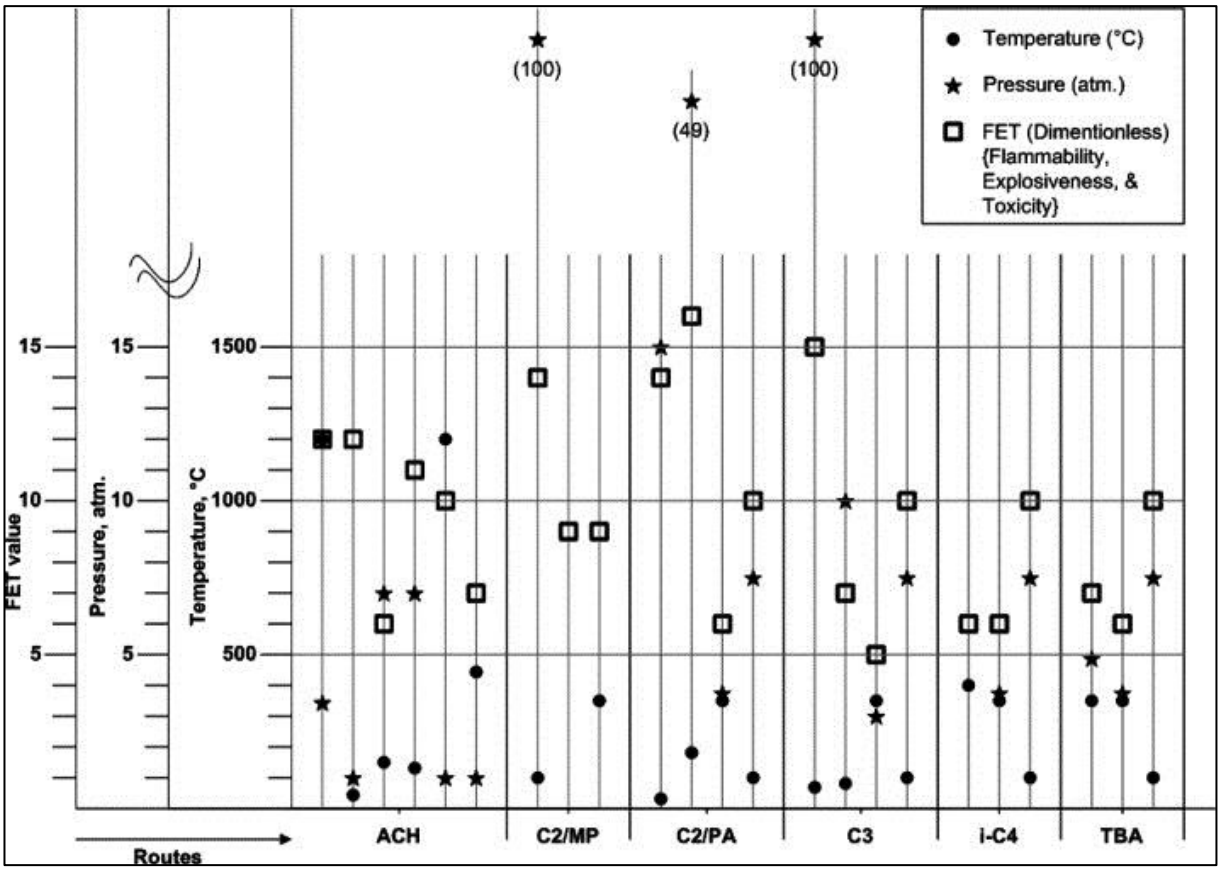

Figure 2: Graphical ISL quantification method [16]

Two years later, in 2005, a new index-approach has been proposed by Khan and Amyotte [17] that is a structured guide word-based similar to HAZOP technique known as "integrated inherent safety index" (I2SI). The developed index was aimed to be applied throughout the life cycle of process design such as the cost model and system design model (Figure 3). The I2SI encompasses two main sub-indices which are hazard index (HI) and inherent safety potential index (ISPI). The HI is designed to measure the damage potential of the process after considering the process and hazard control measures. The ISPI is responsible for the applicability of the inherent safety (or guidewords) to the process.

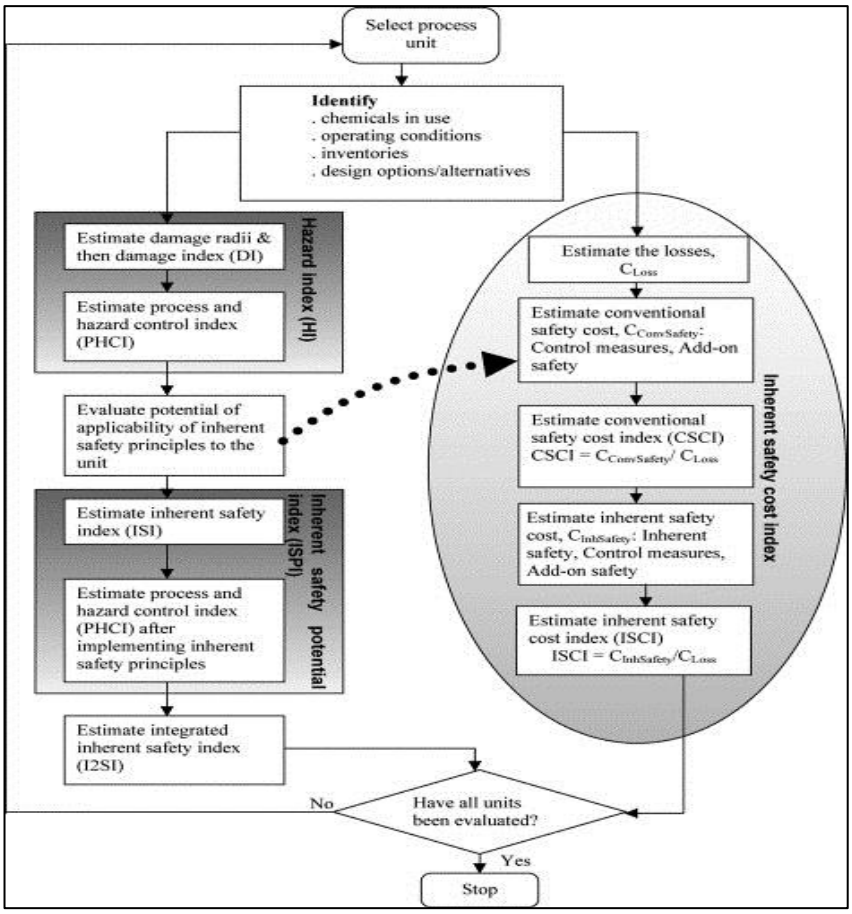

Figure 3: I2SI conceptual framework [17]

