CHAPTER 1

INTRODUCTION

1.1 Chapter overview

This chapter begins by giving a general overview on why safety analysis is important to Chemical Process Industries (CPI), followed by a brief introduction on Inherent Safety (IS) analysis as a new concept in analysing process safety for CPI. Next, a discussion of the research problem statements, research objectives, and scopes, will be provided. An outline of the entire thesis is shown at the end of this chapter.

1.2 The importance of safety analysis in CPI

Historical worldwide disasters, such as the Bhopal toxic release in 1984 that caused more than 16,000 fatalities, the explosion and fire on Piper Alpha causing 167 fatalities in 1988, BP in Texas with 15 fatalities in 2005, and the more recent major explosion and fire at a petroleum storage facility near San Juan, Puerto Rico in 2009, have shown the vulnerabilities of CPI that can cause major loss, of not only human life, but also in terms of assets, company reputation, etc. This is alarming to the authorities as well as the public’s perception that past serious accidents may be repeated in the future, unless continuous efforts to ensure the safety of CPI are properly managed.

Accidents in CPI occur for many reasons, such as the intrinsically hazardous characteristics of the chemicals used, failure to operate equipment correctly in extreme conditions, mechanical failure from stress or fatigue of equipment or workers, human error, and ignorance. A study conducted by Taylor (2007) on accident causes (Figure 1.1), for 121 accidents that were reported to the European Joint Research Centre MARS database under the major hazard scheme, revealed nine general causes of accidents where design and managerial causes were the major contributors, with more than 50%. The study also identified that the lack of safety analysis contributes to the causes of accidents with more than 20%.

The study revealed several important observations, that the risk of accidents in chemical industries could be minimised through consideration of safety issues during the early stages of the CPI lifecycle i.e., the design stage. The management of hazardous activities in CPI is equally important, to ensure that accidents do not happen or repeat themselves.

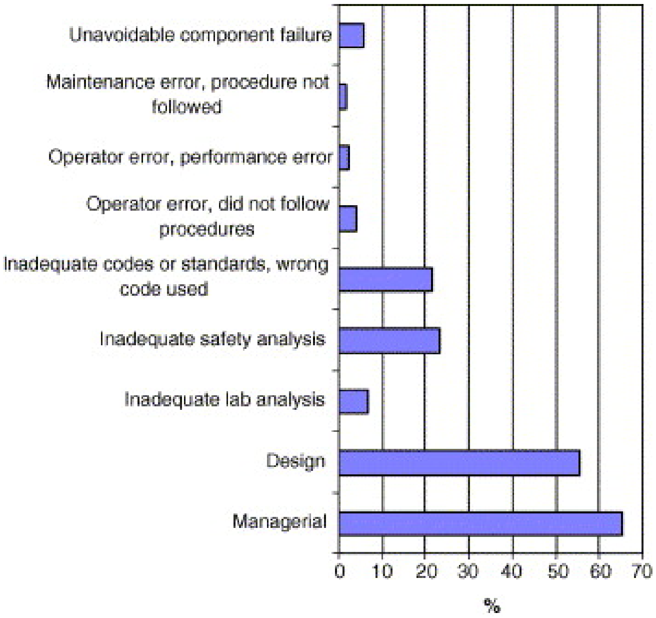


Figure 1.1: Causes of 121 chemical industry accidents, as reported to the MARS accident database (Taylor, 2007)

1.2.1 A paradigm shift in safety analysis by integrating the IS concept

Safety analysis should be performed to identify the best risk reduction strategies, to avoid accidents. Bollinger et al., (1997) classified the strategies to reduce risk, in a declining order of robustness and reliability, as inherent, passive, active, and procedural, which are to be implemented during the design stage. These strategies are known as the conventional safety layers of protection that are commonly considered or applied by CPI and are described in Table 1.1. Although there are multiple-layers of protection available to control hazards, these hazards still remain in the process and through time, the layers of protection are degraded. This commonly translates into terms of failure frequency, and eventually, the actual risk would happen (Hendershot, 1997). For that reason, the ISD concept is introduced as a paradigm shift in safety analysis, where these inherent strategies are believed to lower the hazards and thus, adopt a less complex of control protection to the process unit. Inherent strategies could be achieved through the implementation of Inherent Safety principles, such as *minimise*, *substitute*, *attenuate,* and *simplify* (CCPS, 2009). This safety philosophy was initiated by Trevor Kletz nearly thirty years ago, as the prime strategy to reduce the risk of accidents in CPI. Brief descriptions of the inherent safety principles, are shown in Table 1.2.

The inherent strategy is a prevention concept known as ‘intrinsic safety’ or ‘inherent safety’, rather than typical safety control measures, known as ‘extrinsic safety’. This prevention strategy is highly effective when applied during the early stages of the process’s lifecycle i.e., the process design stage. Furthermore, this prevention concept is identified as an Inherently Safer Design (ISD), because of its approach to avoid or reduce potential incidents, through the elimination or minimisation of hazards at their source. The concept of ISD is derived from the Inherent Safety Principles initiated by Trevor Kletz, which have been further elaborated (Kletz, 1978; Kletz, 1990; CCPS, 2009). Although this safety and loss prevention concept is only theoretical, there are many continuing research efforts attempting to develop a systematic methodology, which can be adopted and applied, particularly during the early stages of design.

Table 1.1: Risk reduction strategies in descending order of reliability (Bollinger et al., 1997)

Strategy	Description
Inherent	Eliminating the hazard by using materials and process conditions, which are non-hazardous, e.g., substituting water for a flammable solvent
Passive	Minimising the hazard by process and equipment design features, which reduce either the frequency or consequence of the hazard, without altering the active function of any device, e.g., providing a diked wall around a storage tank of flammable liquids
Active	Using controls, safety interlocks, or emergency shutdown systems to detect and correct process deviations, e.g., a pump, which is shut-off by a high-level switch in the downstream tank, when the tank is 90% full. These systems are commonly referred to as engineering controls - although human intervention is also an active layer
Procedural	Using policies, operating procedures, training, administrative checks, emergency response, and other management approaches, to prevent incidents or to minimise the effects of an incident, e.g., hot work procedures and permits. These approaches are commonly referred to as administrative controls

Table 1.2: Definition of Inherent strategies based on IS principle (CCPS, 2009; Hendershot, 2000)

Inherent Safety Principle	Description
Eliminate	A strategy to totally eliminate hazards by changing hazardous materials to non-hazardous materials, or chemistry process if applicable
Substitute	A strategy to reduce hazards by replacing hazardous material with less hazardous material, or changing a hazardous process to a less hazardous process
Minimise	A strategy to reduce quantities of hazardous materials within a process by changing the type of process, process unit, or process technology
Moderate	A strategy to reduce hazards by using less hazardous process conditions or less hazardous forms of material
Limit of effect	A strategy to reduce hazards by designing a plant or process to minimise the impact of a release of material or energy
Simplify	A strategy to reduce hazards by designing to eliminate or tolerate operating errors, by making a plant more user-friendly and reliable

The prime objective of the ISD concept is to avoid or eliminate inherent hazards from the source, rather than accepting their existence and designing control systems to manage and contain them. This approach is widely accepted by industries and has proved effective if applied during the early stages of process development, due to potential cost reduction. This concept is believed to minimise potential safety hazards, as well as offer great benefits to a wide range of environmental hazards and reduce energy costs in the process. The ISD concept appears as a subset of ‘green chemistry’ and ‘green engineering’ (Hendershot, 2006).

Amongst the earliest Inherent Safety tools are the Prototype Index of Inherent Safety (PIIS), which was developed by Edwards et al., (1996) and the Inherent Safety Index (ISI) by Heikkila (1999) for application during the process route selection. Many other safety analysis tools have been published that focus mainly on evaluating the inherent safety characteristics of processes quantitatively. Various methods are employed in these tools, and several selected tools will be discussed in detail, especially their differences, in Chapter 2. Regardless of these efforts, there is yet to be an available and established ISD tool, which has been accepted by industry. Among the reasons for this, are that the tools are not supported by a suitable decision making analysis, to select conflicting ISD alternatives, during the early stages of design.

Recently, CCPS (2009) presented a systematic ISD strategy for a loss prevention methodology, which illustrates a desired hierarchical relationship between inherent, engineered, and procedural safety considerations in chemical processes, which was adopted from Amyotte et al., (2007); as shown in Figure 1.2. This framework was developed to promote the utilisation of the ISD concept and its principles, by providing the steps to be taken to analyse hazards through the order of inherent safety, before the design needed to consider other types of layer protection. This is important in determining how “inherently safe is safe enough” for the design or the process (CCPS 2009). However, in order to follow systematic ISD activities, a comprehensive tool to support the evaluation, might be required. The lack of availability of effective tools that are capable of supporting decision making, especially when conflicts exist in design alternatives, is the most contributing reason for the low acceptance of inherent safety within CPI. The potential conflicts, as described in the following section, become the objectives to develop an inherent safety tool that will evaluate the design being As inherently Safer As Practicable (AiSAP) in this research, particularly to support Activity 2; as described in Figure 1.2.

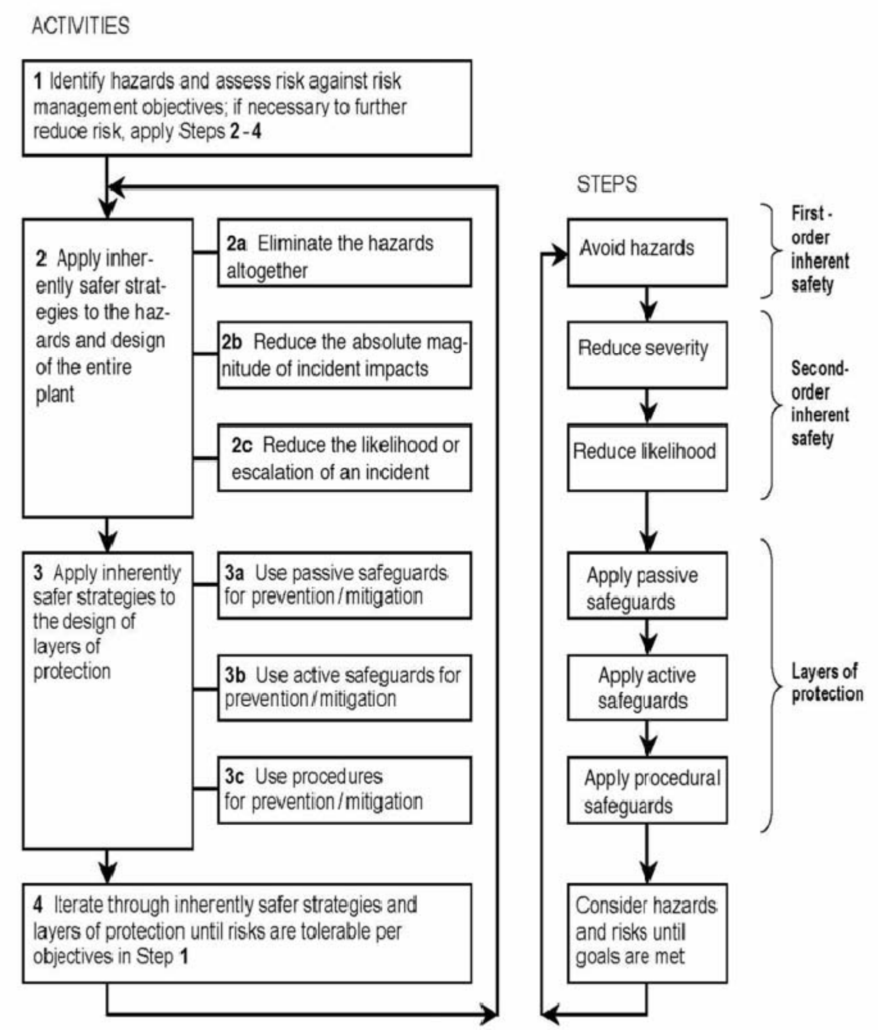


Figure 1.2: Inherent Safety application during Process Risk Management (CCPS, 2008)

1.2.2 Conflicts in Inherent Safety applications

Managing hazard conflicts after attempting the ISD concept, as described in Figure 1.3, is one of the important factors that limits the application of Inherent Safety (IS). In addition, the trade-off issue that may be required has to be dealt with (Khan and

Amyotte, 2003a). The issue of trade-offs has been reviewed by Bollinger et al., (1997). They cited several examples that have been categorised by Khan and Amyotte (2003a), as follows:

- Inherent safety vs. Performance: Aqueous latex paints are inherently safer than solvent based paints, but they may offer poorer performance under certain conditions.
- Inherent safety vs. Environment: Chlorofluorocarbon refrigerants are inherently safer than their alternates, such as ammonia, but are also recognised as being environmentally deleterious to ozone concentrations in the stratosphere.
- Inherent safety principle vs. Inherent safety principle: Supercritical processing, uses relatively non-hazardous materials, such as water and carbon dioxide (application of substitution principle), but may require high temperature and pressure (non-application of moderation principle). A specific example, given by Xu et al., (2003), is where supercritical water oxidation of organic wastes with heavy metals was carried out in a batch reactor operated up to 420^{o}C and 30MPa.
- Hazard vs. Hazard: One solvent choice for an exothermic reaction may be non-volatile, but represents a toxic hazard; an alternative solvent may be less toxic, but have a lower boiling point - leading to the possibility of a pressure hazard, due to the boiling solvent in the event of a runaway reaction.
- Within the inherent safety principle itself: The simplification principle involves a trade-off between the complexity of an overall plant and the complexity within one particular piece of equipment. For example, a reactive distillation process for producing methyl acetate only requires three columns and the associated support equipment. The older process required a reactor, an extractor, and eight other columns, along with the associated support equipment. The new process is simpler, safer, and more economical, but the successful operation of the reactive distillation itself, is more complex and knowledge intensive (Hendershot, 1999).

