Process Safety Conflict Index (PSCI) For Toxic Release

Using Risk Based Approach

by

Nurul Hidayah binti Abu Hanipah

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CERTIFICATION OF APPROVAL

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Approved by,

____

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JULY 2010

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.

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NURUL HIDAYAH BINTI ABU HANIPAH

ABSTRACT

Inherent safety is an important term for development of safety performance indicator. Inherent safety principles are used in order to calculate the safety performance indicator for selected based case. The safety performance indicator has been developed from the traditional approach to the new strategies and tools. In this project, the aim is to develop an inherently safety model by considering the conflicts or tradeoffs that will be arose when a process unit is attempt to apply Inherent Safety Principles. The focus will be narrowed down on analyzing the risk of toxic release. The risk will be calculated by implementing one of available tools for inherent safety. The method that will be used in this project will be similar to the available tools. However, the calculated risk is corresponding to the damage index and the conflict indices which will be developed throughout the project. Thus, conflict index, CI has been developed in taken into accounts the likelihood of conflicts that arise in the design options after considering the inherent safety principles (ISP) which is the measurement of the impact of the ISP analysis to the safety process.

ACKNOWLEDGEMENT

In the name of ALLAH, the Most Gracious, Most Merciful, with His permission, Alhamdulillah this project has completed.

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CHAPTER 1

1 INTRODUCTION

Several established qualitative hazard analysis such as safety reviews, checklist and HAZOP has been used widely during design stage (CCPS, 1992). Although this approach is very efficient and useful, it is believed that inherent safety approach could be better technique. Inherent safer design approach is to eliminate or reduce the hazard by changing the process itself, rather than by adding on additional safety devices and layers of protection (Hendershot. D.C., 1999). Ideally, hazard would be reduced to a level where no protective systems are required because the hazard is too small to be of concern. Even it is not possible, an inherently safer process will allow the number of layers of protection to be reduced. The overall design is therefore more robust from a safety and environmental viewpoint, and is likely to be less expensive to build and operate because of the elimination of complex system.

Inherent safety principles are accomplished throughout the design process stage, from the conception until completion. The four main concepts of inherently safer design are intensification/minimization (to reduce the amount of hazardous material involved in the process as much as possible), attenuation/moderation (to challenge process conditions such as that it renders the substance/process less hazardous), substitution (to use a less hazardous material compared to a more hazardous one) and simplification (to reduce unnecessary complexity and opportunities of human errors). If implemented properly, inherently safer design can achieve higher reduction benefits compared to procedural safety systems (Hendershot, 1997). Inherent Safety Design also has been considered as an inspiring philosophy which could be the bases of sustainability. Despite, these principles will help in reducing hazard by using safer material and operating conditions, minimizing inventory and by designing a simpler and friendlier plant (Palaniappan et al., 2002).

It has been highlighted that the inherent safety concept using technologies and chemical that reduce or eliminate the possibility of an accident. However, in spite of having such advantages, the previous method in inherent safety principles has been limited. Nevertheless, the lacks of recognized methodology or tools to analyze the inherently safer design at the early stage of process design by including the conflict and tradeoffs that arise to process alternatives are the crucial obstacles to the implementation of this safety philosophy. Lack of studies in tradeoffs that may arise in the system has questioned the sustainability and persistency of the selected methods. Thus, there is a need to incorporated safety considerations with the design procedure and apply methods with quantitative estimate the hazard. Process Safety Conflict Index (PSCI) will objectively define and analyzed the tradeoffs and calculated the risk. This integrated study of the risk relative to the base case is calculated and ranked.

However, in this project, the focus will be narrowed down on analyzing the risk of toxic release. The risk will be calculated by implementing one of available tools for inherent safety. The method that will be used in this project will be similar to the available tools. However, the calculated risk is corresponding to the damage index and the conflict indices which will be developed throughout the project. In this context, these quantitative indices provide a good balance in analyzing the conflict that arises in the system and the risk calculated can be rank based on the developed conflict indices. Parallel to this, this method also aimed to be able to calculate the consequences of the base case and also to calculate the likelihood of the conflicts studies that arise in the system while implementing the inherent safety principles. This study also highlighted the integrated study of the risk relative to the base case and the risk will be ranked for decision making procedures.

Overall, objective of these inherent safety principles concepts into the design stage has been approached thoroughly. Finally, a case study of production of methyl methacrylate (MMA) was used to demonstrate the applicability of the proposed method Application of this work; not only to solvent the selection but also other material and parameter selection will be extremely beneficial in early conceptual design for greater impact of inherent safety.

Throughout this report, there are four highlighted chapters that cover the introduction of the project, literature review of related topics and project methodology, results and discussion, and conclusion. The introduction part mainly discussed about the background of the study of the inherent safety and development of the tools, objectives of the projects and the scope of study. Chapter 2 of the report will be described more on the literature review of the inherent safety, the features and various developments from the early days of implementation. The literature reviews will also be covered an accident that happened because of the toxic release.

Also described in this chapter is about the conflict or tradeoffs that will be analyzed and studied. In this part, the details project framework of the study is discussed. In order to determine the best main routes of producing methyl methacrylate (MMA) and ranked the routes in hypothetically safety order, Chapter 4 presents a comparison study in damage index and tradeoffs in each process routes. Finally, the recommendations will be discussed and a conclusion will be stated in this report together with the references used for research work on this project.

CHAPTER 2

2 LITERATURE REVIEW

In this chapter, it contains the literature reviews that taken from several source like journals, book and the internet. The literature reviews includes the critical analysis of the journals taken from various source. The information related to the inherent safety principles that will be apply in this project will be discussed in this chapter. These literature reviews are very important in order to develop the best tools for inherent safety assessment.

2.1 Inherent Safety

Risk reduction strategy is aimed at reducing frequency or mitigating the consequences of potential accidents. One of the strategies in reducing the risk is by applies Inherent Safety Principle in the process design. It is best to implement these principles at the early design stage of process design because their effectiveness in improving process safety can be assessed. (Takriff and Bahnuddin N.N., 2008; Khan and Amyotte, 2002, 2003). In the other hand, a chemical manufacturing process is described as inherently safer if it reduces or eliminates hazards associated with materials and operations used in the process, and this reduction or elimination is a permanent and inseparable part of the process technology.

Inherent safety methodologies are generally regarded as being more reliable and robust because they depend on the physical and chemical properties of the system rather that the proper and timely operation. By considering the approaches such as designing equipment to withstand any reasonably expected explosion pressure to be an example of inherent safety.

2.2 Key Ideas of ISP

Inherently safer design concepts include the following key ideas:

a) Hazard Elimination:
   a. Concept

      Eliminate hazards as a first priority (rather than accepting them and mitigating them as a risk reduction strategy once they exist)
   b. Potential Methods
      - Eliminate the hazardous material
      - Substitute a non-hazardous material
      - Discontinue the operation

b) Consequence Reduction:
   a. Concept

      Hazards cannot be completely eliminated, find less hazardous solutions to accomplish the same design objective by focusing on the consequences
   b. Potential Methods
      - Reduce the quantity of the hazardous material
      - Provide a curbed area with a drain to contain and evacuate a spill and produce a smaller pool area of a spill
      - Separate the operation by adequate spacing to reduce exposure to adjacent operations and personnel

c) Likelihood Reduction:
   a. Concept

      Hazards cannot be completely eliminated and after consideration of consequence reduction, consider ways such to reduce the likelihood of events occurring;
   b. Potential Methods
      - Reduce the potential for human error through simplicity of design
      - Provide redundant alarms

2.2.1 Inherent Safety Principles

The terminology of inherent safety varies throughout the process safety community. Table 1 (Khan and Amyotte , 2002) presents commonly used inherent safety principles or guidewords.

Inherent safety strives to enhance process safety by introducing fundamentally safer characteristics into process design. Implementation of inherent safety means selecting and designing the process to eliminate hazards rather than accepting the hazard and implementing add-on system to control it.

The opportunity for installing the inherent safety features decreases exponentially from conceptual design stage to operational stage. Thus it is best to implement the inherent safety at early stages of process design and to assess their effectiveness in improving in process safety.

Table 1: Inherent Safety Principles (Khan and Amyotte, 2002)

Inherent Safety Principle	***Definition***
Intensification	Reduction in the quantify of hazardous materials
Substitution	Use of safer materials
Attenuation	Operation at comparably safer operating conditions
Limitation of effects	Changing the design and operation for less severe effects
Simplification	Avoidance of complexities

With this approach, the primary concepts may be summarized by four basic principles: minimize, substitute, moderate, and simply. These four building blocks of inherent safety are described below.

- **Minimize**

Use smaller quantities of hazardous substances. This may be achieved through efficient continuous reactors such as stirred tanks, loop reactors or tubular reactor in place of batch reactors. It will also reduce the inventory raw materials and in-process intermediates, and efficient process equipment.