The HI is intended for the base process (any one process option or process setting will be considered as the base operation or setting) and maintain the same for all other possible options. For each option of HI and ISPI are merged to produce a value of the integrated inherent safety index (I2SI) as shown in Equation 2.1.

$$I2SI = \frac{ISPI}{HI} \qquad \text{Eq. 2.1}$$

Both HI and ISPI are range from 1 to 200, where the range has been fixed considering the maximum and minimum likely values of the impacting parameters. This range has shown enough flexibility to quantify the index. As the result, an I2SI has a greater value than unity denotes a positive response of the inherent safety guideword application (inherently safer option). The higher the value of I2SI, the more pronounced the impact of inherent safety.

CHAPTER 3: METHODOLOGY

3.1 Three-Tier Inherent Safety Quantification (3-TISQ)

This new technique of Three-Tier Inherent Safety Quantification (3-TISQ) implements the concept of inherent safety indices (ISI) and combining it with Quantitative Risk Assessment (QRA) which could evaluate the inherent safety level (ISL) at preliminary design stage. Therefore, a framework has been introduced which is able to differentiate ISL of the process routes and followed by the risk assessment for process streams within a process route for toxic release accidents. This framework is an improvement of the Two-Tier Inherent Safety Index (2-TISI) proposed by Leong and Shariff [18]. However, 2-TISI is developed for the case of explosion and never focused on prevention or minimization of major accidents due to toxic release accidents. Hence, for toxic release accidents, 3-TISQ has the similar approach as 2-TISI but with three levels of quantification, i.e. the Toxic Release Route Index (TRRI), Toxic Release Stream Index (TRSI) and Toxic Release Inherent Risk Assessment (TRIRA). The 3-TISQ framework procedure is as shown in Figure 4.

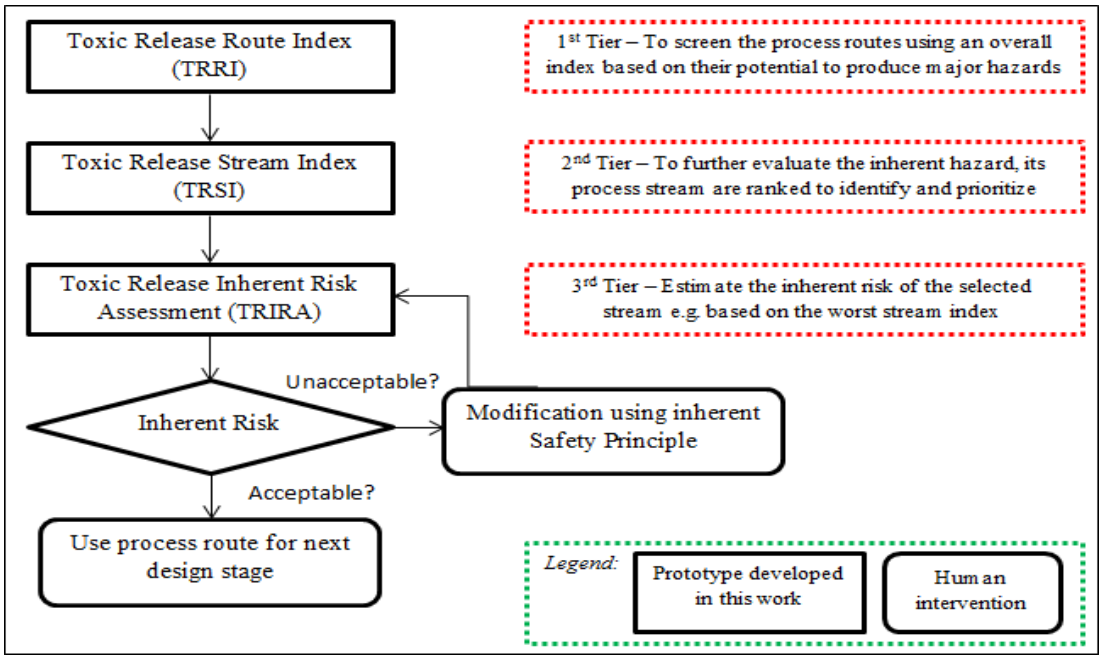

Figure 4: 3- TISQ Framework

3.1.1 Toxic Release Route Index (TRRI)

Practically, the development of Inherent Safety Indices (ISI) is complicated. The inherent safety concept at preliminary design stage identifies that safety should be deliberated and given high attention and priority when selecting the chemical process route. As stated by Edwards and Lawrence [19], the chemical process route, or just 'route', may be defined as the raw material(s) and the sequence of reactions which converts to the desired products.

Toxic Release Route Index (TRRI) embraces the similar technique as Process Route Index (PRI) but TRRI is focusing on toxic release whereas PRI is to assess process route proposed by Leong and Shariff [18] which is for explosion only. TRRI uses representative numerical to present ISL for a process route as the first tier in 3-TISQ. An overall process route index is based on the average value of the relevant parameters that influence the toxic release which is also dimensionless is given in Equation 3.1. The empirical constant, A_0 functions to reduce or increase the magnitude of the resulting numbers in the calculation of TRRI and the magnitude is up to the acceptable level of the end users.

$$TRRI = \left[(average\ density) \times (average\ pressure) \times \left(average\ toxicity\ level(TL)\right)\right] \times A_0$$

Eq. 3.1

All the process parameters can be gained from process design simulator. The relative ranking for the index is similar to the technique by Leong and Shariff [18] to determine the inherently safer route. Therefore, a larger TRRI value indicates that the route is inherently less safe from the toxicity perspective compared to a route having smaller TRRI value.