It is important to highlight that the management of hazard conflicts is not unique to the field of inherent safety, because it is an integral component of all engineering activities (Khan and Amyotte, 2003a). Expert judgements at times may be appropriate to resolve the above conflicts and finally to support the identification of best design alternatives. However, this type of dependency could be minimised if there are supporting tools at hand that inclusively identify the above conflicts and understand the hazards, since this stage is essential to achieve the above objective.

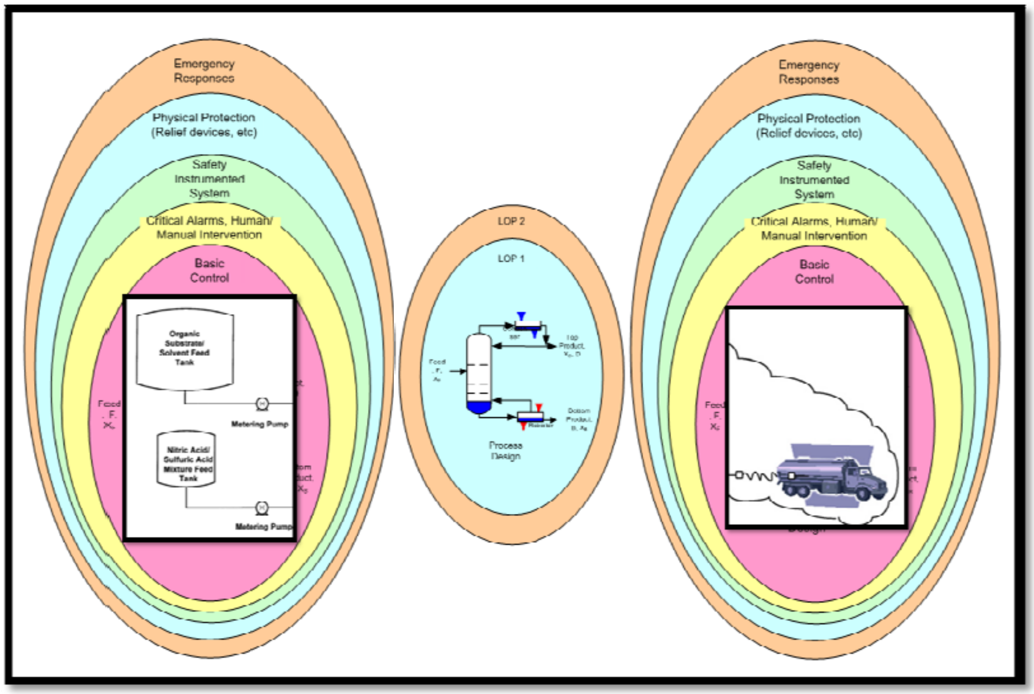


Figure 1.3: Conflicts in the ISD option

1.3 Research problem statement

The application of IS principles and the ISD concept has been proven to reduce the risk of accidents and is economically attractive for the CPI. However, they also suffer from several trade-offs or conflicts that arise from the modification suggested by the concept. A design which is identified to be inherently safer from one hazard could possibly alter the magnitude of other hazards, which were previously not at a critical level. Therefore, an IS tool should emphasise this limitation before a decision can be made, in order to obtain the best ISD alternatives.

Even though many efforts have been made to develop effective IS tools over the years, most of them are still immature and cannot cover all process safety aspects, due to several constraints of the tools. Among the obvious ones is the capability to resolve inherent safety conflicts, after the application of the concept. Others, are the aggregation methods of indices considered in the tools to represent the overall index of IS, but have several drawbacks that could lead to the misinterpretation of the actual overall risk of the design. Moreover, present IS tools do not welcome the generation of ISD alternatives innovatively, but rather by evaluating the available alternatives only. Thus, the research is focused to minimise the limitations of existing IS tools and to develop a simple systematic methodology and practical guidelines preferable by industrial practitioners. The prevailing qualitative technique should also be fully utilised, to a large extent using IS principles, in order to identify and understand hazards effectively.

Risk analysis is commonly performed during the last stage of design, as a consequence to cause fatalities from either individuals or societal exposures of the design evaluation. The estimation of failure frequency in conventional risk procedures is based on historical data, which sometimes does not reflect the actual process conditions; especially batch processes for example. Hence, there is uncertainty in the results values. The risk value is then subjected to a mutual agreement either, in order to accept or reject the design, following the perception or the criteria established by the independent regions or countries. The option to remove or reduce hazards is subject to constraints that are dictated by technical and economic factors at that time, which could be too late to consider for a redesign. Therefore, this research attempts to breach the conservative use of risk concept during the safety analysis. The risk concept is modified in this research to enable its application during the early design stage, to inculcate the easiness concept of ISD to design-out the hazards, and therefore, to address conflicts through the risk concept when the design is modified.

1.4 Research objectives and scope

This research hypothesises that a design can be As inherently Safe As Practicable (AiSAP) during the early stages of the CPI lifecycle, by explicit application of the

ISD concept. This can be achieved by identifying, generating, and evaluating, the design throughout the design process. The design option selected is determined AiSAP, due to extensive use of IS principles and many factors considered during analysis, which not only focus on materials and process factors, but also other contributing design factors, such as transportation, auxiliary units, complexity of control measures, etc. Therefore, the specific objectives of this research are:

- To develop an overall framework that integrates the qualitative and quantitative approaches of IS analysis in identifying, generating, and evaluating the ISD options.
- To develop a qualitative ISD analysis method that aims to identify, generate, screen, and evaluate design options based on the ISD concept in a single tool.
- To develop a quantitative ISD analysis method that incorporates IS principles, in order to assess hazards, generate, and evaluate conflicts in ISD options, based on a risk approach.
- To test the applicability of the above developed tools with various case studies and a comparison study with previous ISD tools.

The developed framework is expected to be able to assist in providing answers to the following questions:

i. Can I eliminate this hazard?
ii. If not, can I reduce the magnitude of this hazard?
iii. Do the alternatives (identified in questions i and ii) increase the magnitude of any other hazards, or create new hazards?
iv. At this point, what technical and management systems are required to manage the hazards that could not be eliminated?

The developed tool is believed to be applicable at any lifecycle stage of CPI. However, to ensure the practicability of the developed methodologies, the research scope is focused at developing a tool suitable to be used during the preliminary design stage e.g., during solvent selection and flow-sheeting development. The scope of hazards concentrates mainly on fire and explosion, since these types of hazard cause the greatest damage and loss, in terms of people, assets, and property. The ISD conflict focuses on the trade-off between Inherent Safety principles and the Inherent Safety principle itself. The computation of the developed models in MS Excel, are based on an index approach for its simplicity, ease of understanding, and is flexible for modification; according to the availability of data during the early design stage. The HYSYS process simulator is used to collect the relevant design properties, by simulating worst case scenarios for the process considered in the case study.

1.5 Outline of the thesis

This thesis is constructed in the following manner. Chapter 2 contains a literature review of conventional safety analysis, an explanation of the ISD concept, and related previous works, which highlight current approaches of Inherent Safety analysis during the design stage and their limitations. The importance of the ISD concept and the urgency of developing an effective methodology to overcome the constraints in evaluating and finding suitable ISD options, are also discussed. Chapter 3 discusses related theories for qualitative and quantitative tools and describes the modifications made to suit this research. In addition, the process hazards and theories related to runaway reaction, combustion, and physical hazards that caused fire and explosions and its formulations, are also discussed. A detailed description of the developed framework, of the integrated ISD qualitative and quantitative tools, is also provided in this chapter. This is followed by its application in a hazardous chemical process during the process development stage through several case studies. The findings and discussions on the applications of the developed methodologies are in Chapter 4. Finally, the conclusion and future works are addressed in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Chapter overview

This chapter provides a review on current practice of safety analysis in CPI especially during design stage. Next, a detailed review on the present tools available to analyse safety is provided. The review includes the conventional methods and also the Inherent Safety analysis methods that embedded ISD concept. The discussion is focused on the concept applied, objectives of the methods and the limitations of the conventional and Inherent Safety tools which lead to the importance of developing a systematic Inherent Safety analysis method in the present research works.

2.2 Current implementation of safety analysis in process design stage

Lifecycle of chemical process plant begins from the synthesis studies of the desired process and its life ends at decommissioning phase after completing the targeted production years. Typical structure of CPI projects are shown in Figure 2.1 and each phase has specific key deliverables which require high level of commitment from various expertise of engineering disciplines, for example, process, mechanical, civil, electrical etc. (CCPS, 1989; Siirola, 1996; Kaibel and Schoemakers, 2002 and Harmsen, 2004). Table 2.1 provides the summary of typical process deliverables throughout the lifecycle of process.

While all phases are equally important in the successful implementation of a CPI project, the initial design phases i.e. process synthesis, preliminary and basic engineering are the more critical ones where various feasibility studies are conducted such as screening of alternatives in terms of chemicals, reactions, process units and control abilities. All of these will determine the profitability outcomes from the project. Since time is the limitation, these design stages require systematic and effective procedures as the guidelines for effective decision making.

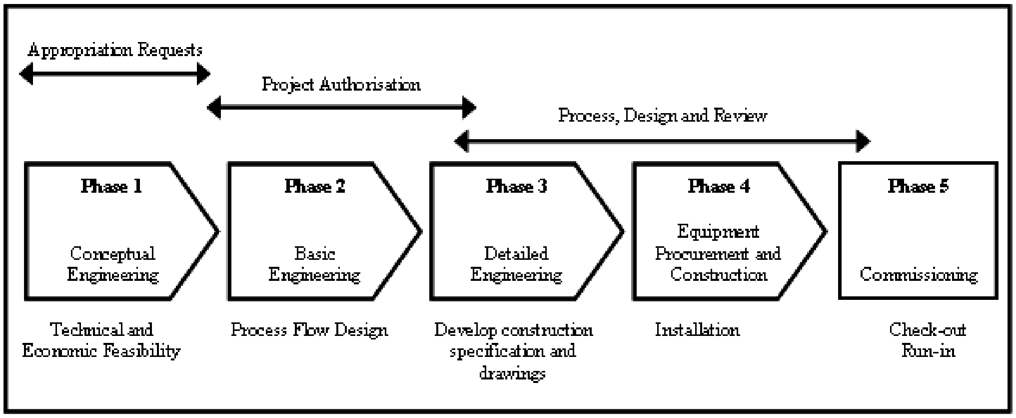


Figure 2.1: Phases of a capital project (CCPS 1989)

The well known preliminary design procedure developed by Douglas (1988) used cost studies as the initial screening to eliminate ideas for designs that are unprofitable. The heuristic procedure is concentrated on finding the best flowsheet during preliminary design stage. The limitation of this procedure is it is not integrated with other important factors such as safety and environmental constraints when defining the flowsheet of the process. It is often occurred that the above factors are considered at the very late stage which will end up with costly design modification in order to capture the safety, health and environmental problems. Thus, in order to avoid uneconomical design, the hazards that have been identified remained in the process and the solution is merely to control the likelihood of hazards to occur through technical safety measures such as added safety instruments which through time could fail and lead to catastrophic accident as described in Section 1.1. Because of this reason, safety became equally important when designing the CPI. It is significant to perform safety analysis throughout the lifecycle of CPI so that able to identify early the effective ways of designing out the hazards during design stage before it is too late.