- **Substitute**

Replace a material with a less hazardous substance. This could be achieved through water based paints and coatings, alternative chemistry using less hazardous materials, and less flammable or toxic solvents. Substitution of innovative chemistries offers the potential for inherent safer and more environmentally friendly process which include electrochemical techniques, series reactions, reaction controlled by microwaves and laser light, use of extremozymes and various innovative catalytic processes.

- **Moderate**

Use less hazardous conditions, a less hazardous form of a material, or facilities which minimize the impact of a release of hazardous material or energy. This could be implemented through dilution, refrigeration of volatile hazardous materials, and granular agricultural product formulations in place of powders.

- **Simplify**

Design facilities which eliminates unnecessary complexity and make operating errors less likely, and which are forgiving errors that are made. On the other hand, simplification sometimes involves a tradeoff between the complexity of an overall plant and complexity within one particular piece of equipment

2.3 The Need for Inherent Safety

An approach safety is an afterthought in the design. A safety review or Process Hazards Analysis (PHA), such as a Hazard and Operability Study (HAZOP) or a What if?/Checklist Study, merely as a project 'check' instead of a preemptive hazards reduction tool. If these studies are done at the latter stages of engineering or during construction, there is a natural tendency to avoid expensive redesign or rework. Inherent safety benefits are often missed.

There may be several explanations for the claim that inherently safer design practices are not being used to their maximum advantage. These may include factors such as:

a) The lack of standardized approaches to commonly applied process hazard analysis studies and a failure to include inherent safety in PHAs
b) The lack of a recognized method for incorporating inherently safer design issues into the process safety management process or a discipline to review the merits of options for inherent safety
c) The lack of safety experience and knowledge to apply these approaches
d) Lack of clear measures of acceptability of risks, thus, teams do not have good rules to follow in risk decision-making.

2.4 Traditional Approaches to Manage Risk

In early 1990s, there were already several existing evaluation methods for process safety such as Dow and HAZOP studies. Unfortunately, they were not directly suitable as analysis tools to be used in preliminary process design. Most of the methods required too detailed qualitative study of all process units, piping and instruments of any chemical process industries. HAZOP method identifies problems that may be caused if the operations do not occur as per design. This is not directly applicable such as for conceptual design. Likewise, FTA (Fault Tree Analysis) and FMEA (Failure Mode Effect Analysis) can be utilized to address different aspects of risk assessment. These methodologies require substantial input from high-quality technical expertise. Also not all methods were suitable for computerized use with simulation and optimization tools.

Hazard and operability (HAZOP) studies will provide information on how a particular accidents occur. The study will focus on determining the frequency of accident occurs. QRA or LOPA (the simplified QRA) studies show how the frequencies are used. In both methods, the frequency of the release is determined using a combination of event trees, fault trees or an appropriate adaptation. Thus in this context, quantitative indices provide a good balance between simplicity and sophistication. The virtues worth are:

a) Quantitative analysis can be worked out quickly, provide a swift means of hazard identification
b) Provide net scores which enable easy interpretation of results: one can just compare the net score with the designated risk levels.
c) Net scores enable comparison of hazards posed by alternatives
d) Do not require high levels of expertise from the user.

2.5 Development of Inherent Safety Approach

Despite the various development efforts on inherent safety assessment in the early design stage that have been put forward by various investigators, minimal work has been carried out to integrate the assessment. There are various inherent safety assessment techniques with different features and requirements throughout these several years. The earliest technique has been developed in early 1993 which is Prototype of Index of Inherent Safety (PIIS). Khan and Amyotte (2000,2003) has also mentioned that the selected approaches or methods have been revised by numerous authors because of their systematic and easy to use tool that may answer most of the safety design questions. Nevertheless, most of the approaches are much similar to the well known and practiced HAZOP study procedure (Khan and Amyotte, 2005).

2.5.1 Advantages and Disadvantages of Available Methods

Table 2: Comparison between Various Tools

Available Tools	***Advantages***	***Disadvantages***	***Indices***	***Conflicts***
Prototype Index of Inherent Safety (PIIS), 1993	Analyze the process routes.	• Very reaction-step oriented and does not consider much other parts of the system such as separation sections. • Does not consider reaction hazards directly but through yields, operating conditions and physical properties.	Process Yield Index	No

Safety Weighted Hazard Index (SWeHI), 1998	• More systematic and reliable methods for hazard identification. • Indicates safety measures needed • Assign penalties.		G factor which includes penalties and core factor.	Yes. Defines as the measure ment control indices.
Inherent Safety Index (ISI), 1999	Consider both chemical and physical inherent safety index.	• Limited range of factors or choice of the materials and the sequence of steps. • Indices have been calculated separately.	Chemical and Reaction Index	No
INSIDE Project Toolkit, 2001	• Consider safety, health and environmental factors in one set of tools. • Reduce layer of protection	Wide range of tools of the particular interest to measure the inherent safety of chemical processes.	Overall index characterize the inherent safety of the overall process.	No
i-Safe, 2002	Identify hazard that associated with reaction and chemical involved in process routes	Does not account safety issues in related to the phase of reaction and operating conditions.	Rank the available process based on the overall reaction index.	No
Integrated Inherent Safety Index (I2SI), 2004	Consider cost index and dispersion of hazard in the damage radii.	Some procedure requires subjective arguments.	Hazard Index, Control Index and Cost Index	No

Integrated Risk Estimation Tool (iRET), 2006	• Risk assessment can be carried out at all stages of design • Immediately analyses risk and consequences level due to process conditions in their design simulation. • Harness full potential of HYSYS such as thermodynamics property.		Probit	No
Toxic Release Consequences Analysis Tool (TORCAT), 2010	• Preliminary analysis with ICON simulation • Evolution of IRET dealing with toxic release		Percentage of fatalities	No

2.6 Design Conflicts and Trade-offs

Design objectives are often in conflict, and may be mutually exclusive. The designer must choose which of the alternative solutions has the best overall balance of characteristics with respect to all of the design objectives. This is true in considering inherently safer processes. Ideally, it is the best to identify inherently safer process alternatives which simultaneously reduce or eliminate all of the potential hazards. Unfortunately, in the real world, this is seldom occurs. A process alternative which is safer with respect to one hazard may increase other hazards. Thus, a designer must identify and consider all of the hazards and apply appropriate decision making tools to identify the best overall solution.

2.6.1 Bottleneck/ Limiting Factors of ISP

The issues of the tradeoffs that arise when attempting to apply ISP are as below:

a. Inherent Safety/ Performance

   Example: Paint A is inherently safer than Paint B, but may offer poor performance under certain conditions.

b. Inherent Safety/ Environment

   Example: Refrigerant C is inherently safer than alternates such as ammonia, but are also recognize as environmentally deleterious to ozone.

c. ISP/ISP

   Example: A process use relatively non-hazardous materials but may require high temperature and pressure.

d. Hazard/Hazard

   Example: A solvent for exothermic reaction may be nonvolatile but represents a toxic hazard.

2.7 Previous incidents related to Toxic Release

2.7.1 Statistic of chemical accidents

Below is the statistic of chemical accidents that frequently happened in United States based on research done by James C. Belke in 2000. Chlorine Dioxide is listed as the chemical that apparently mostly caused accidents per year (J.C. Belke, 2000)

Table 3: Normalized Accident Rates for RMP Chemicals, 1994-1999

Chemical Name	Number of Accidents per process per year	Rank	Number of Accidents per Mlbs stored per Year	Rank
Chlorine Dioxide	0.155	1	1.97	2
Hydrogen Sulfide	0.067	2	0.50	3
Hydrogen Fluoride	0.064	3	0.27	4
Hydrogen Chloride	0.060	4	0.25	5
Titanium tetrachloride	0.056	5	0.090	9
Phosgene	0.044	6	2.49	1

2.7.2 Toxic Release Accidents

In some occurrences, lack of knowledge, technology or implementation of process safety has led to tragic incidents. The table below has shown the analysis of both incidents.

Table 4: Accidents and Causes

Incidents	Type of Hazards	Cause(s)
Bhopal, India Year: 1984 Description: 3800 fatalities and approximately 11000 with disabilities.	Toxic cloud of methyl isocyanides (MIC) gas.	Trigged by water-washing of lines. The water entered the system containing 42 tons of MIC. The resulting exothermic reaction *increased the temperature* inside the tank to over 200 °C (392 °F) and *raised the pressure*. The tank vented releasing toxic gases into the atmosphere.
Seveso, Italy Year: 1976 Description: 250 reported cases of chloracne	Exposure of hazardous TTCD at high concentration, 10 ppm. However, in the higher-temperature conditions associated with the runaway reaction, TCDD production apparently reached 100 ppm or more. The limit of the chemicals is only 1ppm.	The exhaust steam *temperature rising* to around 300°C, heating the reactor wall above the level of the liquid to the same temperature. The residual heat in the jacket then heated the upper layer of the mixture next to the wall to the critical temperature. After seven hours a rapid *runaway reaction* ensued when the temperature reached 230°C.