3.1.2 Toxic Release Stream Index (TRSI)

TRSI is developed using similar approach as Shariff et al. [20] by rank the streams based on the ISL as the second tier in 3-TISQ. TRSI is a single numerical

value to present the ISL in term of relative ranking which also adopts the similar theoretical technique from TRRI.

$$TRSI = \left(I_P \times I_\rho \times I_{TL}\right) \times A_0 \qquad \text{Eq. 3.2}$$

$$I_P = \frac{pressure\ value\ of\ individual\ stream}{average\ pressure\ of\ all\ streams} \qquad \text{Eq. 3.3}$$

$$I_\rho = \frac{density\ value\ of\ individual\ stream}{average\ density\ of\ all\ streams} \qquad \text{Eq. 3.4}$$

$$I_{TL} = \frac{TL\ value\ of\ individual\ stream}{average\ TL\ of\ all\ streams} \qquad \text{Eq. 3.5}$$

The worst stream is given by the highest ISL value which can be considered as the priority stream to be improved using the inherent principles. Therefore, to determine whether the developed TRSI technique can be used to assess and prioritize the process streams for the toxic release cases, it has been compared with PSI proposed by Shariff et al. [20]. For this index, Acrylic Acid Plant is used as a case study and the results shown in Figure 5. By using PEARSON function to calculate correlation coefficient, the trending and correlation between both methods can be evaluated.

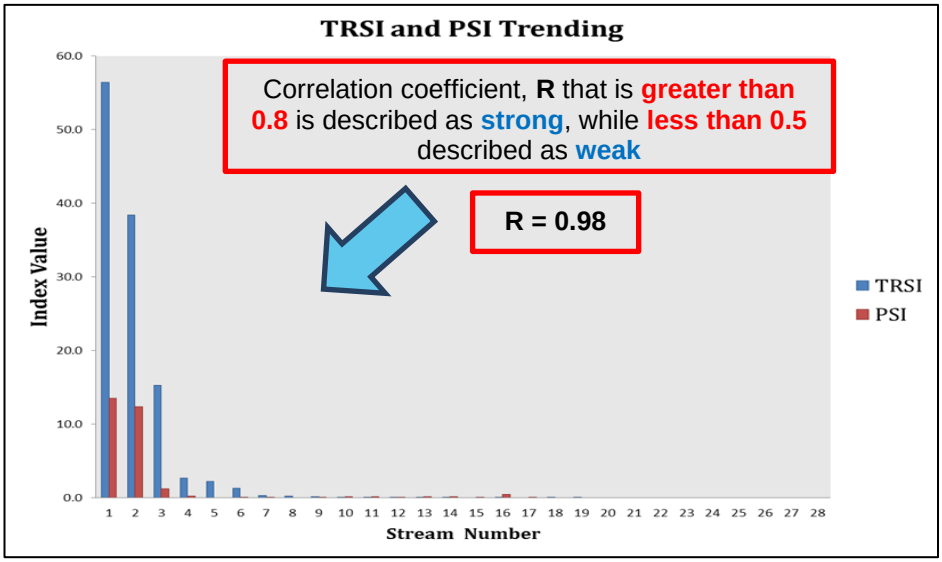

Figure 5: Inherent safety indices for Acrylic Acid streams

3.1.3 Toxic Release Inherent Risk Assessment (TRIRA)

Shariff and Zaini [21] have introduced Toxic Release Inherent Risk Assessment (TRIRA) to determine the inherent risk of toxic release hazard by using the two-region risk matrix as the third-tier in 3-TISQ as given in Figure 6. The framework for inherent risk assessment and also design improvement for the toxic release case is shown in Figure 7.

The two-region risk matrix is introduced in TRIRA due to the absent of safety measures and control mechanisms during preliminary design stage in reducing the risk As Low as Reasonably Practicable (ALARP). Several criteria has been compared between TRIRA technique and QRA in Table 7.The information existing at preliminary design stage will be useful to evaluate the inherent risk of toxic release based on the process conditions of the materials in the process plant.

Likelihood of Occurrence (year-1)	Severity of Occurrence		
	AEGL – 1 [A] (ppm)	AEGL – 2 [B] (ppm)	AEGL – 3 [C] (ppm)
Very High [1]	A1	B1	C1
High [2]	A2	B2	C2
Moderate [3]	A3	B3	C3
Low [4]	A4	B4	C4
Very Low [5]	A5	B5	C5
Unlikely [6]	A6	B6	C6

Legend
Unacceptable
Acceptable

Figure 6: Two region risk matrix for TRIRA [21]