Table 2.1: Lifecycle step of CPI and its process deliverables

Lifecycle Step	Process Engineering Key Deliverables
Chemical route synthesis	- Development of chemical synthesis steps - Selection of best chemical synthesis steps
Preliminary process design	- Function integration - Heuristic selecting unit operations and recycle structure - Superstructure optimisation
Process development	- Experiments for kinetic, physical data - Reaction and separation tests - Pilot plant - Cold flow scale-up tests
Process engineering	- Definition of all equipment and control for accurate economic evaluation
Site integration	- Connect energy and mass flows with other processes and utilities
Detailed engineering	- Definition of all process details to allow purchasing and construction
Plant operations	- Production phase
End of life	- Find second use - Deconstruct and reuse parts

2.3 Conventional safety analysis methods

There are many safety analysis methods used in CPI to analyse safety in order to achieve specific goals and objectives towards reduction of risk in each stage of lifecycle. The most recommended tools by CCPS (1996) and frequently used by CPI for respective plant design stages are summarised in Table 2.2 which also indicates the specific category of each tool. Perry (2008) has classified these tools as the hazard identification and analysis tools (HIA), hazard ranking methods (HR) and logic model methods (LM).

Safety analysis tools in HIA category are generally used to spot out potential hazards from the studied process which becomes a precursor towards detail hazard scenario studies such as in Quantitative Risk Assessment (QRA). The hazards could be prioritised by using safety analysis tools in HR category where the hazard is quantified based on its potential to cause impact to people, properties or the environment. While safety analysis tools in LM category are commonly used in QRA with the objective to understand and estimate cause of failures from the studied process.

Reviews of the above safety analysis tools are given in this chapter starting with safety analysis that used qualitative studies followed by the quantitative methods. The review is focused on the objectives, techniques applied and outcomes from the safety tools. Research observations on their applicability to analyse inherent safety and generating inherent strategies are also discussed for each safety tool.

Table 2.2: Safety analysis tools at various project stages (CCPS, 1996)

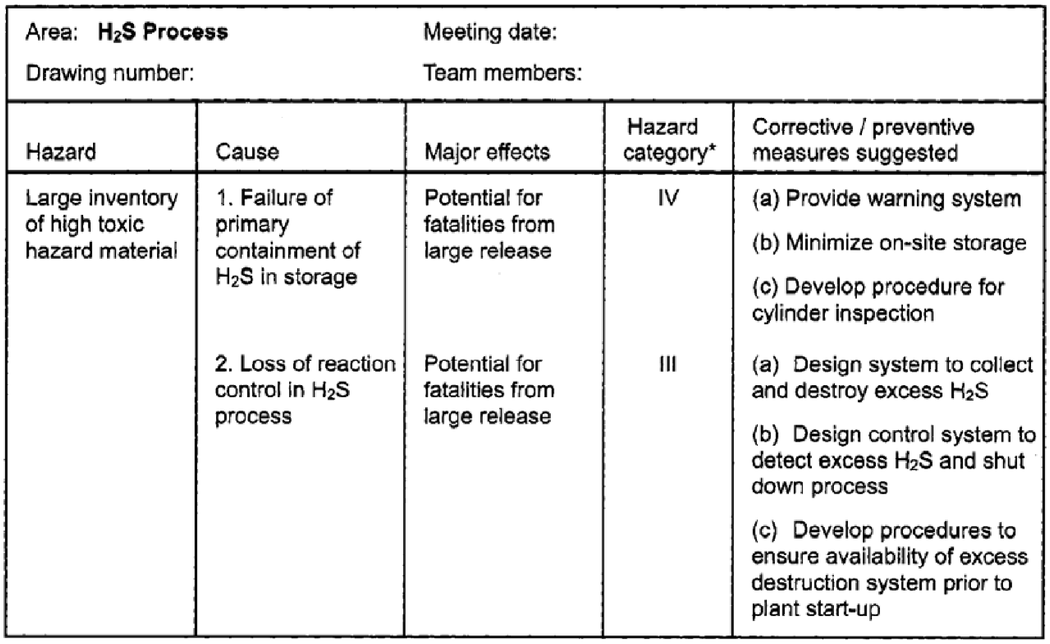
Project Stages	Hazard Analysis	Category of Analysis
Preliminary Engineering	Preliminary Hazard Analysis	HIA
Basic Engineering	DOW Fire and Explosion Index	HR
	Chemical Exposure Index	HR
Detailed Design	Hazard and Operability Studies	HIA
	Failure Mode Effects and Critical Analysis	HIA
	Fault Tree Analysis	LM
	Event Tree Analysis	LM
	Quantitative Risk Assessment	Combination of all
Equipment Procurement and Construction	Checklist and What-If Review	HIA
Commissioning	Pre-start up safety review	HIA

2.3.1 Preliminary Hazard Analysis (PreHA)

PreHA is used to identify hazards during early design stage particularly in research and development or preliminary design phase (CCPS, 2008). Generally, this tool is used when fewer details are available on the design and operating procedures. The tool used qualitative technique to broadly overview potential hazards from overall process and chemicals involved and rank them based on previous experiences or accidents. In order to conduct an effective PreHA, the study requires at least basic information such as chemicals, reactions, process parameters as well as the major types of equipment e.g. vessels, heat exchangers etc. Then risk reduction measures are suggested which include design modifications, passive and active safety measures.

Although PreHA could identify design criteria or alternatives that could eliminate or reduce those hazards, some experience is required in making such judgements (CCPS, 2008). Table 2.3 shows a typical PreHA table to document the outcomes from the discussion of the PreHA's team which will be used in detail hazard analysis.

Table 2.3: Example of Preliminary Hazard Analysis Worksheet (CCPS, 2008)



Area: **H_2S Process** Meeting date:

Drawing number: Team members:

Hazard	Cause	Major effects	Hazard category*	Corrective / preventive measures suggested
Large inventory of high toxic hazard material	1. Failure of primary containment of H_2S in storage	Potential for fatalities from large release	IV	(a) Provide warning system (b) Minimize on-site storage (c) Develop procedure for cylinder inspection
	2. Loss of reaction control in H_2S process	Potential for fatalities from large release	III	(a) Design system to collect and destroy excess H_2S (b) Design control system to detect excess H_2S and shut down process (c) Develop procedures to ensure availability of excess destruction system prior to plant start-up

* Hazard Category: I - negligible, II - marginal, III - critical, IV - catastrophic

2.3.2 Hazard and Operability Studies (HAZOP)

HAZOP is one of the most used safety analysis methods in CPI. This qualitative study is performed by stimulating the imagination of a group of people through theapplication of guidewords on potential of deviation from the design or process intention that could lead to undesirable consequences. Example of guidewords is given in Table 2.4 with illustration of suitable process parameters.

HAZOP study is a systematic procedure in searching potential hazards and operability problems from one vessel to another and from one pipe to another called as "study nodes". For an effective HAZOP study, Imperial Chemical Industries (ICI) originally defined the HAZOP study technique to require that HAZOP studies to be performed by an interdisciplinary team to trigger hazards out from the studied process. A brainstorming session is conducted by people that are knowledgeable and highly experienced about the process and HAZOP study. Another important requirement for a complete HAZOP study is essentially to have a final process planning with flowsheets and Process Piping and Instrumentation Diagram (P&ID). Figure 2.2 shows the overview of HAZOP study technique, however, CCPS (2008) stated that the activities listed as "Follow-up" are not actually part of the HAZOP methodology and are not necessarily the responsibility of the HAZOP study team.

Table 2.4: Some HAZOP guidewords used in conjunction with process parameters (CCPS, 2008)

Guideword	**Meanings**	**Comments**
No, Not, None	Complete negation of design intentions	No part of intention is achieved and nothing else occurs
More	Quantitative increases	Quantities and relevant physical properties such as flowrates, heat, perssure
Less	Quantitative decreases of any relevant physical parameters	Same as above
As well as	Qualitative increase	All design and operating intentions are achieved as well as some additional activity
Part of	A qualitative decrease	Some parts of the intention are achieved, others are not
Reverse	Logical opposite of intention	Activities such as reverse flow or chemical reaction or poison instead of antidote
Other than	Complete substitution	No part of intention is achieved; something quite different happens

HAZOP is effective to recognise hazards from potential operational failures that could lead to accident regardless of the stage of hazard review performed. Although HAZOP is one of the simplest approaches yet easy to understand for hazard identification, the identified risk reduction measures through these tools usually aimed at passive, active engineered and procedural strategies rather than eliminating the hazards inherently through changes in design. Even if there are changes being proposed, it is considered as major changes which come too late and costly to be done. Table 2.5 shows an example of HAZOP study table with results focused on passive, active and procedural strategies. Apart from the effort to automate HAZOP, the method has not changed. However its application has been abused nowadays by users who claim to perform HAZOP but instead only do simple line diagram revisions (Kletz, 1999).

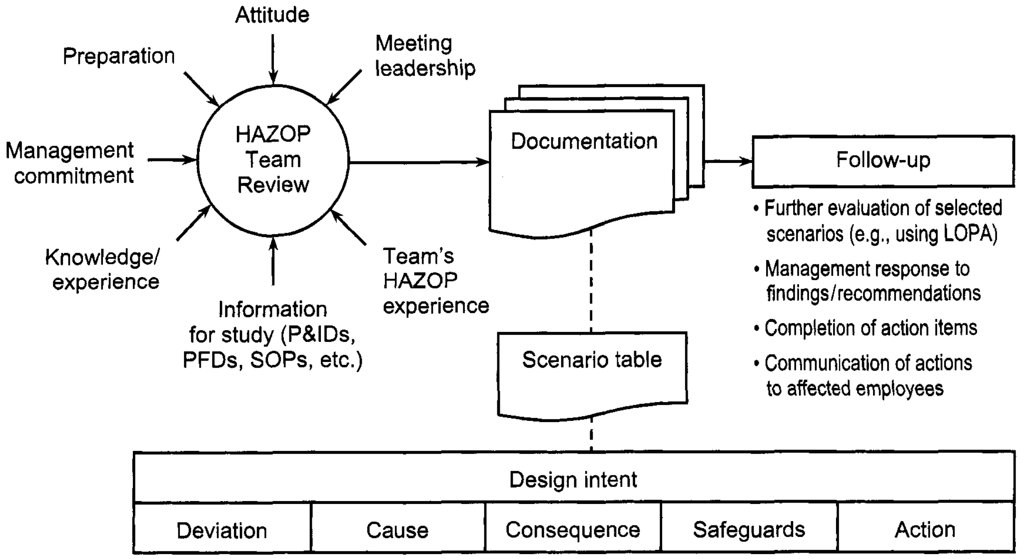
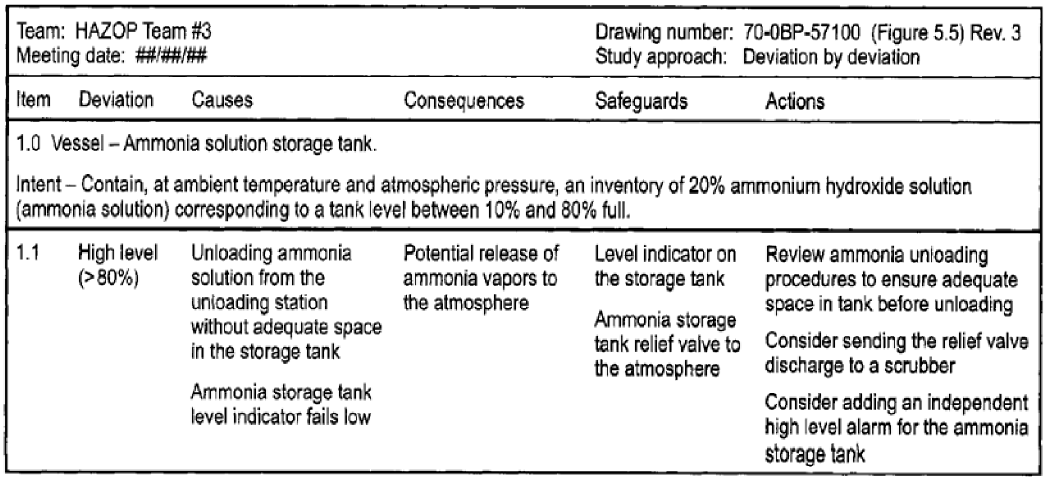