CHAPTER 3

3 METHODOLOGY/PROJECT WORK

A new framework and a prototype tool were developed to allow enhanced safety features to be incorporated in safety design. The framework will assesses risk level associated with various options in a fast and efficient manner. This framework is aim to provide clear strategies to implement risk and consequences assessment studies at various design stages. The framework was then translated into a risk estimation tools to allow the immediate analysis of risk and consequences levels.

Process Safety Conflicts Index (PSCI) is a new develop framework that aims at providing a concept that calculates conflicts or tradeoffs that arise after implementing Inherent Safety Principles to a desired process unit. It simultaneously integrates this PSCI information with safety measures as they ought to be. PSCI in quantified in a manner similar to toxic damage index (TDI) of the HIRA system that has been used in Safety Weighted Hazard Index (SWeHI) by Faisal I. Khan et al. methods.

SWeHI concepts is generally regarded as being more reliable and robust because they depend on the physical and chemical properties of the system rather that the proper and timely operation. However, with some additions and modifications in the methodology, PSCI can be determined by integrating the conflict indicator and damage index. Thus, it is the best option for calculating the damage index, DI in this project.

In SWeHI framework, damage index is denoted by B, which is the quantitative measure of the damage that may be caused by a unit/plant. It is measured in terms of area under 50% probability of damage. B has two components; B1 addresses damage due to fire and explosion while B2 considers damage due to toxic release and dispersion. Thus, our main focus in this project is the damage index, DI or denoted by B2 factor in SWeHI framework.

The parameter DI quantifies radius of the area (in meters) affected lethally by a toxic load at 50% probability of causing fatality. This index is similar to the toxic damage index of the HIRA system. This factor is derived using transport phenomena and empirical models based on the quantity of chemical(s) involved in the unit, the physical state of the chemical(s), the toxicity of the chemical(s), the operating conditions and the site characteristic.

The dispersion is assumed to occur under slightly stable atmospheric conditions to represent a median of high instability and stability. Furthermore, such conditions are often prevalent during accidents – as happened at Bhopal, Basel and Panipat. (Khan et al, 2001).The estimation of DI is done with one core factor, named as the G factor, and several penalties. The G factor takes into account the following conditions (Khan et al, 2001):

a) During the accidental release of super-heated liquid from the unit, where a part of the liquid would flash into vapor and the remaining part would form a liquid pool and evaporate.
b) The release gas would directly lead to dispersion in atmosphere and would cause build-up of lethal of toxic load.
c) Liquified gases would have two-phase release, followed by dispersion and build up of toxic load.
d) Pyrophilic solids would give toxic vapours

3.1 Damage Index

In this project, the focus is narrowed down to the dispersion of toxic release in the quantify radius of area that is lethally by a toxic load at 50% possibility of fatalities. The core factor, G is also the core factor for SWeHI and it is forms the base or the 'core weight' that provides to the several of penalties. The systematic procedure to quantify the damage index, DI is presented in Figure 3.

$$\text{Core factor, } G = S \times m$$

The value of S is dependent on the release conditions which can be arrived to a value by using Table 5 and m is denoted as anticipated release rate, kgs-1.

Table 5: Guidelines to assign the value to the factor S

NFPA Rank	Liquid	Liquefied gas	Gas	Solid
4	4.0	8.0	13.4	0.1300
3	0.40	0.80	1.34	0.0130
2	0.20	0.40	0.67	0.0060
1	0.07	0.10	0.25	0.0025

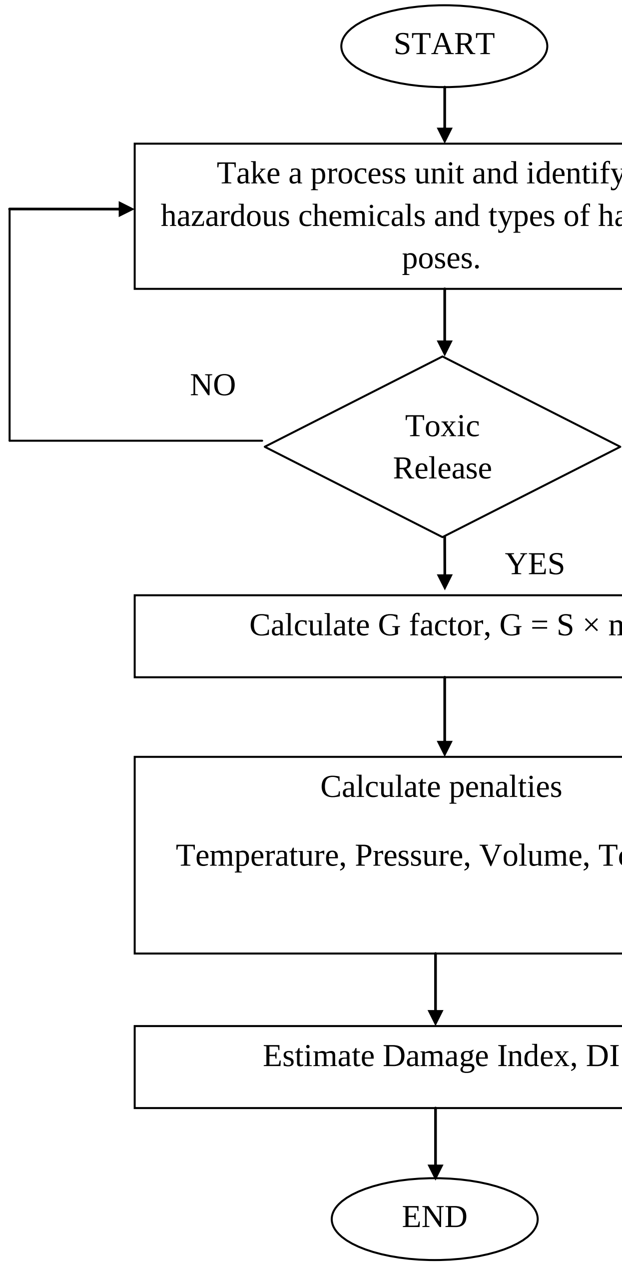


Figure 1: Estimating Damage Index, DI

Several penalties have been taken into account such as operating temperature, operating pressure, inventory and the toxicity of chemicals. The effects of temperature and pressure are estimated through pnr1 and pnr2 respectively and these are the derivations of TCPA, OSHA and several authors (Khan et al., 2001).

The conditions of estimating those penalties are as follows:

<u>Temperature</u>

if (chemical is flammable)

if (fire point > temperature > flash point)

pnr1 = 1.45

if (0.75 auto ignition temperature > temperature > fire point)

pnr1 = 1.75

if (temperature > 0.75 auto ignition temperature)

pnr1 = 1.95

or if (chemical is toxic or corrosive)

if (temperature > 4 x ambient temperature)

pnr1 = 1.55

or if (temperature > 2 x ambient temperature)

pnr1 = 1.35

or pnr1 = 1

<u>Pressure</u>

if(VP >AP)

if (PP > 3.0 > AP)

pnr2 = h1(PP)

or pnr2 = 1.3

or if(PP < VP)

pnr2 = -h2(PP) where PP <0.3 x AP

Otherwise

pnr2 = 1.2

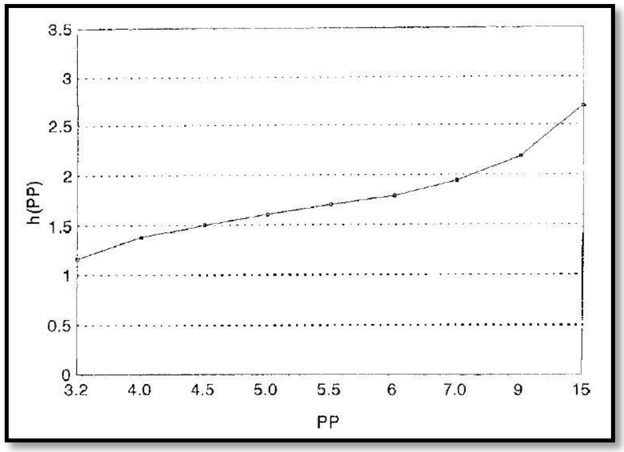


Figure 2: Penalty due to severity of pressure (above atmospheric pressure)