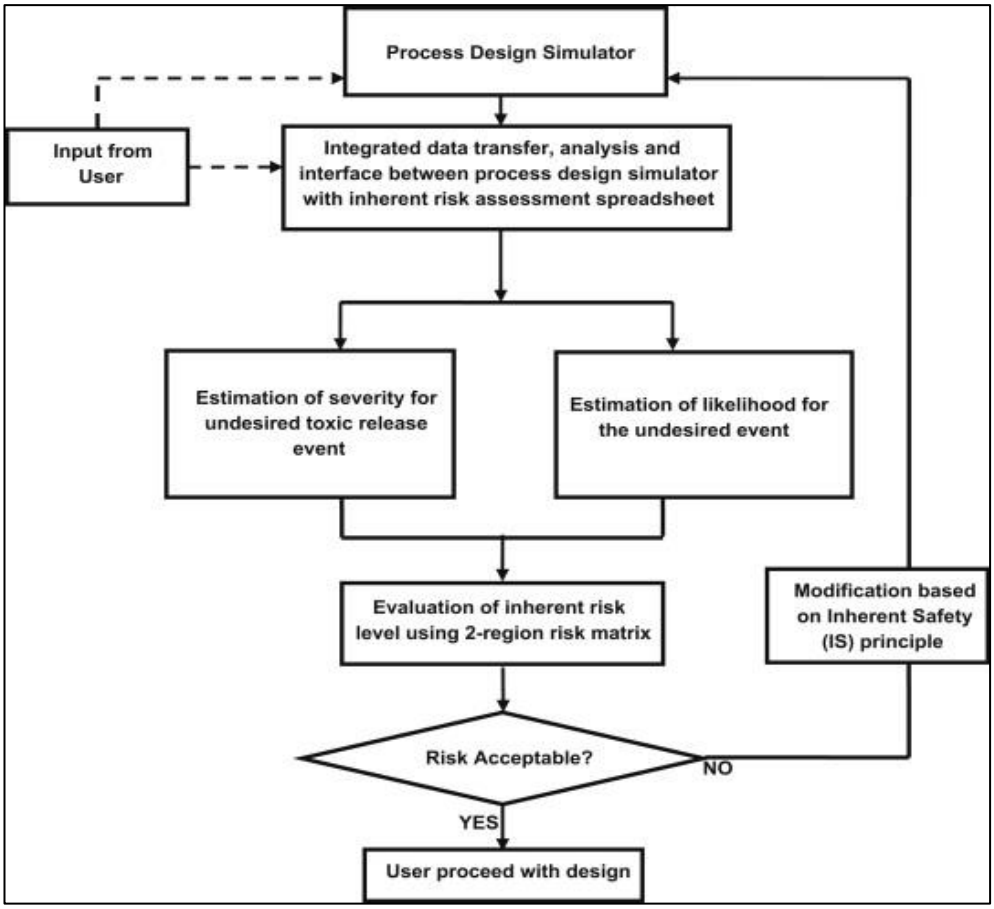

Figure 7: TRIRA framework concept [21]

Table 7: Comparison between QRA and TRIRA [21]

Criteria	QRA	TRIRA
Stage to be applied	Coarse (preliminary) QRA during Front End Engineering Design (FEED) and detailed QRA during operation stage	During preliminary design/simulation stage
Purpose	To measure risk for credible major accident events and benchmark	To proactively identify risk, inherent to the design intention based on the developed risk matrix and manage the risk by adopting inherent safety principles
Regulatory requirements	Required by regulatory agencies, for example Department of Occupational Safety & Health in Malaysia and the Health and Safety Executive in the UK	No regulatory requirement
Information required	Process & instrumentation diagrams (P&ID), process conditions, reliability data and historical weather data	Simulation data on process conditions, approximate reliability data, piping and equipment sizing
Scenario	Only few credible scenario including worst case to be studied in detail	Worst case scenario
Duration of analysis	Relatively long depending on the size of the plant	Relatively quick as it is carried out in parallel with simulation work
Result representation	3-region Frequency-Number (F-N) curve covering tolerable, tolerable with ALARP and intolerable regions	2-region risk matrix covering acceptable and unacceptable regions

3.2 Key Milestone

Table 8 shows the key milestone throughout the project.

Table 8: Key Milestone

Semester	Task	Completion
May 2014	Selection of Project Topic	Week 2
	Preliminary research work	Week 5
	Submission of extended proposal	Week 6
	Proposal Defense	Week 8
	Submission of Interim Draft Report	Week 13
	Submission of Interim Draft Report	Week 14
September 2014	Submission of Progress Report	Week 8
	Pre-SEDEX	Week 11
	Submission of Draft Report	Week 12
	Submission of Dissertation (soft bound)	Week 13
	Submission of Technical Paper	Week 13
	Oral presentation	Week 14
	Submission of Project Dissertation (hard bound)	Week 15

3.3 Gantt-Chart

Table 9 shows the Gantt chart for FYP 1.

Table 9: Gantt-Chart of FYP 1

Activities	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14
First meeting with coordinator and supervisor														
Problem statement and analysis of project														
Preliminary research work and literature review														
Submission of extended proposal defense														
Oral proposal defense presentation														
Preparation of Interim Report														
Submission of Interim Draft Report														
Submission of Interim Final Report														

Legend: Progress Suggested milestone

Table 10 shows the Gantt chart for FYP 2.

Table 10: Gantt-Chart of FYP 2

Activities	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15
Project work continues															
Submission of Progress Report															
Project work continues															
Pre-SEDEX															
Submission of Draft Report															
Submission of Dissertation (soft bound)															
Submission of Technical Paper															
Oral presentation															
Submission of Project Dissertation (hard bound)															

Legend: Progress Suggested milestone

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Overview

In this chapter, a case study will demonstrate the application of the Three-Tier Inherent Safety Quantification (3-TISQ) for designing an inherently safer process plant. It is concluded that 3-TISQ has the potential to assist design engineers to measure the potential risks during the preliminary design stage. Besides, it can also provide preliminary toxic release consequence analyses. Therefore, with all the knowledge available to the design engineers, they can choose for potential inherently safer design for the process plant.

4.2 Case Study: Application of 3-TISQ to quantify the inherent safety level (ISL)

The recent case study is based on acrylic acid via propylene oxidation process simulation by Shariff et. al. [22]. It is designed to demonstrate the application of 3-TISQ for quantifying the inherent safety level (ISL) which the main target is on toxic release at preliminary design stage. Briefly, acrylic acid is commonly produced by partial oxidation of propylene. In this route, the typical mechanism for producing acrylic acid has two-step process in which propylene is first oxidized to acrolein and then further oxidized to acrylic acid [23].

Referring to Figure 8, propylene is partially oxidized to acrolein in CRV101 and further converted in CRV 102 to become acrylic acid. During the process, the gaseous product from CRV102 is partly quenched and passed through A101, the scrubber tower. Next, the liquid stream from the A101's bottom is combined with the liquid stream from the V101 and passed to two distillation columns in series for purification. For the last step, T101 is responsible to separate water from the mixture of water and acrylic acid in stream 23 and achieved 99.6% purity. In this preliminary design, T102 is added for further acrylic acid purification from 99.6% to 99.9% by a distillation process.

From this process simulation, analysis has been done by applying the first tier of 3-TISQ and the Toxic Release Route Index (TRRI) overall index calculated is 1.73. In order to prioritize the stream, identify the 'worst' stream and list down the streams that have low or hazardless by using the second tier of 3-TISQ which is Toxic Release Stream Index (TRSI) to rank the process streams within the process route. From Table 11, the TRSI calculation shows that stream 18 has the highest score amongst the process streams in the simulation followed by stream 23 and 26 respectively. This indicates that stream 18 is the most hazardous if toxic release occurs.