Figure 2.2: Overview of the HAZOP study technique (CCPS, 2008)

Table 2.5: Sample deviation from the HAZOP study table for the DAP process example (CCPS, 2008)



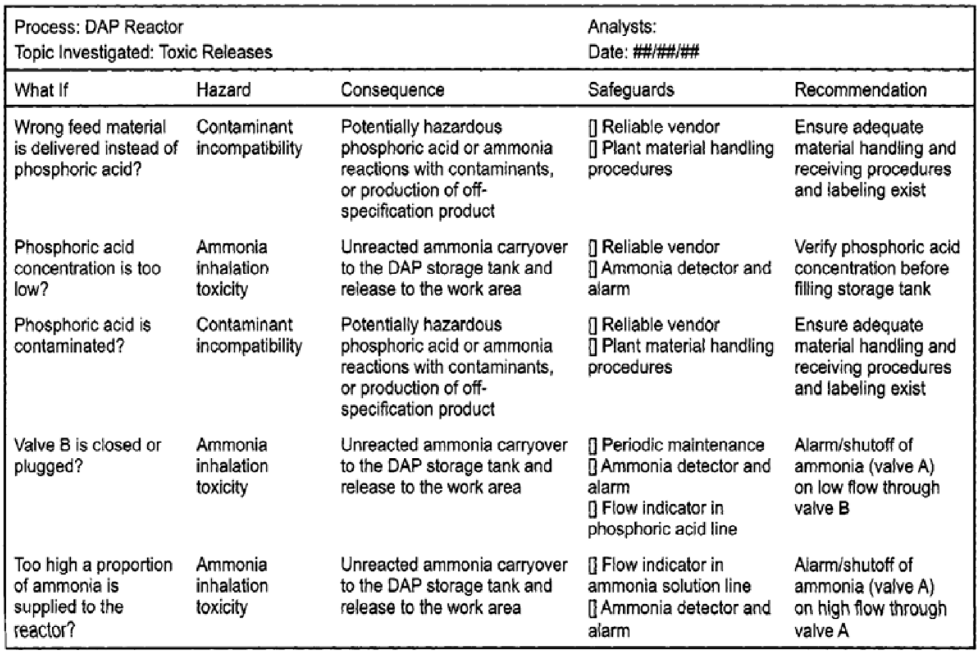
Team: HAZOP Team #3 Meeting date: ##/##/##				Drawing number: 70-0BP-57100 (Figure 5.5) Rev. 3 Study approach: Deviation by deviation	
Item	Deviation	Causes	Consequences	Safeguards	Actions
1.0 Vessel – Ammonia solution storage tank. Intent – Contain, at ambient temperature and atmospheric pressure, an inventory of 20% ammonium hydroxide solution (ammonia solution) corresponding to a tank level between 10% and 80% full.					
1.1	High level (>80%)	Unloading ammonia solution from the unloading station without adequate space in the storage tank Ammonia storage tank level indicator fails low	Potential release of ammonia vapors to the atmosphere	Level indicator on the storage tank Ammonia storage tank relief valve to the atmosphere	Review ammonia unloading procedures to ensure adequate space in tank before unloading Consider sending the relief valve discharge to a scrubber Consider adding an independent high level alarm for the ammonia storage tank

2.3.3 What-If/Checklist Analysis

The identification of hazards in this qualitative method is by considering the general types of incidents that can occur in a process via development list of What-if questions format. In addition, a Checklist technique is used to cover any gaps that were not addressed by the What-if method. This hybrid method is conducted through brainstorming session and works best when performed by an experienced team in the studied process.

The outcomes from this method are commonly a generated table that contains What-if questions as the initiating causes, effects, safeguards and action items. This method also often used as a pre-cursor to more detailed hazard analysis studies since the method provides less details of output. Table 2.6 and 2.7 are the examples of What-if Analysis table and Checklist table, respectively as shown in CCPS (2008).

Table 2.6: Example of What-if Analysis (CCPS, 2008)

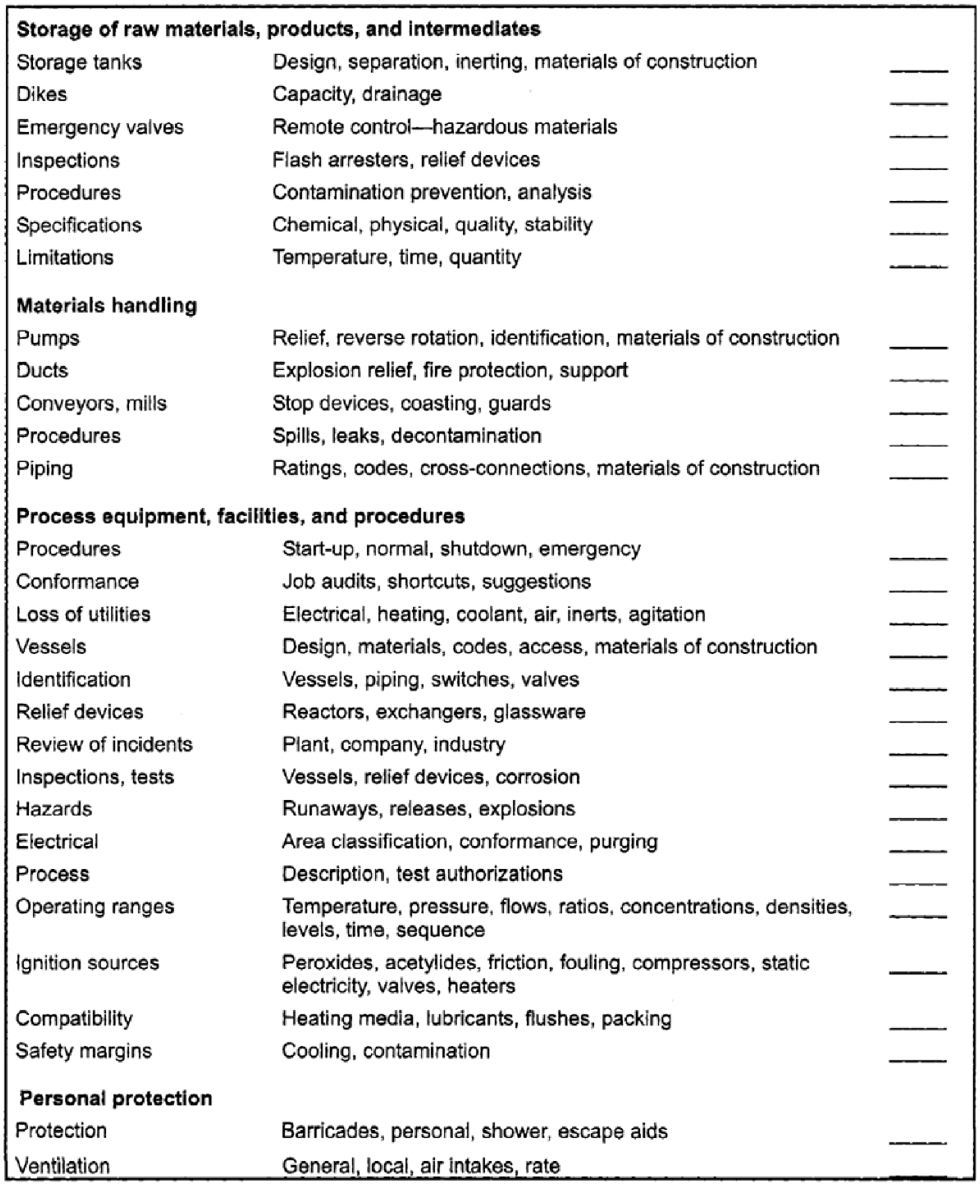


Process: DAP Reactor
Topic Investigated: Toxic Releases
Analysts:
Date: ##/##/##

What If	Hazard	Consequence	Safeguards	Recommendation
Wrong feed material is delivered instead of phosphoric acid?	Contaminant incompatibility	Potentially hazardous phosphoric acid or ammonia reactions with contaminants, or production of off-specification product	☐ Reliable vendor ☐ Plant material handling procedures	Ensure adequate material handling and receiving procedures and labeling exist
Phosphoric acid concentration is too low?	Ammonia inhalation toxicity	Unreacted ammonia carryover to the DAP storage tank and release to the work area	☐ Reliable vendor ☐ Ammonia detector and alarm	Verify phosphoric acid concentration before filling storage tank
Phosphoric acid is contaminated?	Contaminant incompatibility	Potentially hazardous phosphoric acid or ammonia reactions with contaminants, or production of off-specification product	☐ Reliable vendor ☐ Plant material handling procedures	Ensure adequate material handling and receiving procedures and labeling exist
Valve B is closed or plugged?	Ammonia inhalation toxicity	Unreacted ammonia carryover to the DAP storage tank and release to the work area	☐ Periodic maintenance ☐ Ammonia detector and alarm ☐ Flow indicator in phosphoric acid line	Alarm/shutoff of ammonia (valve A) on low flow through valve B
Too high a proportion of ammonia is supplied to the reactor?	Ammonia inhalation toxicity	Unreacted ammonia carryover to the DAP storage tank and release to the work area	☐ Flow indicator in ammonia solution line ☐ Ammonia detector and alarm	Alarm/shutoff of ammonia (valve A) on high flow through valve A

While this method may be used at any stage of process's life time, the method is still proposing risk reduction measures for controlling the hazards identified rather than the inherent strategies which are more effective to eliminate the hazards. In addition, the method is not systematic, requires multidisciplinary team and relies mainly on their expertise and experience (CCPS, 2008).

Table 2.7: Examples of Checklist table



Storage of raw materials, products, and intermediates		
Storage tanks	Design, separation, inerting, materials of construction	_____
Dikes	Capacity, drainage	_____
Emergency valves	Remote control—hazardous materials	_____
Inspections	Flash arresters, relief devices	_____
Procedures	Contamination prevention, analysis	_____
Specifications	Chemical, physical, quality, stability	_____
Limitations	Temperature, time, quantity	_____
Materials handling		
Pumps	Relief, reverse rotation, identification, materials of construction	_____
Ducts	Explosion relief, fire protection, support	_____
Conveyors, mills	Stop devices, coasting, guards	_____
Procedures	Spills, leaks, decontamination	_____
Piping	Ratings, codes, cross-connections, materials of construction	_____
Process equipment, facilities, and procedures		
Procedures	Start-up, normal, shutdown, emergency	_____
Conformance	Job audits, shortcuts, suggestions	_____
Loss of utilities	Electrical, heating, coolant, air, inerts, agitation	_____
Vessels	Design, materials, codes, access, materials of construction	_____
Identification	Vessels, piping, switches, valves	_____
Relief devices	Reactors, exchangers, glassware	_____
Review of incidents	Plant, company, industry	_____
Inspections, tests	Vessels, relief devices, corrosion	_____
Hazards	Runaways, releases, explosions	_____
Electrical	Area classification, conformance, purging	_____
Process	Description, test authorizations	_____
Operating ranges	Temperature, pressure, flows, ratios, concentrations, densities, levels, time, sequence	_____
Ignition sources	Peroxides, acetylides, friction, fouling, compressors, static electricity, valves, heaters	_____
Compatibility	Heating media, lubricants, flushes, packing	_____
Safety margins	Cooling, contamination	_____
Personal protection		
Protection	Barricades, personal, shower, escape aids	_____
Ventilation	General, local, air intakes, rate	_____

2.3.4 Dow Fire and Explosion Index (Dow F&EI)

Dow F&EI (Dow, 1994a) is a Hazard Ranking tool that is most often used in CPI as one way to communicate to management on the quantitative hazard potential of fire and explosion. Other similar concepts of hazard indices are Dow Chemical Exposure Index (Dow CEI) (Dow, 1994b) and Mond Fire, Explosion and Toxicity Index (ICI,

1993) which deals on toxicity and combination of both F&E and toxicity, respectively.