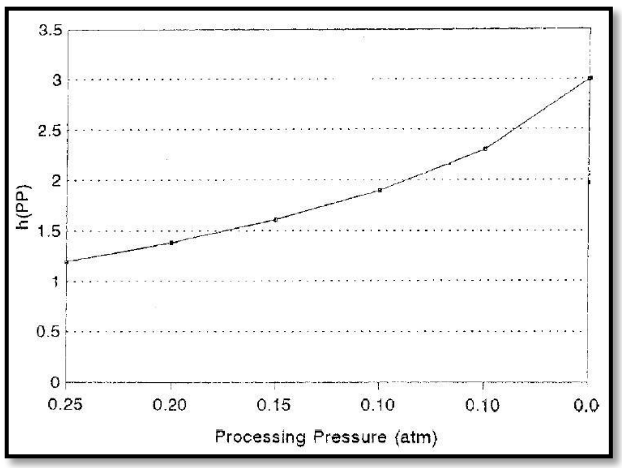
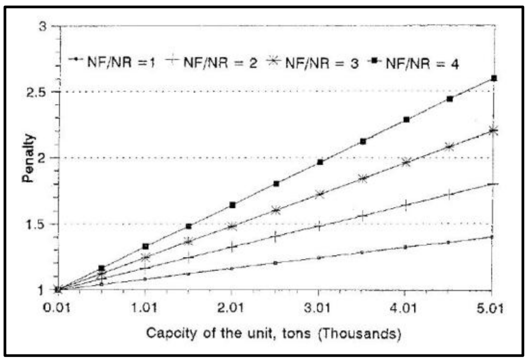
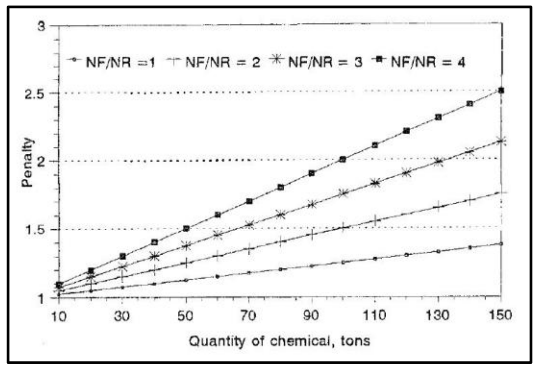


Figure 3: Penalty due to severity of low pressure (under vacuum)

<u>Volume</u>

Storage tank	Unit involve physical changes
The effect due to the quantity of the chemical handled in the unit (capacity of the unit)	*It is similar to the one for storage units except that a more pronounced impact has been taken into account.*
Pnr3=fqur(quantity in tons)	Pnr3=fqur(quantity in tons)
	
Penalty due to quantity of chemical handled in storage unit	Penalty due to quantity of chemical handled in the unit involving physical changes

<u>Toxicity</u>

Due to the toxicity of a chemical is access NFPA-49 health factor (NH) as

$$Pnr4 = Maximum\ (1, 0.6 \times NH)$$

Finally, the G factor and the penalties are combined to give damage index, B2 using the following equation:

$$B2 = a(G \times pnr1 \times pnr2 \times pnr3 \times pnr4 \times pnr5)^{b}$$

Where a and b are constant and are estimated empirically by studying release and dispersion of a range of chemicals. Those appropriate values of a and b are estimated as:

$$a = 25.35$$

$$b = 0.425$$

Damage index is then generated by generalizing B2 to a fix value line.

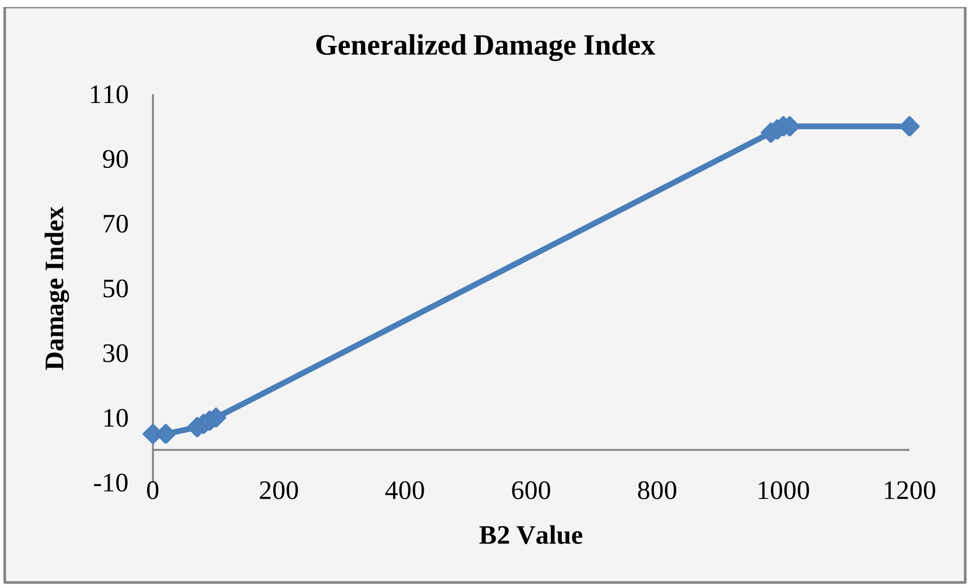


Figure 4: Generalized Damage Index.

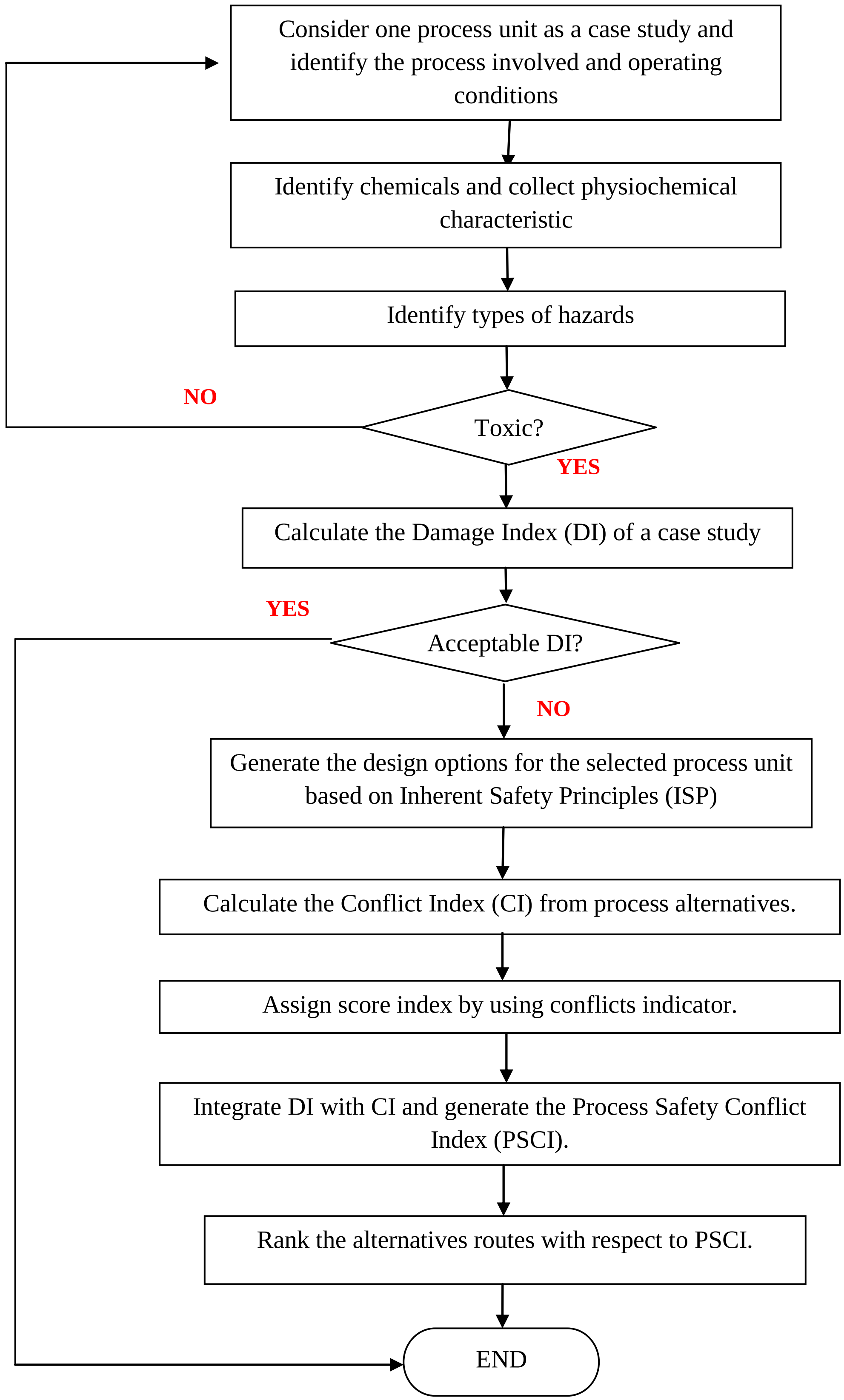


Figure 5: Finalize Conflict or Tradeoffs analysis.

3.2 Conflicts Indicator

The conceptual framework of the PSCI is shown in Figure 6. This framework comprised two main sub-indices; a damage index, DI and the conflict index, CI. The damage index has been calculated at the very first part of the framework. The step-by-step methodology of calculating damage index (DI) has been shown in Figure 5. Conflict index, CI has been developed in taken into accounts the likelihood of conflicts that arise in the design options after considering the inherent safety principles (ISP). It is a measurement of the impact of the ISP analysis to the safety process. The conflict indicator has been developed and shown in Table 5.