Table 11: Inherent safety indices for Acrylic Acid streams

Acrylic Acid Stream [24]	Process Stream Index (PSI) [20]		**Toxic Release Stream Index (TRSI)**
	Calculated index value		Calculated index value
1	0.11		0.09
2	0.00		0.00
3	0.00		0.00
4	0.00		0.00
5	0.08		0.07
6	0.00		0.00
7	0.08		0.03
8	0.05		0.02
9	0.00		0.00
10	0.12		0.06
11	0.00		0.00
12	0.12		0.06
13	0.13		0.07
14	0.04		0.13
15	0.00		0.00
16	0.09		0.32
17	0.00		0.01
18	**13.54**		**56.42**
19	0.00		0.00
20	0.00		0.00
21	0.00		2.22
22	0.00		0.17
23	12.52		38.39
24	0.00		0.00
25	0.10		1.31
26	1.16		15.27
27	0.20		2.68
28	0.44		0.03

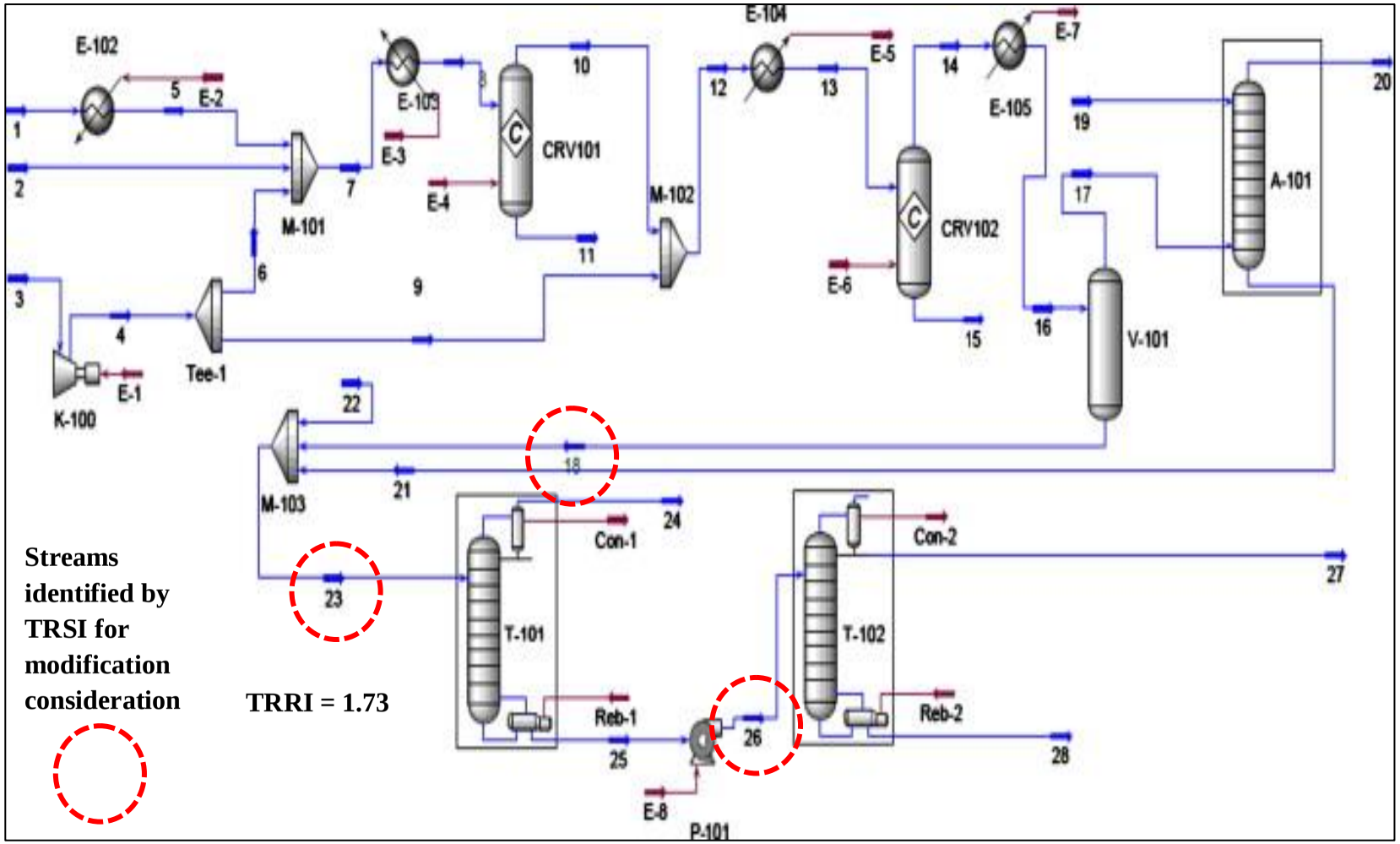

Figure 8: Acrylic acid production base using HYSYS proses design simulation [23]

Followed by the third tier of 3-TISQ which is Toxic Release Inherent Risk Assessment (TRIRA), it has been carried out to evaluate the risk that is inherent to the process conditions and composition using i-TORSET (Figure 9) for the severity. i-TORSET severity estimation for stream 18 was calculated in the Appendix B while the probability of toxic release is calculated using i-TORFAT (Figure 10). i-TORFAT is a fault tree analysis (FTA) which is a simplified basis to describe a likelihood toxic release event developed by Khan and Abbasi [25] and Khan et. al. [26]. Once the probability of the top event has been determined, it can be used to assess the likelihood of occurrence. The likelihood of occurrence was developed based on MIL-STD-882D standard [27]. The summary of the Acute Exposure Guideline Level (AEGL) value for acrylic acid is given in Table 12. From the calculated severity in Appendix B and probability, the results were combined on a two-region risk matrix (Figure 11). The background of the risk matrix was explained in section 3.1.3. From Figure 11, it can be concluded that the inherent risk of the stream 18 is in the ACCEPTABLE region.