There are substantial researches attempted to improve and apply Dow F&EI as an IS tool. Etowa et al. (2002) claims Dow F&EI could quantify IS aspects through evaluation of inventory, temperature and pressure of the studied process. Suardin et al. (2007) recently have proposed to include Dow F&EI as a safety metric in their optimization framework. Recently, the Likely-Loss Fire and Explosion Index (LL-FEI) by Jensen and Jorgensen (2007) introduced a new relationship for estimation of the damage factor used in the Dow F&EI, which provides an estimate of risk of losses from fires and explosions. Earlier on, Hendershot (1997) reported that Dow F&EI and Dow CEI can measure inherent process risks that give unitless index value for ranking the various options at early design stage. However, the information on process design required by Dow F&EI has to be fully in place to make it applicable on the design.

Therefore, they are unsuitable for measuring the level of inherent safety at the preliminary design and preliminary process development stages, where the use of such indices is most useful (Lees, 2005). Furthermore, the weighting factors used to combine the sub-indices in the Dow F&EI method suffered from controversy and Kletz recommends that the method should be used cautiously keeping in mind that some of the numbers are arbitrary (Loss Prevention, 1980).

Dow F&EI is applied in this research as a tool to determine consequence from the case studies conducted in this work. The damage index obtained from Dow F&EI is used as the base guideline to evaluate the accuracy of the developed tool since Dow F&EI is widely used in chemical process industry. This tool is commonly used to rank the relative hazards in a plant specifically the relative magnitude of flammable hazards based on process unit. A process unit is defined as any major item of process equipment typically available in process plant such as reactor, distillation, storage tank, unloading facility etc. Therefore in this research, the steps in Dow F&EI procedures are referred up to the determination of the index value as shown in Figure 2.3.

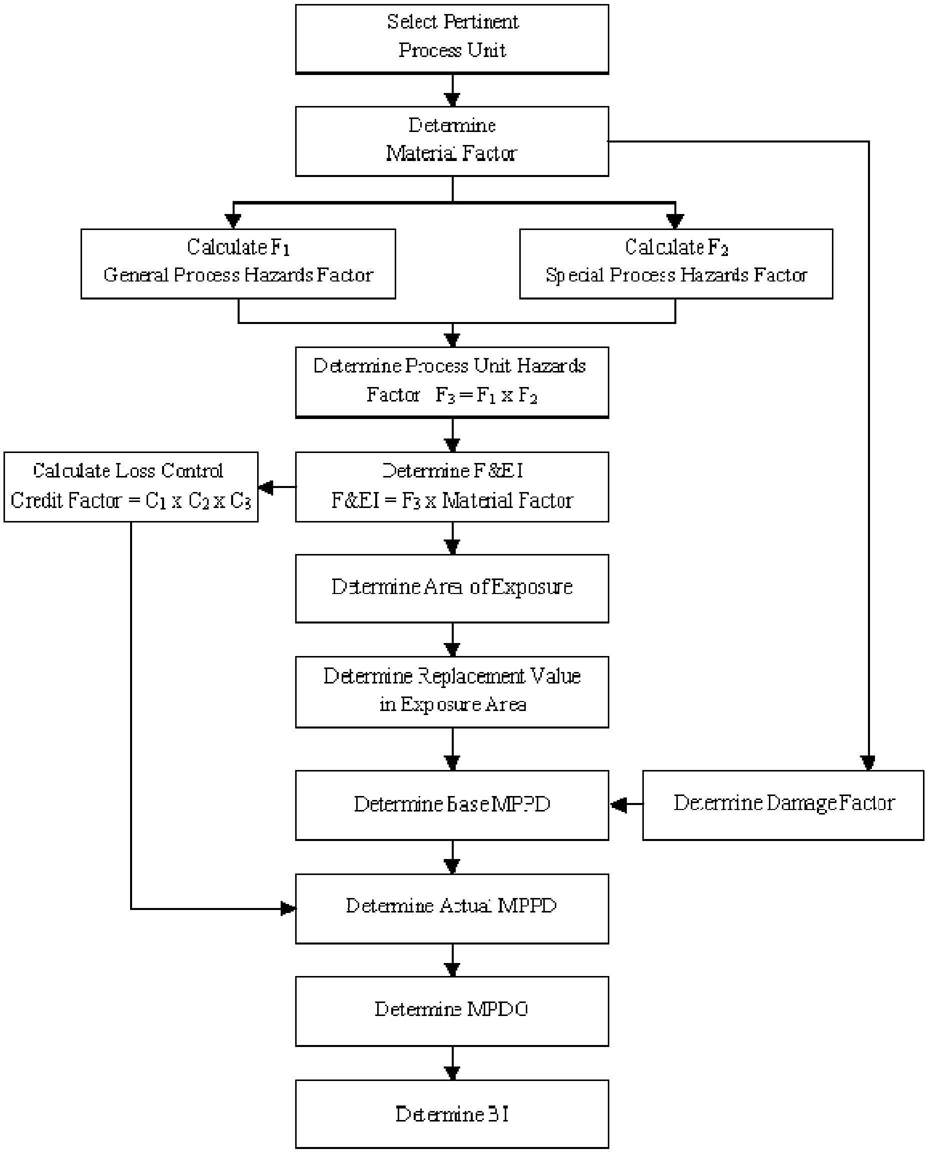


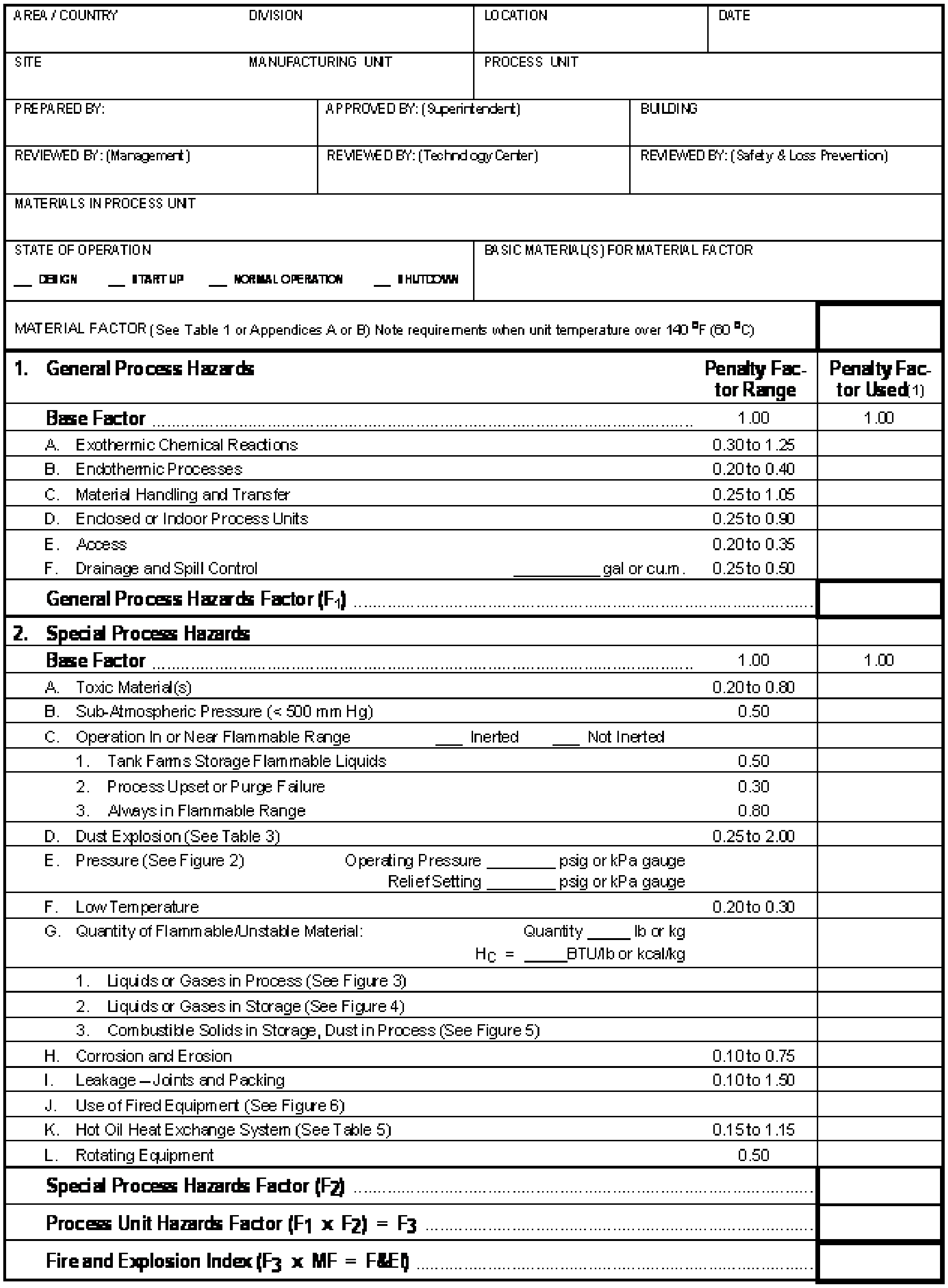
Figure 2.3: Dow F&EI procedure (CCPS, 1994)

Dow F&EI determined the hazard level of a process plant by identifying equipment that could contribute to an incident by estimating potential damage from the equipment. As shown in Figure 2.3, the resulting product of Dow F&EI is based on Material Factor (MF) and Process Hazard Factor (PHF). MF is the basic starting value in calculating the Dow F&EI. MF is referred as the flammability and instability level of substances involved in the equipment which denotes the intensity of energy release from the most hazardous material or mixture of materials present in significant quantity in the equipment. It is a function of the National Fire Protection Association (NFPA) N_F and N_R ratings. These are flammability and reactivity (or instability) ratings respectively. If the process operates at over 60^oC (140^oF), then the MF is adjusted for temperature since fire and reaction hazards increase markedly with temperature. The guideline includes instructions on how to determine the MF for mixtures and for materials not included in the table. For example the MF for gasoline is 16 while propane is 21.

PHF is obtained from the hazard penalty given for General Process Hazards and Special Process Hazards based on the information from the studied equipment. Figure 2.4 shows the detail criteria of penalty factors and the penalty range for each category. General Process Hazards represent as F_1 deal with differences in type of reactions, material handling and transfer, enclosed or indoor process units, access to the process units, drainage and spill control. While Special Process Hazards known as F_2 consider factors for toxic materials, sub-atmospheric pressure, operation in or near flammable range, dust explosion, relief pressure, low temperature, quantity of flammable and unstable materials, corrosion and erosion, leakage at joints and packing, use of fired heaters, hot oil system and rotating equipment. Detailed instructions and correlations for determining the F_1 and F_2 are provided in the complete guidelines of Dow F&EI (CCPS, 1994). Then, the Process Unit Hazards represent by F_3 is obtained from the multiplication of F_1 and F_2. The Dow F&EI is estimated from the multiplication of F_3 with MF and finally is referred to Table 2.8 which provides the degree of hazard based on the index value.