Table 6: Conflict Indicator

Score	Reactant Temp.		Op. Pressure	Inventory	NF	NR
1	$T < T_f$	$T_b > 90$ ˚C	P < 1 atm	$m < m_c$	0 , 1	0 , 1
2	$T_{fire} > T > T_f$	$T_b = 60$˚C – 89˚C	P = 1 atm – 35 bar	$m = 2 – 3\ m_c$	2	2
3	$0.75\ T_{auto} > T > T_{fire}$	$T_b = 38$˚C – 59˚C	P = 3501 kPa – 200bar	$m = 4 – 6\ m_c$	3	3
4	$T > 0.75\ T_{auto}$	$T_b < 38$ ˚C	P > 200 bar	$m > 7\ m_c$	4	4

The conflict studies are then being evaluated by calculating the penalties. The penalties that have been taken into account are as in the conflict indicator table. Scores are assigned to each of the reactants in the process including case study and process alternatives. Total of conflict penalties is calculated to generate C2.

∑ CT (Temperature) = Score of conflict indicator for temperature of a reactants in a process unit

∑ CP (Pressure) = Score of conflict indicator for pressure of a reactant reactants in a process unit

∑ CF (Flammability) = Score of conflict indicator for flammability of a reactant reactants in a process unit

∑ CR (Reactivity) = Score of conflict indicator for reactivity of a reactant reactants in a process unit

∑ CIV (Inventory) = Score of conflict indicator for inventory of a reactant reactants in a process unit

Thus,

$$\boldsymbol{C2 = \sum CT + \sum CP + \sum CF + \sum CR + \sum CIV}$$

Conflict Index (CI) is then generated by generalizing C2 to a fix value line.

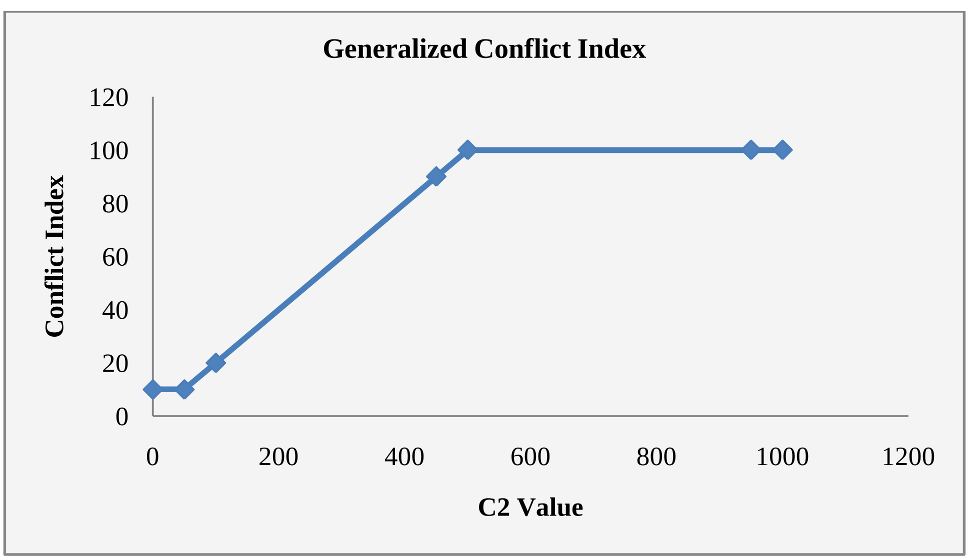


Figure 6: Generalized Conflict Index.

Table 7: Conflict Index Table

Design options \ Conflicts	CT	CP	CF	CR	CIV	C2	Conflict Index (CI)
AltA/1	CT_1	CP_1	CF_1	CR_1	CIV_1		
AltA/2	CT_2	CP_2	CF_2	CR_2	CIV_2		
AltA/3	CT_3	CP_3	CF_3	CR_3	CIV_3		
AltA/4	CT_4	CP_4	CF_4	CR_4	CIV_4		
Total Alt A	$\sum CT$	$\sum CP$	$\sum CF$	$\sum CR$	$\sum CIV$		

3.2.1 Choosing indicators

Temperature and pressure are the dominant parameter in a reaction. Extreme temperature and pressure will lead to runaway reaction that may cause toxic hazards release to the environment. As temperature of the chemical is increases, the flammability range will also increase as well. High pressure also significantly gives impact to the flammability limit. Upper Flammability Limit of certain chemicals increase as pressure is increased. This will broaden the flammability range as well.

High capacity equipment will give impact to safety. The capacity range is depends on the type of equipment that is used in the certain reaction. High volume of chemicals in process unit will release an anticipated amount of mass release to the environment. Not only those, the reactivity and the flammability of the chemicals also play important roles in prediction of damage and conflict index. For example, the high flammability chemical has low flammability point. The low flammability point means that they are easy to ignite even in room temperature. On the other hand, high reactivity chemical will lead a rapid reaction. This type of reaction will lead to increase temperature and pressure as well as volume.

Thus, despite of all the importance of these four main parameters, they are been used in predicting Conflict Index (CI) which play important roles in Process Safety Conflict Index (PSCI).

3.3 PSCI Index Table

PSCI Index Table is generated to calculate the safety index of the process by integrated the damage index and the conflict index. PSCI Index is denoted as a multiplication of conflict index and damage index of the process route.

PSCI = Damage Index (DI) × Conflict Index (CI)

Conflict studies end by rank the design options based on PSCI Index that has been calculated. Small value of PSCI Index indicates that the safer design options. Thus, PSCI will rank the design option as 1 and otherwise.

3.4 Case Study Selection

There are three (3) options of a case study that has been considered to suit this proposed tools. Narrowing down the focus to toxic release, author has come to three viable case studies that will be discussed further.

3.4.1 Option 1: Ammonia production process

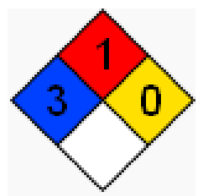
Ammonia is easily recognized by its pungent, penetrating, suffocating odor. Its common forms are anhydrous ammonia (without water) and ammonium hydroxide or aqua ammonia (a solution of ammonia and water). At standard conditions, atmospheric pressure and 32F, ammonia is a light gas. Exposure to ammonia vapors or liquid has potential for serious injury or fatality. Thus, ammonia is also categorized as a hazardous chemical by referring to NFPA 704.

NFPA Rating for Ammonia

Health = 3

Fires = 1

Reactivity = 0



3.4.2 Option 2: Methyl methacrylate (MMA) process

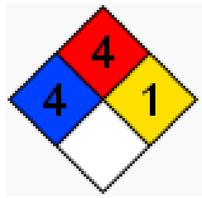
The main reaction of producing Methyl Methacrylate or MMA is by using acetone cyanohydrins (ACH), which is classified as an extremely hazardous substance. The principal hazards of ACH arise from its ready decomposition on contact with water, which releases highly toxic cyanide. Hydrogen cyanide is commonly listed amongst chemical warfare agents that cause general poisoning and skin blisters. Under the name prussic acid, HCN has been used as a killing agent in whaling harpoons. Hydrogen cyanide gas in air is explosive at concentrations over 5.6%, equivalent to 56000 ppm.

NFPA Rating for Hydrogen Cyanide (HCN)

Health = 4

Fires = 4

Reactivity = 1

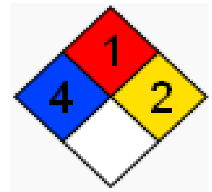


NFPA Rating for Acetone cyanohydrin (ACH)

Health = 4

Fires = 1

Reactivity = 2



Option 3: Polycarbonate production process

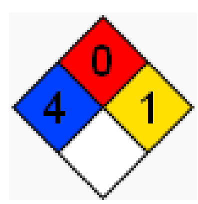
One of the main reactant in producing polycarbonate is phosgene. Phosgene is an insidious poison as the odor may not be noticed and symptoms may be slow to appear. Phosgene can be detected at 0.4 ppm, which is four times the Threshold Limit Value. Its high toxicity arises by the action of the phosgene on the proteins in the pulmonary alveoli, which are the site of gas exchange: their damage disrupts the blood-air barrier causing suffocation. Phosgene detection badges are worn by those at risk of exposure. Thus, phosgene is also categorized as a hazardous chemical by referring to NFPA 704.

NFPA Rating for Phosgene

Health = 4

Fires = 0

Reactivity = 1



CHAPTER 4

4 RESULTS AND DISCUSSIONS

After several analyses, Option 2 (As per discuss in Chapter 2) has been selected as the case study due to its practicality to the project. The toxicity of the hydrogen cyanide (HCN) in the production of MMA is noted as the very hazardous chemicals. A complete study of this case study is conducted to demonstrate the efficacy of the proposed conflict studies.