Input Data				Result					
Composition		Acrylic Acid							Clear Data
Total Release	Q*m	5.11	kg	Stability Class			F		
Molecular Weight	MW	72.06		Assumed wind speed, μ:			2	m/s	
Temperature	T	298	kg	Dispersion Coefficients:					
Pressure	P	1	atm		Sigma y:	σy	11	m	Import Data
Release Height	H	0	m		Sigma z:	σz	3.8	m	
Distance Downwind	x	1200	m	Downwind concentration:		C	0.001419	kg/m^3	
Distance Off Wind	y	0	m				1418.757	mg/m^3	
Distance Above Ground	z	0	m	PPM:			481.4614	ppm	Calculate
				The time required for the center to arrive			10	min	
				Probit			-4.7		
				Percent of Fatalities			0		
				AEGL			3		

Figure 9: Severity estimation for stream 18 rupture occurrence (i-TORSET)

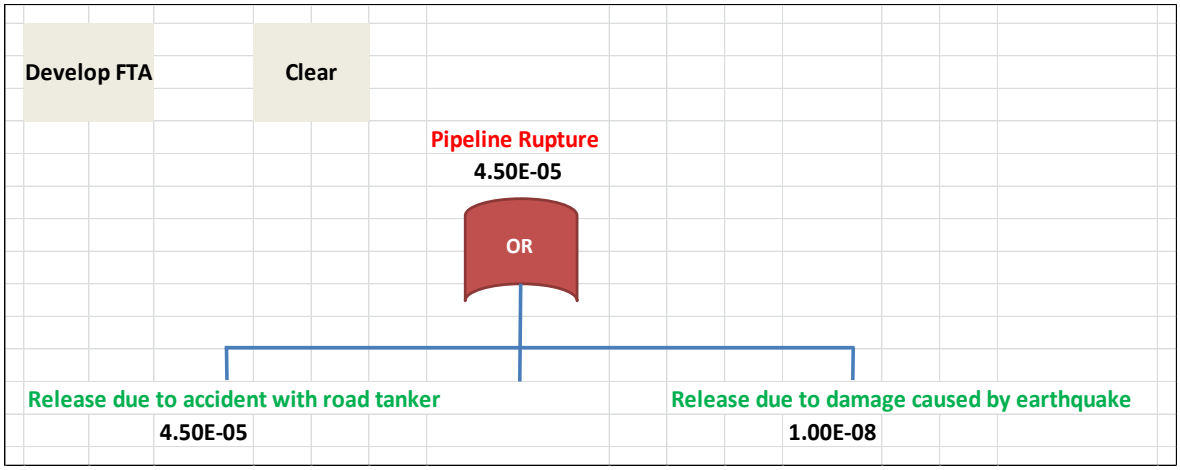

Figure 10: i-TORFAT likelihood estimation for stream 18 rupture occurrence [25] & [26]

Table 12: Likelihood ratings [27]

Likelihood of occurrence	Likelihood of event occurring/year
Very high	$10^{-0} \geq P\ 10^{-1}$
High	$10^{-1} \geq P\ 10^{-2}$
Moderate	$10^{-2} \geq P\ 10^{-3}$
Low	$10^{-3} \geq P\ 10^{-4}$
Very low	$10^{-4} \geq P\ 10^{-5}$
Unlikely	$10^{-5} \geq P\ 10^{-6}$

Table 13: Acute Exposure Guideline Level (AEGL) value for acrylic acid

Chemical name: Acrylic Acid (in ppm)					
	10 min	30 min	60 min	4 hr	8 hr
AEGL-1	1.5	1.5	1.5	1.5	1.5
AEGL-2	68	68	46	21	14
AEGL-3	480	260	180	85	58

Source: http://www.epa.gov/opptintr/aegl/pubs/results23.htm (retrieved on 10 November 2014)

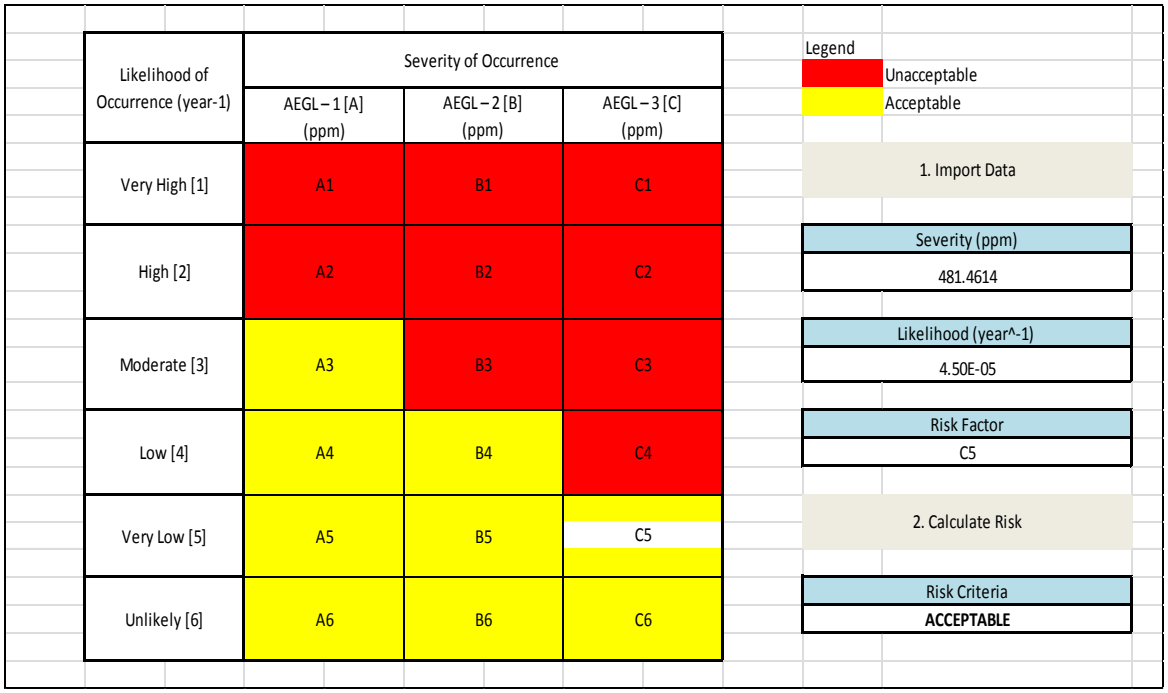

Figure 11: Inherent risk estimation from TRIRA for stream 18 rupture occurrence

CHAPTER 5: CONCLUSION AND RECOMMENDATION

The growth of chemical, oil and gas industries since 1960s has seen an increasing number of major accidents where it now comprises complex processes to achieve desired products. Some of examples of previous major accidents which gave historic impact to human has triggered the engineers to be more serious and aware about safety in the process industries, were discussed in section 1.1. A few general safety and hazard assessments tools used in industries were briefly described in section 2.2. Although implementing these techniques to yield the best results during the early stage, however, these techniques are not suitable to apply at preliminary design stage due to unavailability of required data.