Table 2.8: Dow F&EI to estimate degree of hazard (Crowl and Louvar, 2002)

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



AREA / COUNTRY	DIVISION	LOCATION	DATE
SITE	MANUFACTURING UNIT	PROCESS UNIT	
PREPARED BY:	APPROVED BY: (Superintendent)	BUILDING	
REVIEWED BY: (Management)	REVIEWED BY: (Technology Center)	REVIEWED BY: (Safety & Loss Prevention)	
MATERIALS IN PROCESS UNIT			
STATE OF OPERATION __ DESIGN __ START UP __ NORMAL OPERATION __ SHUTDOWN		BASIC MATERIAL(S) FOR MATERIAL FACTOR	
MATERIAL FACTOR (See Table 1 or Appendices A or B) Note requirements when unit temperature over 140 °F (60 °C)			

1. General Process Hazards	**Penalty Factor Range**	**Penalty Factor Used**(1)
Base Factor	1.00	1.00
A. Exothermic Chemical Reactions	0.30 to 1.25	
B. Endothermic Processes	0.20 to 0.40	
C. Material Handling and Transfer	0.25 to 1.05	
D. Enclosed or Indoor Process Units	0.25 to 0.90	
E. Access	0.20 to 0.35	
F. Drainage and Spill Control __________ gal or cu.m.	0.25 to 0.50	
General Process Hazards Factor (F_1)		
2. Special Process Hazards		
Base Factor	1.00	1.00
A. Toxic Material(s)	0.20 to 0.80	
B. Sub-Atmospheric Pressure (< 500 mm Hg)	0.50	
C. Operation In or Near Flammable Range ___ Inerted ___ Not Inerted		
1. Tank Farms Storage Flammable Liquids	0.50	
2. Process Upset or Purge Failure 3. Always in Flammable Range	0.30 0.80	
D. Dust Explosion (See Table 3)	0.25 to 2.00	
E. Pressure (See Figure 2) Operating Pressure ________ psig or kPa gauge Relief Setting ________ psig or kPa gauge		
F. Low Temperature	0.20 to 0.30	
G. Quantity of Flammable/Unstable Material: Quantity _____ lb or kg H_C = _____ BTU/lb or kcal/kg		
1. Liquids or Gases in Process (See Figure 3)		
2. Liquids or Gases in Storage (See Figure 4)		
3. Combustible Solids in Storage, Dust in Process (See Figure 5)		
H. Corrosion and Erosion	0.10 to 0.75	
I. Leakage – Joints and Packing	0.10 to 1.50	
J. Use of Fired Equipment (See Figure 6)		
K. Hot Oil Heat Exchange System (See Table 5)	0.15 to 1.15	
L. Rotating Equipment	0.50	
Special Process Hazards Factor (F_2)		
Process Unit Hazards Factor ($F_1 \times F_2$) = F_3		
Fire and Explosion Index ($F_3 \times MF$ = F&EI)		

(1) For no penalty use 0.00.

Figure 2.4: Documentation form for Dow F&EI (CCPS, 1994)

2.3.5 Fault Tree Analysis (FTA)

Fault Tree Analysis is one of the Logic Model tools that is frequently used to analyse potential of failure through deductive method where the top event is given and analysis focuses on the search of the causes that may trigger it. The qualitative study is done with the help of logic symbol to represent "AND" and "OR" gates to identify the possible combination of hazardous events that could cause the top event to occur. Once the fault tree is completed, the quantitative evaluation is possible through calculation on frequency of failure of the top event starting from the frequency of the initiating events. Example of Fault Tree Diagram is shown in Figure 2.5.

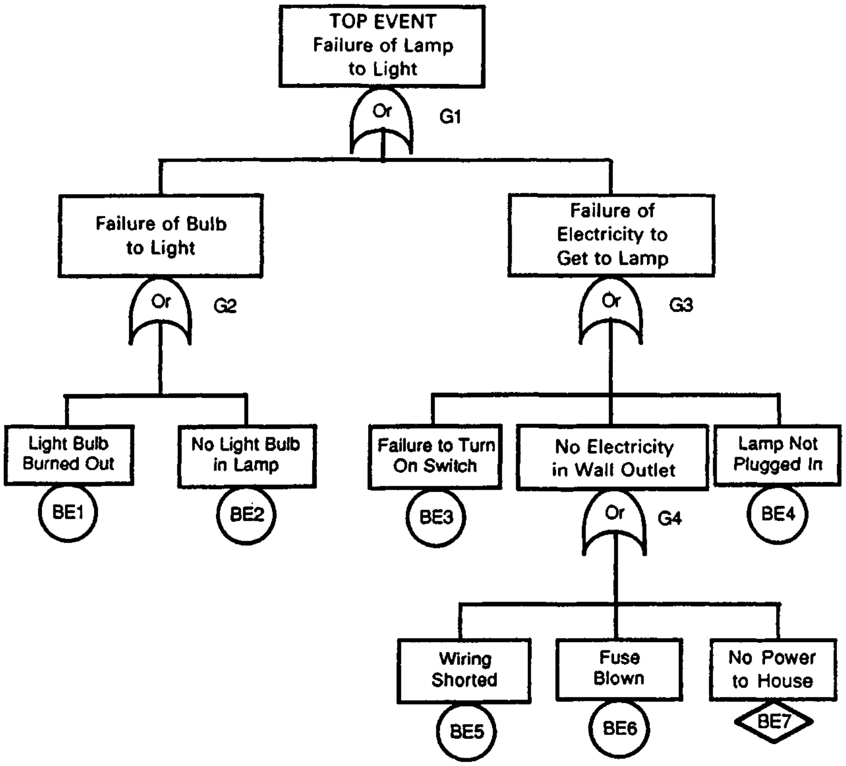


Figure 2.5: Example of Fault Tree Analysis (CCPS, 2000)

The method is comprehensive due to its applicability to combine both qualitative and quantitative studies. However, the analysis commonly stopped at the failure of elementary devices such as valves, pumps or control instruments as the basic events (Stoessel, 2008). The results would end up to the recommendations on secondary safety strategies such as to provide back up pumps or to increase the maintenance frequency of the pump rather than the primary safety strategies. Furthermore, the method is highly dependence on statistical data of the failure frequency which is specific to the process condition studied. The reference for this type of data is not always available and often has to be estimated thus increasing the uncertainty of the analysis (Khan and Abbasi, 1998; CCPS, 1993).

2.3.6 Quantitative Risk Assessment (QRA)

The ultimate result from safety analysis is to identify and quantify risk indicator. Risk is commonly defined as a measure of human injury, environmental damage or economic loss in terms of both the incident likelihood (probability) and the magnitude of the loss or injury (consequence) (CCPS, 2000). The common concept to achieve low risk is by identifying the answer of the following questions:

- How frequent is the scenario?
- How bad are the consequences?

Thus, risk is influenced by a combination of potential severity presents in the process and probability of the severity to happen based on the rate of recurrence of failures or exposures which these two parameters must be estimated effectively.

In CPI, risk could be analysed by following the Quantitative Risk Assessment (QRA) technique to find the risk reduction measures that economically practicable to achieve according to the As Low As Reasonably Practicable (ALARP) concept. A typical process flow diagram for Chemical Process Quantitative Risk Analysis (CPQRA) is shown in Figure 2.6 while ALARP concept based on definitions from HSE UK (2001), Lees (1996) and Shell (2001) is shown in Figure 2.7. The risk outcomes are presented in the mode of potential fatalities for individual and societal potential risk. Then, the risk values are referred to the tolerability criteria which differ from one region to another. Examples of risk acceptance criteria are shown in Table 2.9.

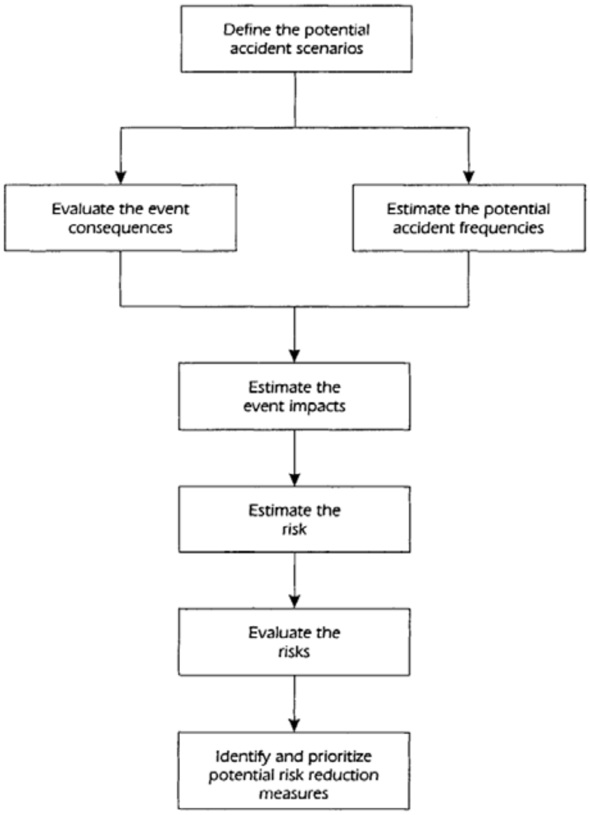


Figure 2.6: Chemical process quantitative risk analysis (CCPS, 2000)

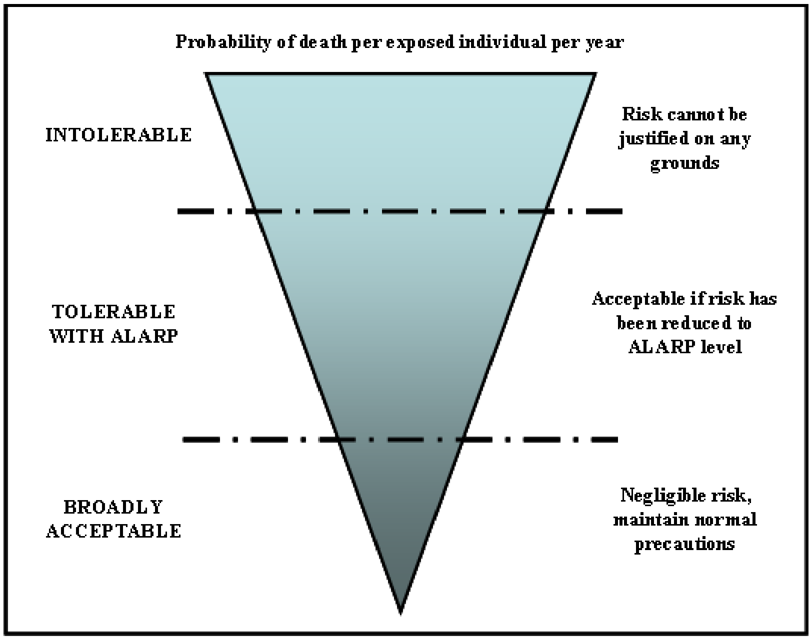


Figure 2.7: ALARP concept applied by CPI (HSE UK, 2001; Lees, 1996 and Shell, 2001)

Table 2.9: Individual risk acceptance criteria for different regions or countries

Country/Region	Individual Risk Criteria			Source of references
	Not tolerable	Tolerable with ALARP	Tolerable or broadly acceptable	
Russia	$>10^{-5}$	10^{-5} to 10^{-6}	$<10^{-6}$	Clark (2001)
Argentina	none	none	$<10^{-6}$	Clark (2001)
The Netherlands	$>10^{-6}$	10^{-6} to 10^{-8}	$<10^{-8}$	DNV (1993)
UK	$>10^{-5}$	10^{-5} to 10^{-6}	$<10^{-6}$	HSE (2001)
Western Australia	$>10^{-5}$	10^{-5} to 10^{-6}	$<10^{-6}$	DNV (1993)
Malaysia	10^{-3}	10^{-3} to 10^{-6}	$<10^{-6}$	DOE (2004)

QRA is a safety analysis tool that is mostly used in CPI due to regulations requirement to submit a written Safety Report, for example in Malaysia, under the Control of Industrial Major Accident and Hazards (CIMAH) Regulations 1996 (OSHAct, 1994). QRA is performed by systematically prioritises the identified hazards using risk-based through numerical estimation of incident frequency and consequences. The consequences commonly represented in the form heat radiation and overpressure for fire and explosion, respectively. For toxic effect, the consequence results normally shown as the downwind concentration that would cause fatality to human. Because of intensive data is involved, QRA is most comfort to be applied at a later stage of process design when detail design properties and information on frequency of failures is available. In addition, this method is widely used at operation stage which normally requires industry to fulfil regulation requirements such as renewal of safety accreditation when there are modifications made to the plant or simply for safety certification for every five years. Therefore, there are many commercial software that have been developed to aid QRA such as Software for the Assessment of Flammable, Explosive and Toxic Impact (SAFETI) which at present is known as Phast and PhastRisk as the newer version developed by Det Norske Veritas (DNV) and Fire, Release, Explosion and Dispersion (FRED) by Shell. These tools are very helpful provided that all detail information about the process, frequency of failure and safety data are available. Otherwise, the outcomes of risk value suffered from numerous uncertainties.

In brief, the concept is used to assist the CPI practitioners in deciding the suitable risk reduction strategies based on the present available technology and approved cost to minimise the risk. However, the QRA results are normally used to prove the acceptability of the hazardous process through evaluating the proposed control measures whether these safety measures are enough to reduce the risk rather than focusing more on how the risk can be reduced. Hence, this type of mindset and perception becomes one of the contributing factors to the reoccurrence of accidents in CPI.