4.1 Production of Methyl Methacrylate (MMA)

Methyl methacrylate is an important monomer which is widely used in producing acrylic plastic or producing polymer dispersions for paints and coating. The world production capacity has been almost doubled in the past 15years and reached about 2.2 million tons per year. The demand of MMA is still expected steady growth in the future. Most manufacturers in the world today adopted the commercialized method of producing MMA in 1937 by the acetone cyanohydrins (ACH) process.

4.2 ACH process routes details

The main reaction of producing Methyl Methacrylate or MMA is by using acetone cyanohydrins (ACH), which is classified as an extremely hazardous substance. The principal hazards of ACH arise from its ready decomposition on contact with water, which releases highly toxic cyanide. Hydrogen cyanide is commonly listed amongst chemical warfare agents that cause general poisoning and skin blisters. Under the name prussic acid, HCN has been used as a killing agent in whaling harpoons. Hydrogen cyanide gas in air is explosive at concentrations over 5.6%, equivalent to 56000 ppm.

Table 8: Methyl Methacrylate process of ACH method

Route/ Step	**Reactants**	**Products**	**Reaction Phase**	**Temp. (^0C)**	**Pressure bar**	**Yield (%)**	**ΔHr kJ/kg**
ACH	**Acetone cyanohydrin (ACH)**						
1	CH_4 NH_2, Oxygen	hydrogen cyanide	Gas	1200	3.4	64	-3757
2	Aceton, HCN	ACH	Liquid	29 - 38	1	91	-458
3	ACH, Sulphuric acid	HMPA/ HMPASE	Liquid	130 - 150	7	98	v.exot
4	HMPA/HMPASE , CH_3OH	MMA	Liquid	110 - 130	7	100	small
5	H_2SO_4, NH_4HSO_4, O_2, CH_4	SO_2, CO_2, N_2	Gas	980 - 1200	1	100	-1520
6	Ssulphur dioxide, Oxygen	Sulphur trioxide	Gas	405 – 440	1	99.7	-1229

Despite of using high toxicity level of reactants such as hydrogen cyanide and acetone cyanohydrins, this method is operated at high temperature (up to 1200˚C) and this may lead to run away reactions. This high toxicity profile of ACH process route makes this route as the best and viable case study for implement Process Safety Conflict Index (PSCI).

4.3 Process Alternatives of Producing MMA

Although the ACH method was the only industrial process until 1982 for manufacturing MMA, there are problems of shortage of toxic hydrogen cyanide (HCN) supply and of dealing with the large quantities of ammonium bisulfate waste. Till today, many efforts have been continuously put into the development of placing this ACH process.

New commercialized processes have been developed until now, such as:

a) Ethylene based via propionaldehyde
b) Ethylene based via methyl propionate
c) Propylene based
d) Direct oxidation process consists of catalytic, isobutylene
e) Direct oxidation process consists of catalytic, tert-butanol (TBA) oxidation

These five (5) new alternatives are accomplished by application of inherent safety principles (ISP) throughout the design process, from conception until completion. These principles help avoid or reduce hazards by using safer materials and operating conditions, minimizing inventory and by designing a simpler and friendlier plant. The reactions involved in each process route along with the information used for PCIS analysis are shown in Appendix A.

PSCI identifies hazards that are associated with the reaction and chemicals that involved in the process route and ranks the available process routes. Information used for analysis is reaction conditions, materials involved, phase of reactions, unit process involved and process yield.

4.4 Index Calculation for Production of MMA

4.4.1 Case Study: Acetone Cyanohydrin (ACH) Route

Case study of toxic release is assumed on the hole in the tank. Damage index (DI) and Conflict Index (CI) are calculated by using the developed method. The PSCI value represents the safety performance of the process route. The PSCI value of the case study will be compared to the other PSCI alternatives routes value.

The penalties are determined and damage index (DI) has been calculated in Table 9. It is found that the calculated damage index (DI) of ACH Route is rather high and therefore the alternative routes of production of MMA are required.

Table 9: Damage Index (DI) of ACH Process Route

Process Route	Core Factor	pnr1	pnr2	pnr3	pnr4	B2
ACH/1	0.437	1.55	1.30	1.05	1.80	31.4
ACH/2	0.751	1.10	1.20	1.17	2.40	39.2
ACH/3	2.310	1.55	1.20	1.08	2.40	70.6
ACH/4	-	-	-	-	-	0.0
ACH/5	0.615	1.55	1.20	1.06	1.80	35.3
ACH/6	0.357	1.55	1.30	1.03	1.80	28.6
Total B2						**205.10**
Damage Index (DI)						**20.51**

Further considerations of conflicts that arise in the process route are determined by using the conflict indicator in Table 6. The Conflict Index has been determined and summarized in Table 10. If the evaluated Conflict Index is high, therefore it is also indicates the parameter that can be improved for further consideration in the process route.

Table 10: Conflict Index (CI) of ACH Process Route

Process Route	**CT**	**CP**	**CF**	**CR**	**CIV**	**C2**
ACH/1	12	6	6	3	3	30
ACH/2	6	2	7	4	2	21
ACH/3	4	4	2	4	2	16
ACH/4	5	4	5	2	2	18
ACH/5	10	4	7	5	4	30
ACH/6	8	2	2	2	2	16
Total C2						**131**
Conflict Index (CI)						**26.20**

The inherent risk assessment is continued by integrating Damage Index and Conflict Index. PSCI value for ACH Process Route is calculated in Table 11 below

.

Table 11: PSCI of ACH Process Route

Damage Index (DI)	**20.51**
Conflict Index (CI)	**26.20**
PSCI	**537.36**

4.4.2 Alternatives Routes

The application of Conflict Index (CI) and PSCI are illustrated through the comparison of the case study and the other alternative routes. The DI and CI for individual routes options were calculated in Table 12 and Table 13 respectively.

Table 12: Damage Index (DI) of alternatives routes

Process Route	Core Factor	pnr1	pnr2	pnr3	pnr4	B2	Total B2	Damage Index
Ethylene via based propionaldehyde								
C2PA/1	0.416	1.35	1.20	1.22	2.40	33.8	**147.1**	**14.71**
C2PA/2	0.547	1.55	3.88	1.15	1.80	57.4		
C2PA/3	0.537	1.20	1.20	1.06	1.80	33.4		
C2PA/4	0.238	1.35	1.20	1.09	1.80	22.5		
Ethylene via based methyl propionate								
C2PA/1	0.320	1.35	1.20	2.36	2.40	40.1	**40.1**	**5.00**
C2PA/2	-	-	-	-	-	0.0		
C2PA/3	-	-	-	-	-	0.0		
Propylene based								
C3/1	10.7	1.35	1.20	1.18	2.40	132.0	**240.5**	**24.05**
C3/1	0.351	1.35	1.20	1.18	2.40	31.0		
C3/2	0.289	1.10	1.20	1.20	1.80	23.3		
C3/3	0.467	1.55	1.20	1.08	1.80	31.7		
C3/4	0.238	1.35	1.20	1.09	1.80	22.5		
Isobutylene based								
iC4/1	-	-	-	-	-	0.0	**55.9**	**5.569**
iC4/2	0.537	1.55	1.20	1.06	1.80	33.4		
iC4/3	0.238	1.35	1.20	1.09	1.80	22.5		
Tert-butanol (TBA) based								
TBA/1	-	-	-	-	-	0.0	**55.9**	**5.569**
TBA/2	0.537	1.55	1.20	1.06	1.80	33.4		
TBA/3	0.238	1.35	1.20	1.09	1.80	22.5		

Table 13: Conflict Index (CI) of alternatives routes

Process Route	CT	CP	CF	CR	CIV	C2	Total C2	Conflict Index
Ethylene via based propionaldehyde								
C2PA/1	9	6	12	4	9	40	**112**	**22.40**
C2PA/2	7	6	5	3	6	27		
C2PA/3	6	4	4	2	6	22		
C2PA/4	4	4	6	3	6	23		
Ethylene via based methyl propionate								
C2PA/1	9	9	12	4	9	43	**90**	**18.00**
C2PA/2	8	2	5	2	6	23		
C2PA/3	7	2	6	3	6	24		
Propylene based								
C3/1	7	9	10	3	6	35	**95**	**19.00**
C3/2	4	4	4	3	4	19		
C3/3	7	4	3	2	4	20		
C3/4	4	4	6	3	4	21		
Isobutylene based								
iC4/1	8	2	5	2	2	19	**56**	**11.20**
iC4/2	6	4	4	2	2	18		
iC4/3	4	4	6	3	2	19		
Tert-butanol (TBA) based								
TBA/1	7	4	4	2	2	19	**56**	**11.20**
TBA/2	6	4	4	2	2	18		
TBA/3	4	4	6	3	2	19		

The PSCI scores of every alternatives route are given in the following table and the alternatives routes has been ranked with respect to the case study.