Thus, the 3-TISQ is developed to allow design engineers to integrate inherent safety indices with inherent risk assessment for implementing the inherent safety features efficiently and cost efficient. 3-TISQ has three levels of quantification which are Toxic Release Route Index (TRRI), Toxic Release Stream Index (TRSI) and Toxic Release Inherent Risk Assessment (TRIRA). The TRRI was compared against previous research which is Process Route Index (PRI) by Leong and Shariff [18] and produces good results which are in-line with PRI since TRRI and PRI have the ability to quantify properties of the mixture in a route. Followed by TRSI, also was compared against the Process Stream Index (PSI) developed by Shariff et. al. [20] and produces results that are in good agreement with PSI since TRSI and PSI have the ability to measure the properties of the mixture in a stream. Furthermore, TRIRA is added as the third tier in this framework to be used as an integrated tool during process simulation to apply the principles of inherent safety. 3-TISQ also has been tested to acrylic acid plant as the case study to proof the capability of this new framework to quantify consequence of toxic release.

For the next improvement, 3-TISQ has the potential to determine the consequence analysis for other type of hazard since the present work only presented the consequences and risk assessment for toxic release. Due to this, it is recommended to propose a complete development of this model for other hazards

and integrate them using two-region risk matrix inherent risk assessment. Besides, in the future, cost analysis can be include which can calculate the potential risks associated with the cost especially risk in the operation of the process plant, risk to environment, risk to assets and equipment and risk to financial performance. By integrating some additional data and enhancements the methodology, 3-TISQ is capable of being extended to include cost evaluation.

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APPENDIX A

DETAILS OF SIX METHYL METHACRYLIC (MMA) ROUTES

Appendix A: Details of six MMA routes [16]

Route 1: Acetone cyanohydrin based route (ACH)

Step 1: $2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$
Methane + ammonia + oxygen → hydrogen cyanide + water Gas phase, pressure: 3.4 atm, temperature: 1200 °C, yield: 64%

Step 2: $(CH_3)_2CO + HCN \rightarrow (CH_3)_2COHCN$
Acetone + hydrogen cyanide → acetone cyanohydrin
Liquid phase, pressure: atm, temperature: 29–38 °C, yield: 91%

Step 3: $2(CH_3)_2COHCN + H_2SO_4 + 2H_2O \rightarrow (CH_3)_2COHCONH_2 + (CH_3)_2COHCONH_2 \cdot H_2SO_4$
$\xrightarrow{\text{Heat}} CH_2{=}C(CH_3)CONH_2 + CH_2{=}C(CH_3)CONH_2 \cdot H_2SO_4 + 2H_2O$
Acetone cyanohydrin + sulphuric acid + water
→ 2-hydroxyl-2-methyl propionamide + 2-hydroxyl-2-methyl propionamide sulphate
→ methacrylamide + methacrylamide sulphate + water
Liquid phase, pressure: 7 atm, temperature: 130–150 °C, yield: 98%

Step 4: $CH_2{=}C(CH_3)CONH_2 + CH_2{=}C(CH_3)CONH_2 \cdot H_2SO_4 + 2CH_3OH + H_2SO_4 \rightarrow$
$2CH_2{=}C(CH_3)COOCH_3 + 2NH_4HSO_4$
Methacrylamide + methacrylamide sulphate + methanol + sulphuric acid → MMA + ammonium bisulphate Liquid phase, pressure: 7 atm, temperature: 110–130 °C, yield: 100%

Step 5: $H_2SO_4 + 2NH_4HSO_4 + 3O_2 + CH_4 \rightarrow 3SO_2 + CO_2 + N_2 + 8H_2O + O_2$
Sulphuric acid + ammonium bisulphate + oxygen + methane
→ sulphur dioxide + carbon dioxide + nitrogen + water + oxygen Gas phase, pressure: atm, temperature: 980–1200 °C, yield: 100%

Step 6: $2SO_2 + O_2 \rightarrow 2SO_3$
Sulphur dioxide + oxygen → sulphur trioxide
Gas phase, pressure: atm, temperature: 405–440 °C, yield: 99.7%

Route 2: Ethylene (via methyl propionate) based route (C2/MP)

Step 1: $CH_2{=}CH_2 + CO + CH_3OH \rightarrow CH_3CH_2COOCH_3$
Ethylene + carbon monoxide + methanol → methyl propionate Liquid phase, pressure: 100 atm, temperature: 100 °C, yield: 89%

Step 2: $6CH_3OH + O_2 \rightarrow 2CH_3OCH_2OCH_3 + 4H_2O$
Methanol + oxygen → methylal + water
Vapour phase, pressure: ?, temperature: ?, yield: ?

Step 3: $CH_3CH_2COOCH_3 + CH_3OCH_2OCH_3 \rightarrow CH_2{=}C(CH_3)COOCH_3 + 2CH_3OH$
Methyl propionate + methylal → MMA + methanol Liquid phase, pressure: ?, temperature: 350 °C, yield: 87.4%

Route 3: Ethylene (via propionaldehyde) based route (C2/PA)

Step 1: $CH_2{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CHO$
Ethylene + carbon monoxide + hydrogen → propionaldehyde Gas phase, pressure: 15 atm, temperature: 30 °C, yield: 90.7%

Step 2: $CH_3CH_2CHO + CH_2O \rightarrow CH_2{=}C(CH_3)CHO + H_2O$
Propionaldehyde + formaldehyde → methacrolein + water
Liquid phase, pressure: 49 atm, temperature: 160–185 °C, yield: 98.2%

Step 3: $2CH_2{=}C(CH_3)CHO + O_2 \rightarrow 2CH_2{=}C(CH_3)COOH$
Methacrolein + oxygen → methacrylic acid
Gas phase, pressure: 350 atm, temperature: ?, yield: 57.75%

Step 4: $CH_2{=}C(CH_3)COOH + CH_3OH \rightarrow CH_2{=}C(CH_3)COOCH_3 + H_2O$
Methacrylic acid + methanol → MMA + water
Liquid phase, pressure: 6.8–7.5 atm, temperature: 70–100 °C, yield: 75%

Route 4: Propylene based route (C3)

Step 1: $CH_3CHCH_2 + CO + HF \rightarrow (CH_3)_2CHCOF$
Propylene + carbon monoxide + hydrogen fluoride → isobutyrl fluoride Liquid phase, pressure: 90–100 atm, temperature: 70 °C, yield: 94.5%