A well-driven risk analysis not only leads to a safer process but also to an economical process since the process will be more reliable and gives rise to less productivity losses (Stoessel, 2008). Risk analysis plays an important role during process design as it is a key element in process development especially in the definition of risk reduction or process control strategies to be implemented. Thus, a conventional risk concept can be modified and integrated at early stage of design not only to understand the effective control measures for the process but also to support the decision making in achieving a design that is as inherently safer as possible.

2.4 Present safety analysis that incorporate ISD concept

At present, there were many attempts made to develop safety analysis tools that incorporate ISD concept in lifecycle of CPI. Among the efforts are the developments of tools to quantify Inherent Safety characteristics in process design alternatives particularly during process route selection. The approaches and level of applications throughout the process lifecycle of these tools are varied but most of them are aimed at application during process development design stage. Since process design at early stage is suffers from the deficiency of process information and safety properties, most of the above tools use indexing approach to represent the quantification process.

In general, the developed tools can be categorised into two approaches; qualitative and quantitative approaches which can be further classified into four main types of tool; Qualitative-based Analysis, Overall Hazard-based Index, Consequence-based Index and Risk-based Index which are applied for evaluating IS aspects in process design. Table 2.10 provides the summary of hazard criteria applied in the above tools. Since the main focus of the present research is to develop an ISD tool that combines both qualitative and quantitative approaches, the review of the available ISD methods is begin with the efforts made to develop Inherent Safety tools using qualitative techniques followed by the other three methods. Brief discussion on the objective, scope, structure and the way Inherent Safety aspects considered in each tools are given in this chapter.

2.4.1 Qualitative-based Analysis

At present, the common approach to analyse inherent safety qualitatively is using the IS Checklist technique. Checklist is intended to prompt lateral thinking by questioning the rationale behind each alternative and identify the possible alternatives. Among the earlier methods are the inherent safety checklists developed by Bollinger et al. (1996) and CCPS (1996) that provide extensive questions related to inherent safety as the guidance to implement inherent safety during process design. Besides, a set of checklists developed by CCPS (1998) for specific types of process equipment such as heat transfer equipment, mass transfer equipment etc. are suggested and the options are not only for inherent strategies but also covering passive, active and procedural safety measures. Furthermore, there are inherent safety-based checklists developed for incident based investigation and process safety management developed by Goraya et al. (2004) and Amyotte et al. (2007) respectively. This qualitative method is obviously suitable to be applied during incident investigation as the aftermath or reactive approach to avoid the reoccurrence of the accidents.

AIChE (2001) has developed an EHS (environment, health and safety) review namely MERITT (Maximising EHS Returns by Integrating Tools and Talents) that integrates skills and tools of EHS in a single unified approach. Several of the above conventional safety tools such as HAZOP are also described in MERITT. Basically, MERITT provides a comprehensive references and procedures of EHS tools and not merely to evaluate risk from the options.

2.4.2 Overall Hazard-based Index

The developed hazard indices, thus far, measured the characteristics of inherent safety by aggregating scores of the chemical and process parameters which becomes an overall scores of index to determine the inherently safeness of the process. The first invented quantitative methodology is Prototype Index of Inherent Safety (PIIS) developed by Edwards et al. (1999) and Inherent Safety Index (ISI) by Heikkila et al. (1999) which apply a hazard-based indexing score through penalising the hazard identified in the chemicals and process parameters in order to identify the inherently safer process route option at design research stage. Subsequently, Gentile et al. (2001) proposed a hazard index that used fuzzy logic system to reduce uncertainties in score values through implementation of if-then rules and continuous changes in scoring the index. They utilised ISI by Heikkila et al. (1999) as the platform to analyse inherent safety characteristics at process route stage. Khan and Amyotte (2002, 2004) presented a detail review of the above tools and techniques.

Further extension is made by Palaniappan et al. (2002) who developed an expert system, called *i*Safe to automate the ISI (Heikkila et al., 1999) for inherently safer route selection and flow-sheeting development. Other approach used to measure inherent safety is a graphical method developed by Gupta and Edwards (2003) for process route selection that are also referred to process and operating parameters such as temperature, pressure and hazardous characteristics of the process. In addition, these values are plotted on a graph together with other design options to give better view for the comparison analysis to identify the inherently safer process alternatives.

INSIDE (Inherent SHE in Design) project sponsored by the European Community Commission has developed a set of tools namely INSET Toolkit (1998) to identify the inherently safer design options throughout the life of a process and to evaluate the options via concept of safety performance indices. The various inherent safety, health and environmental aspects of a process are evaluated using separate indices and no attempt is made to combine the indices into single overall measure.

2.4.3 Consequence-based Index

Consequence-based index is an analysis of potential severity of an accident in terms of the impact of a release of different inventories of hazardous material and process at

Table 2.10: Summary of approach and hazard criteria used in Quantitative Inherent Safety Tools

Quantitative Inherent Safety tools	Technique	Process Information					Hazard Categories														
							Fire/Explosion									Reaction/Decomposition						
		Inventory	Temperature	Pressure	Volume	Mass	Vapour pressure	Boiling point	NFPA-F	Flash point	Risk phrase	LEL	UEL	Boiling point	Auto-ignition	NFPA-R	Risk phrase	Heat of combustion	Heat of main reaction	Heat of side reaction	Type of main reaction	Type of side reaction
Prototype Index for Inherent Safety (PIIS) by Edwards et al. (1999)	Overall Hazard Score	A	x	x						x		x	x	x								
Inherent Safety Index (ISI) by Heikkila et al. (1999)	Overall Hazard Score	A	x	x						x		x	x	x					x	x		
Fuzzy Logic-based Inherent Safety Index by Gentile et al. (2001)	Overall Hazard Score (used ISI as basis)	A	x	x						x		x	x	x					x	x		
iSafe – Inherent Safety Expert system by Palaniappan et al. (2002)	Overall Hazard Score (used ISI as basis)																					
Process Stream Index (PSI) by Leong and Shariff (2009)	Overall Hazard Score (used ISI as basis)	A	x	x								x	x									
Dow Fire & Explosion Index (DOWF&EI) by Dow Chemical (1994)	Consequence-based (fire and explosion only)	A	x	x					x	x				x				x			x	
Integrated Inherent Safety Index (I2SI) by Khan and Amyotte (2005)	Consequence-based (fire, explosion, toxic, environment)	M	x	x	x	x	x		x	x					x	x		x	x		x	x
Inherent Safety Index Module (ISIM) by Leong and Shariff (2007)	Consequence-based (used ISI as basis for VCE only)																					
KPI for Inherent Safety by Tugnoli and Cozzani (2009)	Consequence-based (fire, explosion, toxic)	M	x	x		x					x											
Rapid Risk Analysis Based Design (RRABD) by Khan and Abbasi (1998)	Risk –based (ALARP principle)										x											
Inherent Risk Assessment (IRA) by Leong and Shariff (2009)	Risk-based (ALARP principle for VCE only)										x	x	x									

various temperature and pressure conditions to predict potential energy that would cause safety effects such as fire, explosion and toxic releases from the process.

This type of approach is devised in the inherent safety tools to identify the inherently safer design alternatives. In this vein, the Rohm and Haas Major Accident Prevention Program (MAPP) encouraged the inherently safer process development by requiring accident consequence analysis (Renshaw, 1990).

Among the tools that utilises this approach is the Integrated Inherent Safety Index (I2SI) by Khan and Amyotte (2004). The quantification of hazard in I2SI is based on potential energy and penalties from Safety Weighted Hazard Index (SWeHI) methodology developed by Khan et al. (2001). The outcome from the combination of the above factors is known as damage radii in unit meter. The higher damage radii value means the further the damage would be caused from the potential energy contained in the process unit. Other uniqueness of SWeHI method which is worth mentioning is that the estimation of potential damage involves the safety characteristics of the process unit which is categorised into five different groups i.e. storage units; units involving physical operations such as heat transfer; units involving chemical reactions; transportation units and other hazardous units such as boilers etc.

Comparison performance of SWeHI with other index methods such as Dow F&EI, Mond Index and ISI are provided in Khan et al. (2003a) which shows that SWeHI may be considered more robust than the Dow and Mond Indices in terms of its ability to weigh hazards against the effectiveness of safety measures and provide a single score for the trade-off required. SWeHI also does not require a case-to-case calibration as the magnitude of the index directly signifies the level of hazard. Based on the above advantages, the quantification of consequence using SWeHI is modified and applied to the current research work. The detailed description of I2SI and SWeHI is available in 2.4.3.1.

In this research, I2SI and SWeHI methods are revised to suit the objective and scope of works. These modified tools are aimed to be applied at quantitative stage to estimate the potential damage and generate the ISD alternative to eliminate or reduce the risk from fire and explosion hazards. Detail descriptions of the customised quantitative tool are available in section 4.4 and also in its subsections of Chapter 4.

The I2SI also integrates inherent safety potential and economic evaluations in a single tool to identify the inherently safer process option that is not only safer but cost optimum in terms of loss due to consequence damage. This tool can be utilised during process development stage since the method is focused on the potential severity from a process unit.

On the other hand, there are also other tools such as the Integrated Risk Estimation Tool (iRET) developed by Shariff et al. (2005) and the Inherent Safety Index Module (ISIM) developed by Leong and Shariff (2008) which were developed to evaluate process design alternatives on potential impact from consequences of vapour cloud explosion through the integration of process design simulator with the ISI method developed by Heikkila (1999). The integration works have simplified the design modification activities when considering process safety issues at early stage of design. While recently, Tugnoli and Cozzani (2009) introduced another way to assess the inherent safety of process alternatives based on consequence estimation using key performance indicator. This tool used loss of containment approach to estimate potential consequences to humans and their escalation effects. Specific credit factors are assigned for some categories of process equipment based on the expected release and failure frequency data reported for standard technologies in several publications. It can be observed that this tool requires extensive information for probability values to illustrate the risk of hazards.

Although the above tools could identify design alternatives that are inherently safer than others, they are not fully transparent in dissecting the potential conflicts or trade-offs among the ISD options such as the potential of hazard transfer to other site of processes. This constraint leads to other difficulties during decision making.

2.4.3.1 Integrated Inherent Safety Index (I2SI)

I2SI is developed by Khan and Amyotte (2004) to evaluate inherent safety characteristics in chemical process particularly during preliminary process design stage. The index method is intended ultimately to be applicable throughout the life cycle of process design. The main reasons of adopting the I2SI concept were because of the following features:

- I2SI utilised inherent safety guidewords similar to the well-accepted and practiced HAZOP procedure as such it can be used with minimum amount of expertise
- The index can be easily adapted to the specific design issues of different phases of the design lifecycle such as layout design while maintaining the same general structure (Tugnoli et al., 2008)
- The index can be applied quickly and simple since the inputs required are based on readily available and estimable database
- Quantitative scores enable easy interpretation of results and comparison of the inherent safety potential posed by available alternatives, thus, helping in design decision making

The preliminary framework of I2SI is illustrated in Figure 2.8. The evaluation comprised of two main sub-indices; Hazard Index (HI) is for the identification of hazard by estimating damage potential in a single process unit after considering the process and hazard control measures. The second sub-index is the Inherent Safety Potential Index (ISPI) which is intended to measure the applicability of the inherent safety principles (or guidewords) to the process.

The HI is calculated for the base process (any one process option or process setting will be considered as the base operation setting), and remains the same for all other possible options. The two indices are then combined to yield a value of the integrated index as shown in Equation (2.1):

$$\mathrm{I2SI} = \frac{\mathrm{ISPI}}{\mathrm{HI}} \tag{2.1}$$

Both the ISPI and HI range from 1 to 200; the range has been fixed considering the minimum and maximum likely values of the impacting parameters. This range gives enough flexibility to quantify the index. As evident, an I2SI value greater than unity denotes a positive response of the inherent safety guidewords application (i.e.

an inherently safer option). The higher the value of the I2SI, the more pronounced the inherent safety impact.