Table 14: PSCI Scores of Every Process Routes

Process Routes	Damage Index (DI)	Conflict Index (CI)	PSCI	Rank
ACH	20.51	26.20	537.36	6
C2/PA	14.71	22.40	329.50	4
C2/MP	5.00	18.00	90.00	3
C3	24.05	19.00	456.95	5
i-C4	5.57	11.20	62.37	1
TBA	5.57	11.20	62.37	1

4.5 The approach for evaluation of the index based methods

Inherent Safety Index (ISI) by Heikilla, Prototype Index Inherent Safety (PIIS) by Edward and Lawrence and i-Safe by Palaniappan indices were calculated for MMA subprocesses by using the same consistent input that has been used in PSCI approach. This was necessary to allow the comparison on the same basis.

The indices of subprocess and process routes have been compared with each other and with expert evaluations. These expert evaluations were arrange by Lawrence(1996). The expert jury consisted of eight experts from industry and academia including Prof. Kletz, Lees and Duxbury. The expert evaluated the process from three points of views:

a) Major accidents
b) Medium scale event
c) Unplanned event that causes loss of production and a disruption to local population but not dangerous.

However, since different index methods have different scales and their direct comparison is not possible. Thus, at this stage, only rank comparison can be analyzed and the summary of the comparison is summarized in Table 15.

Table 15: Comparison between PSCI indices with other indices

Ranking	ISI	PIIS	i-SAFE	EXPERT	PSCI
1	TBA & iC4	TBA	TBA	TBA	TBA & iC4
2	TBA & iC4	iC4	C2/MP	iC4	TBA & iC4
3	C2/MP	C2/MP	iC4	C2/MP	C2/MP
4	C2/PA & C3	C3	C3	C2/PA	C2/PA
5	C2/PA & C3	C2/PA	C2/PA	C3	C3
6	ACH	ACH	ACH	ACH	ACH

Conflict Index (CI) is a measure of the number of conflict that arises in the process route. The index considers parameters such as boiling temperature, auto-ignition temperature, flash temperature, fire temperature, operating pressure, inventory and also the flammability and reactivity rating. However, based on the ranking of the process routes, by using PSCI method gave quite similar ranking to Expert, although PSCI could not make any difference between TBA and iC4.

This is because the subprocesses for both TBA/1 and iC4/1 are operated at the same range operating conditions. Both reactants in subprocesses have low toxicity rating and high flammability rating that will results in same DI and CI. However, it should be noticed that, the differences of the top processes TBA and iC4 is quite small in expert evaluation (Values of 57.0 and 60.3, respectively.)

Thus, based on the index calculation, it can be concluded that TBA process route and iC4 process route are the inherently safer routes and ACH process route is the most hazardous one. The TBA and iC4 routes are a three-step process while the ACH process route is six-step process.

Other process alternatives can also be ranked on index evaluations as shown in Table 15. It can be seen that the ISI evaluation is not dissimilar to expert ranking, although in two cases ISI gave the same index value for two processes. However, in PIIS evaluation, there are two differences and in i-Safe four differences to expert ranking.

4.6 Summary of general observation of the indices

Figure 16: Summary of general observation of the indices

Indices	Observations
Prototype Index Inherent Safety (PIIS)	Very step oriented and does not consider separation sections at all. Does not consider hazards at all Lacks of inventory evaluation Very straightforward and fast to use
i-Safe	Step oriented index and easy to use Covered reaction hazards Lacks of inventory evaluation and does not consider separation sections
Inherent Safety Index (ISI)	Largest set of sub indices More factors are covered Process diagram is needed for the equipment index Information is not readily available
Process Safety Conflict Index (PSCI)	Step oriented and does not consider separation Covered reaction hazards and inventory evaluation Straightforward and easy to use Data is available from Material Safety Data Sheet and process literature More factors are covered as it also covers the conflict that may arise in the system

CHAPTER 5

5 CONCLUSIONS

Inherent safety evaluations can be made in a reasonable accuracy with the index method discussed. When process safety ranking is considered, ISI and PCSI gave quite similar ranking to experts although both ISI and PCSI could make no difference between two processes. Both ISI and PCSI could not differentiate between TBA and iC4 process routes. PCSI, however, is able to differentiate other process precisely and give similar ranking to experts. It has to be noted that neither the experts were very common on the evaluations and rankings.

The inaccuracy of the indices is related to differences of their sub index structure and properties. In PCSI, the evaluation is oriented reaction steps even it is not considered the separation process. However, more factors are covered as it also covers the conflict that may arise in the system. Not only that, it is the simplest and easiest method to evaluate process routes. All data is available from Material Safety Data Sheet and process literature and more factors are covered as it also covers the conflict that may arise in the system. Despite PCSI widest range of indices, PCSI come with more accurate results compared with the others.

CHAPTER 6

6 RECOMMENDATIONS

Nevertheless, the method described has some limitations. This is a preliminary attempt to incorporate conflict arise in the system with the inherent safety, which has not yet been extensively approached by previous studies. Some aspects for development in future studies are as shown below:

a) The conflict index that has been applied here does not explicitly include wide factors or parameters in the process routes. The parameters that can be include in the conflict analysis are the site characteristic, population, reaction type, heat capacities, phase change and the transportation routes. Such evaluation need to be included in the future

b) Detail analysis on index scores should be evaluated. Since the different index method have different scales and their direct comparison is not possible. Thus, the index score of each method should be normalized to allow direct comparisons.

c) An approach called integrated cost index can be integrated in this study so that, the optimization of inherent safer design with economic evaluation is incorporated.

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APPENDIX A

1. Reaction Routes

Route/ Step	Reactants	Products	Reaction Phase	Temperature (˚C)	Pressure (bar)	Yield (%)	ΔHr kJ/kg
ACH	**Acetone cyanohydrin (ACH)**						
1	**CH_4 NH_2, Oxygen**	hydrogen cyanide	Gas	1200	3.4	64	-3757
2	**Aceton, HCN**	ACH	Liquid	29 - 38	1	91	-458
3	**ACH, Sulphuric acid**	HMPA/HMPASE	Liquid	130 - 150	7	98	v.exot
4	**HMPA/HMPASE, CH_3OH**	MMA	Liquid	110 - 130	7	100	small
5	**H_2SO_4, NH_4HSO_4, O_2, CH_4**	SO_2, CO_2, N_2	Gas	980 - 1200	1	100	-1520
6	**Ssulphur dioxide, Oxygen**	Sulphur trioxide	Gas	405 – 440	1	99.7	-1229
C_2/PA	**Ethylene based via propionaldehyde**						
1	**Ethylene, CO, Hydrogen**	Propionaldehyde	Gas	100	15	90.7	-2162
2	**Propionaldehyde, CH_2O**	Methacrolein	Liquid	160 – 185	49	98	-1070
3	**Methacrolein, Oxygen**	Methacrylic acid	Gas	350	3.7	58	-2855
4	**Methacrylic acid, CH_3OH**	MMA	Liquid	70 – 100	6.8 – 7.5	75	653
C_2/MP	**Ethylene based via methyl propionate**						
1	**Ethylene, CO, Methanol**	Methyl Propionate	Liquid	100	100	89	-2019
2	**Methanol, Oxygen**	Methylal	Gas	350 – 470	1 – 4.5	79	-1997
3	**Methyl Propionate, Methylal**	MMA	Gas	350	low	87	483
C_3	**Propylene based**						
1	**Propylene, CO, HF**	Isobutyryl fluoride	Liquid	70	120	95	-835
2	**Isobutyryl fluoride, Water**	Isobutyric acid	Liquid	40 – 90	10	96	exot
3	**Isobutyric acid, Oxygen**	Methacrylic acid	Gas	320 – 354	2.5 – 3	61	-883
4	**Methacrylic acid, Methanol**	MMA	Liquid	70 – 100	6.8 – 7.5	75	653
i-C_4	**Isobutylene based**						
1	**Isobutylene, Oxygen**	Methacrolein	Gas	395	1 – 1.5	42	-1659
2	**Methacrolein, Oxygen**	Methacryllic acid	Gas	350	3.7	58	-1656
3	**Methacryllic acid, Methanol**	MMA	Liquid	70 –100	6.8 – 7.5	75	490
TBA	**Tertiary butyl alcohol (TBA) based**						
1	**TBA, Oxygen**	Methacrolein	Gas	350	4.8	83	-1165
2	**Methacrolein, Oxygen**	Methacryllic acid	Gas	350	3.7	58	-1656
3	**Methacryllic acid, Methanol**	MMA	Liquid	70 – 100	6.8 – 7.5	75	490