Step 2: $(CH_3)_2CHCOF + H_2O \rightarrow (CH_3)_2CHCOOH + HF$
Isobutyrl fluoride + water → isobutyric acid + hydrogen fluoride Liquid phase, pressure: 10 atm, temperature: 40–90 °C, yield: 96.2%

Step 3: $2(CH_3)_2CHCOOH + O_2 \rightarrow 2CH_2=C(CH_3)COOH + 2H_2O$
Isobutyric acid + oxygen → methacylic acid + water
Vapour phase, pressure: 2.5–3 atm, temperature: 320–354 °C, yield: 70.5%

Step 4: $CH_2=C(CH_3)COOH + CH_3OH \rightarrow CH_2=C(CH_3)COOCH_3 + H_2O$
Methacrylic acid + methanol → MMA + water
Liquid phase, pressure: 6.8–7.5 atm, temperature: 70–100 °C, yield: 75%

Route 5: Isobutylene based route (*i*-C4)

Step 1: $(CH_3)_2CCH_2 + O_2 \rightarrow CH_2CCH_3CHO + H_2O$
Isobutylene + oxygen → methacrolein + water
Vapour phase, pressure: ?, temperature: 395 °C, yield: 41.8%

Step 2: $2CH_2CCH_3CHO + O_2 \rightarrow 2CH_2CCH_3COOH$
Methacrolein + oxygen → methacrylic acid
Vapour phase, pressure: 3.7 atm, temperature: 350 °C, yield: 57.75%

Step 3: $CH_2=C(CH_3)COOH + CH_3OH \rightarrow CH_2=C(CH_3)COOCH_3 + H_2O$
Methacrylic acid + methanol → MMA + water
Liquid phase, pressure: 6.8–7.5 atm, temperature: 70–100 °C, yield: 75%

Route 6: Tertiary butyl alcohol based route (TBA)

Step 1: $(CH_3)_3COH + O_2 \rightarrow CH_2CCH_3CHO + 2H_2O$
Tertiary butyl alcohol + oxygen → methacrolein + water Vapour phase, pressure: 4.8 atm, temperature: 350 °C, yield: 83%

Step 2: $2CH_2CCH_3CHO + O_2 \rightarrow 2CH_2CCH_3COOH$
Methacrolein + oxygen → methacrylic acid
Vapour phase, pressure: 3.7 atm, temperature: 350 °C, yield: 57.75%

Step 3: $CH_2=C(CH_3)COOH + CH_3OH \rightarrow CH_2=C(CH_3)COOCH_3 + H_2O$
Methacrylic acid + methanol → MMA + water
Liquid phase, pressure: 6.8–7.5 atm, temperature: 70–100 °C

APPENDIX B

ESTIMATION OF RELEASE, DISPERSION AND TOXIC EFFECT CRITERIA FOR STREAM 18 ACRYLIC ACID SIMULATION

Appendix B: Estimation of Release, Dispersion and Toxic Effect Criteria from stream 18 Acrylic Acid Simulation

Calculation:

1) Discharge rate of acrylic acid through a rupture of 100 mm pipeline diameter at $T = 65^{o}C$ and $P_1 = 200$ kPa

Data:

Diameter of the pipe, 100 mm = 0.1 m, $A = 0.007855\ m^2$

Acrylic acid heat capacity ratio, $k = 1.17$

Discharge coefficient, $C_D = 1$

Ideal gas constant, $R_g = 8314\ Pa.m^3 / kg\text{-}mole.K$

Molecular weight of propane, $M = 72.06$ kg / kg-mole

Gravitational constant, $g_c = 1$

Calculation of mass release of acrylic acid vapour [1]

$$m_{choked} = C_D A P_1 \sqrt{\frac{k g_c M}{R_g T_1}\left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}} = \mathbf{5.11\ kg/s}$$

Assumption

a) The worst case scenario is assumed to originate from 100 mm diameter pipeline rupture since there is an uncertainties arise due to an incomplete understanding or the availability of the geometry of the release, that is the hole size. [28]
2) Downwind concentration of acrylic acid from 1200 m distance of source release

By using equation stated in [1] to calculate downwind concentration:

$$\langle C \rangle(x, y, z, t) = \frac{G^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} exp\left\{-\frac{1}{2}\left[\left(\frac{x-ut}{\sigma_x}\right)^2 + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right]\right\}$$

Data:

Total release, G^*	= 5.11 kg
Sigma y, σ_y	= 11 m
Sigma z, σ_z	= 3.8 m
Distance downwind, *x*	= 1200 m
Distance off wind, *y*	= 0 m
Distance above ground, *z*	= 0m
Time since the release of puff cloud, *t*	= 10 minutes

Downwind concentration center at 1200 m from source release = **481.4614 ppm**

Assumption:

a) The release is assumed to disperse at ground level, coordinates fixed at release point, constant wind only in *x* direction, constant wind velocity *u* with maximum concentration occurring at the centre of the puff cloud ($x = ut$, $y = 0$, $z = 0$ in equation above) and $\sigma_x = \sigma_y$ [1]
b) The wind class stability F at the distance of $x = ut = 1200$ m with $u = 2$ m/s wind speed. This is the distance for the 10 minutes duration of the accidental released in the case of the worst condition [28]
c) The mass of material release is calculated at the instant the rupture occurs, with the discharge rate decreasing as a function of time as the pressure within the pipeline decrease i.e. 5 kg of material release is assumed from 5 kg/s release [28]

3) Toxic Effect Criteria Calculation

From Table 4.2, the AEGL value for Acrylic acid is **AEGL-3** by referring the value **481.4614 ppm** from downwind concentration calculation.

Probit function in a term of describing the fatalities by toxic release is calculated using equation below

$$P_r = A + B \ln(c^n t)$$

For acrylic acid,
A = -27.3, B = 1.7 and *n* = 1.8 according to
http://www.epa.gov/oppt/aegl/pubs/tsd304.pdf

From the equation stated above, probit calculation for acrylic acid at 1200 m = **-4.7**

For spreadsheet computations, equation below is used to get the percent of fatalities:

$$P = 50\left[1 + \frac{P_r - 5}{|P_r - 5|} erf\left(\frac{|P_r - 5|}{\sqrt{2}}\right)\right]$$

After calculation, the percent of fatalities for acrylic acid at 1200 m = **0%**