2. Anticipated mass release

Process Route	Reactants		Density (g/cm3)	Mass (kg)	Mass (tonne)
ACH	**Acetone cyanohydrin**				
1	Methane	CH4	0.00072	13447.95158	13.44795
	Ammonia	NH3	0.6096	12666.18575	12.66619
	Oxygen	O2	0.00143	6740.785728	6.740786
2	Acetone	CH3COCH3	0.7924	7980.212478	7.980212
	Hydrogen Cyanide	HCN	0.6873	17147.27121	17.14727
3	Acetone cyanohydrin	ACH	0.932	5446.104703	5.446105
	Sulphuric acid	H2SO4	1.84	2362.819845	2.36282
4	2-hydroxy -2methyl propionamide (Hexamethylphosphoramide - HMPA)	HMPA (C6H18N3OP)	1.03	2280.688997	2.280689
	Methanol	CH3OH	0.7945	14466.00314	14.466
5	Sulphuric acid	H2SO4	1.84	2362.819845	2.36282
	Oxygen	O2	0.00143	7242.042824	7.242043
	Methane	CH4	0.00072	14447.96573	14.44797
	Ammonium Sulfate	NH4HSO4	1.769	2013.251415	2.013251
6	Sulfur dioxide	SO2	1.381	3617.629884	3.61763
	Oxygen	O2	0.00143	3621.021412	3.621021
C2/PA	**Ethylene based via propionaldehyde**				
1	Ethylene	C2H4	0.001178	22031.64543	22.03165
	Carbon monoxide	CO	0.00125	22063.10797	22.06311
	Hydrogen	H2	0.00009	306541.4952	306.5415
2	Propionaldehyde	C3H6O	0.7975	10640.2833	10.64028
	Formaldehyde (37%solution)	CH2O	0.7428	20581.75096	20.58175
3	Methacrolein	C4H6O	0.847	8817.310443	8.81731
	Oxygen	O2	0.00143	9656.057099	9.656057
4	Methacrylic acid	C4H6O2	1.015	7178.557457	7.178557
	Methanol	CH3OH	0.7945	19288.00419	19.288
C2/MP	**Ethylene based via methyl propionate**				
1	Ethylene	C2H4	0.001178	135314.7925	135.3148
	Carbon monoxide	CO	0.00125	135508.0303	135.508
	Methanol	CH3OH	0.7945	118463.793	118.4638
2	Methanol	CH3OH	0.7945	43082.63256	43.08263
	Oxygen	O2	0.00143	7189.414308	7.189414
3	Methyl propionate	CH3CH2CO2CH3	0.9147	6047.082609	6.047083
	Methylal	HCH(OCH3)2		7001.550504	7.001551
C3	**Propylene based**				
1	Propylene	C3H6	0.509	11956.52887	11.95653

	Carbon monoxide	CO	0.00125	17962.53963	17.96254
	Hydrofluoric acid			25143.96477	25.14396
2	Isobutyryl fluoride	(CH3)2CHCOOF		27951.7075	27.95171
	Water	H2O	0.9963	27951.7075	27.95171
3	Isobutyric acid	C4H8O2	0.9487	5710.256895	5.710257
	Oxygen	O2	0.00143	7861.417735	7.861418
4	Methacrylic acid	C4H6O2	1.015	7178.557457	7.178557
	Methanol	CH3OH	0.7945	19288.00419	19.288
i-C4	**Isobutylene based**				
1	Isobutylene	C4H8	0.5948	11013.85946	11.01386
	Oxygen	O2	0.00143	19312.1142	19.31211
2	Methacrolein	C4H6O	0.847	8817.310443	8.81731
	Oxygen	O2	0.00143	9656.057099	9.656057
3	Methacrylic acid	C4H6O2	1.015	7178.557457	7.178557
	Methanol	CH3OH	0.7945	19288.00419	19.288
TBA	**Tertiary butyl alcohol (TBA) based**				
1	Tertiary butyl alcohol	(CH3)3COH	0.789	8337.663982	8.337664
	Oxygen	O2	0.00143	19312.1142	19.31211
2	Methacrolein	C4H6O	0.847	8817.310443	8.81731
	Oxygen	O2	0.00143	9656.057099	9.656057
3	Methacrylic acid	C4H6O2	1.015	7178.557457	7.178557
	Methanol	CH3OH	0.7945	19288.00419	19.288

3. Vapor Pressure at selected Temperature (Perrys Handbook)

Vapor pressure = exp A

where, A = [C1 + (C2/T) + (C3 ln T) + C4(T)^C5]

$$\text{Vapor pressure} = \exp A$$

$$A = \left[C1 + (C2/T) + (C3 \ln T) + C4(T)^{C5} \right]$$

Reactants	C1	C2	C3	C4	C5	Vapor Pressure (kPa)
Methane	39.205	-1324.4	-3.4366	3.10E-05	5	n/a
Ammonia	90.483	-4669.7	-11.607	1.72E-02	1	850.462727
Oxygen	51.245	-1200.2	-6.4361	2.84E-02	1	163653.2368
Acetone	69.006	-5599.6	-7.0985	6.22E-06	2	24.54664239
Hydrogen Cyanide	36.75	-3927.1	-2.1245	3.89E-17	6	81.1491799
Methanol	81.768	-6876	-8.7078	7.19E-06	2	12.78584119
Sulfur Dioxide	47.365	-4084.5	-3.6469	1.80E-17	6	334.7328247
Ethylene	74.242	-2707.2	-9.8462	2.25E-02	1	6286.41814
Carbon monoxide	45.698	-1076.6	-4.8814	7.57E-05	2	1072066.652
Hydrogen	12.69	-94.896	1.1125	3.29E-04	2	2.43711E+17
Propionaldehyde	80.581	-5896.1	-8.9301	8.22E-06	2	34.17570292
Formaldehyde	101.51	-4917.2	-13.765	2.20E-02	1	440.3188829
Methyl Propionate	70.717	-6439.7	-6.9845	2.01E-17	6	8.761058136
Propylene	57.263	-3382.4	-5.7707	1.04E-05	2	1020.590093
Water	73.649	-7258.2	-7.3037	4.17E-06	2	2.31762099
Isobutryic acid	110.38	-10540	-12.262	1.43E-17	6	0.117458059
Isobutylene	102.5	-5021.8	-13.88	2.03E-02	1	259.5443935
tert-butyl alcohol (TBA)	172.31	-11590	-22.118	1.37E-05	2	4.009942502

4. Density at selected temperature

Density = C1/ [C2] ^ (1 + (1- (T/C3)^C4)

Reactants	MW	C1	C2	C3	C4	Density (g/cm3)
Methane	**16.043**	2.9214	0.28976	190.56	0.28881	n/a
Ammonia	**17.03**	3.5383	0.25443	405.65	0.2888	0.60957959
Oxygen	**32**	3.9143	0.28772	154.58	0.2924	n/a
Acetone	**58.08**	1.2332	0.25886	508.2	0.2913	0.792421303
Hydrogen Cyanide	**27.027**	1.3413	0.18589	456.65	0.28206	0.687321031
Methanol	**32.042**	2.288	0.2685	512.64	0.2453	0.794488225
Sulfur Dioxide	**64.065**	2.106	0.25842	430.75	0.2895	1.381091352
Ethylene	**28.054**	2.0961	0.27657	282.34	0.29147	n/a
Carbon monoxide	**28.01**	2.897	0.27532	132.92	0.2813	n/a
Hydrogen	**2.016**	5.414	0.34893	33.19	0.2706	n/a
Propionaldehyde	**58.08**	1.296	0.26439	504.4	0.29417	0.797505223
Formaldehyde	**30.026**	1.9415	0.22309	408	0.28571	0.742822833
Methyl Propionate	**88.106**	0.9147	0.2594	530.6	0.2774	0.914675622
Propylene	**42.081**	1.4094	0.26465	365.57	0.2985	0.509032224
Water	**18.015**	5.459	0.30542	647.13	0.081	0.996328258
Isobutryic acid	**88.106**	0.88575	0.25736	605	0.26265	0.948700398
Isobutylene	**56.108**	1.1454	0.2725	417.9	0.28186	0.594757479
tert-butyl alcohol (TBA)	**74.123**	0.9212	0.2544	506.21	0.276	0.788966096

APPENDIX B

1. **Milestone for Process Safety Conflict Indicator (PCSI) for Toxic Release using Risk-based Approach (January 2010)**

	Detail/Work	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	**Selection of Project Topic** ***Topic: Development of Safety Performance Indicator for Toxic Release using Risk-based Approach***								**Mid - Semester Break**							
2	**Preliminary Research Work**															
3	**Project Work**															
	a. Literature Review															
	b. Develop Tools															
4	**Submission of Progress Report**									√						
5	**Seminar**									√						
6	**Project Work Continues**															
	e. Get information of a based study															
	f. Study of a based case															
7	**Submission of Interim Report Final Draft**															√
8	**Oral Presentation**															√

2. Milestone for Process Safety Conflict Indicator (PCSI) for Toxic Release using Risk-based Approach (July 2010)

	Detail/Week	1	2	3	4	5	6		7	8	9	10	11	14	18	19
1	Get information of a case study							Mid Semester Break								
2	Study of a case study															
3	Submission of Progress Report 1					√										
4	Test tool to a case study															
5	Test tool to design options															
6	Submission of Progress Report 2									√						
7	Seminar															
8	Poster Exhibition											√				
9	Submission of Dissertation (Soft Bound)													√		
10	Oral Presentation														√	
11	Submission of Dissertation (Hard Bound)															√