The indexing procedure for HI in I2SI composed of two sub-indices; a damage index (DI) and a process and hazard control index (PHCI). The damage index is a function of four important parameters namely, fire and explosion, acute toxicity, chronic toxicity and environmental damage. The DI is computed for each of these parameters using the curves in Figure 2.9(a)-(c) and 2.10(a)-(c) which effectively convert damage radii to damage indices by scaling up to 100. Figure 2.9(a)-(c) were developed for the scenarios of fire and explosion, toxic release and dispersion for acute as well as chronic cases. In order to get DI value, the damage radii need to be known, thus, it can be calculated using the Safety Weighted Hazard Index (SWeHI) approach (Khan et al., 2001). SWeHI used a consequence based approach in estimating the hazards. The SWeHI methodology involved three main steps:

i) Quantification of core factors (energy factors in the case of fire and explosion hazards and G factor in the case of toxic hazards) according to process unit type i.e. reaction, storage, etc.
ii) Assignment of penalties considering external forcing factors such as operating conditions and environmental parameters
iii) Estimation of damage radii using core factors and penalties. This damage radii represents the radius of the area in meters that is lethally affected by the hazards load having a 50% probability of causing fatality or damage. In risk analysis, the effects due to fire and explosion are commonly represented as heat thermal radiation and overpressure, respectively. The levels of fatality rate with regard to the above effects are commonly referred as in the guidelines (Lees, 1996) as shown in Table 2.11. Thus, the 50% probability of fatality in this method is referred as 30 kW/m^2 and 20.5 psi for fire and explosion, respectively.

In SWeHI, the quantification of potential damage based on energy factors and penalties are uniquely developed according to the type of process units commonly involved in the chemical process industries by taking into account the potential energy from chemical, physical and reaction conditions in the process unit. Thus, several energy factors and penalties could be considered and may have different formulation to estimate the penalties in the process unit while others may not necessarily contain the similar conditions. The process units themselves are divided into five different groups as follows:

i) Storage units

ii) Units involving physical operations such as heat transfer, mass transfer, phase change, pumping and compression

iii) Units involving chemical reactions

iv) Transportation units

v) Other hazardous units such as furnaces, boilers, direct-fired heat exchangers, etc.

Table 2.11: Level and fatality rate based on thermal radiation and overpressure (Lees, 1996)

Factors	**Fatality rate (%)**	**Level**
Thermal radiation (kW/m^2)	1 (Threshold)	4
	20	12
	40	20
	50	30
	100	37.5
	100	Engulfed in flames
Overpressure (psi)	1 (Threshold)	14.5
	10	17.5
	50	20.5
	90	25.5
	99	29.0

The formulation to estimate the core factors considered in this hazard index are defined into four energy factors; F_1, F_2, F_3 and F_4 which take into account the chemical, physical and reaction energy, respectively. The factor F_1 is calculated using the following equation:

$$F_1 = 0.1M \times \frac{H_c}{K} \tag{2.2}$$

where M is mass of chemical, kg or mass release rate, kg/s; H_c is heat of combustion, kJ/kg and K is a constant, 3.148.

The other two energy factors, F2 and F3 account for physical energy where its total effect is highly reliant to the pressure values and process units which could lead to combination of either one energy factor or both factors after comparing the pressure values. These factors are computed as below:

$$F_2 = \frac{6}{K} \times PPV = 1.304 \times 10^{-3} PP \times V \tag{2.3}$$

$$F_3 = 1.0 \times 10^{-3} \times \frac{1}{(T + 273)} \times (PP - VP)^2 \times V \tag{2.4}$$

where PP is process pressure; V is volume of the chemical, m^3; T is temperature, ^{o}C and VP is vapour pressure, kPa.

These mathematical definitions for the energy scores are derived from well-tried and tested thermodynamics expression models for isentropic expansion of pressurised gases and liquids, transport phenomena, heat transfer and fluid dynamics (Management of Process Hazards, 1990; Green Book, 1992; Lees, 1997; Scheffler, 1994; Fire and Explosion Guidelines, 1994; Crowl and Louvar, 2002).

Besides the above factors, the energy factor, F4 is incorporated in units involving chemical reactions to represent energy released due to runaway reactions. This factor is estimated as:

$$F_4 = M \times \frac{H_{rxn}}{K} \tag{2.5}$$

where H_{rxn} is heat of reaction, kJ/kg; M and K are as defined in Equation 2.2.

Other than these four energy factors, penalties have been assigned to account for the impact of various parameters on the total damage potential. For example, the penalties considered for process units involving chemical reaction such as reactor are described here.

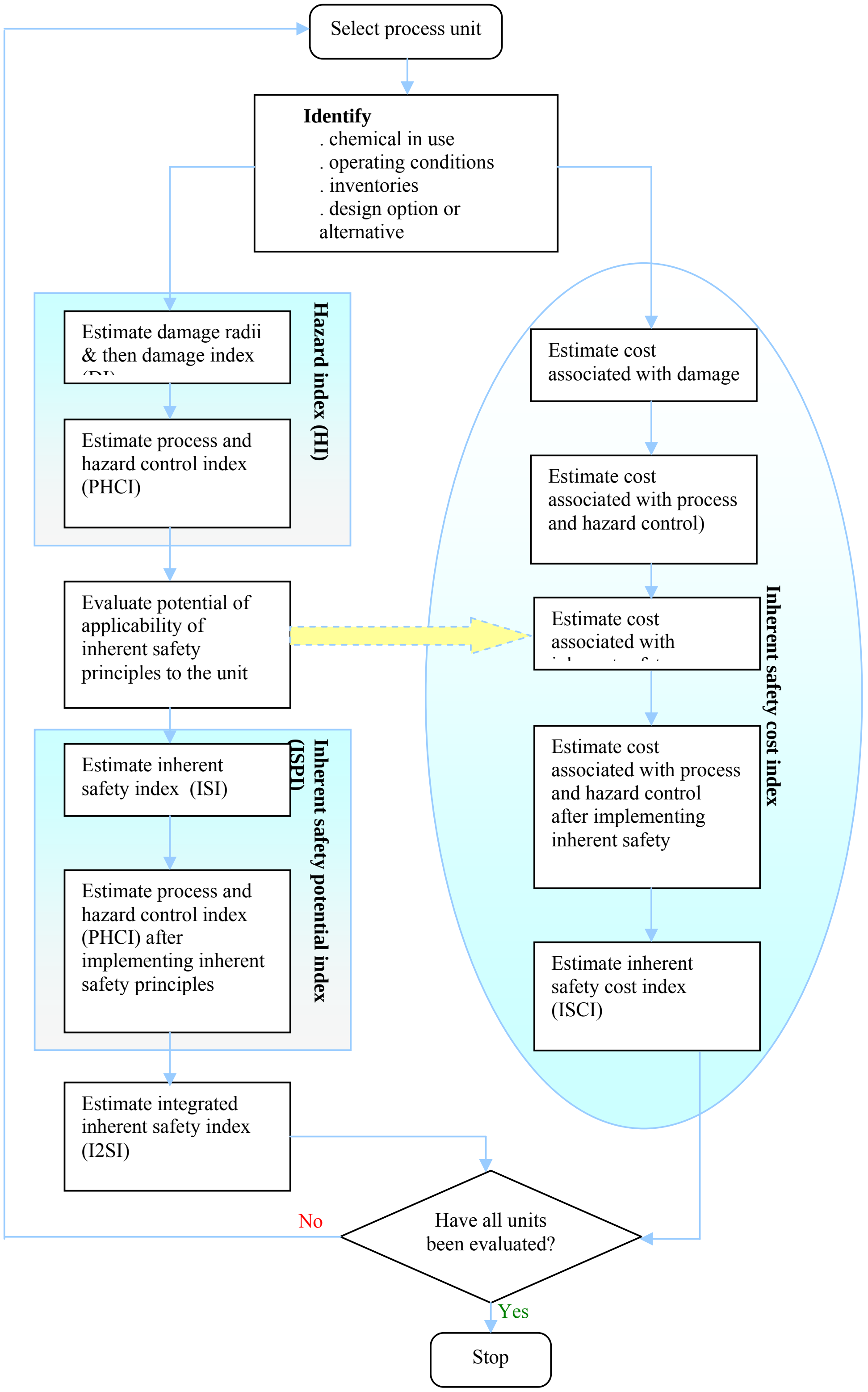


Figure 2.8: I2SI Framework (Khan and Amyotte, 2005)

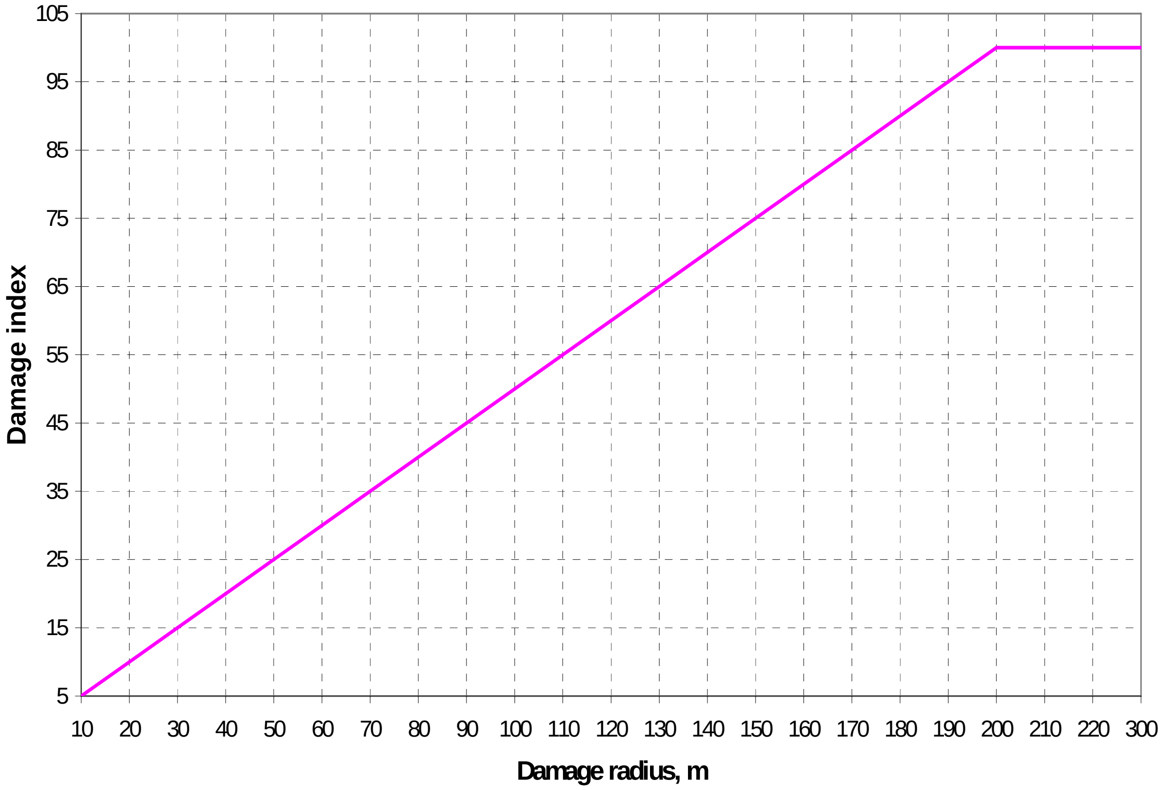


Figure 2.9a: Damage index (DI) graph for fire and explosion.

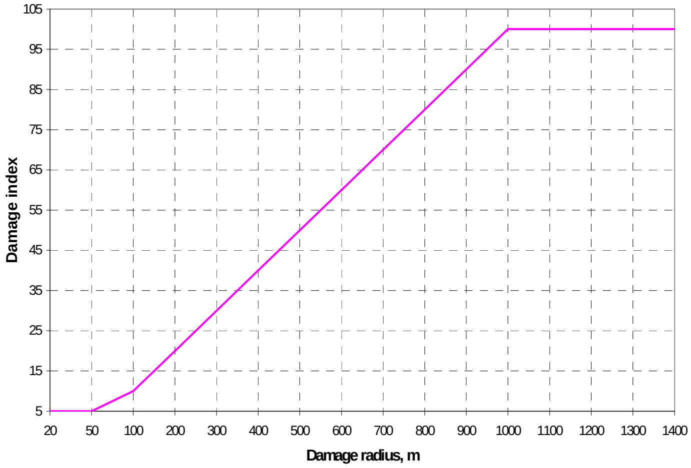


Figure 2.9b: Damage index (DI) graph for acute toxicity.

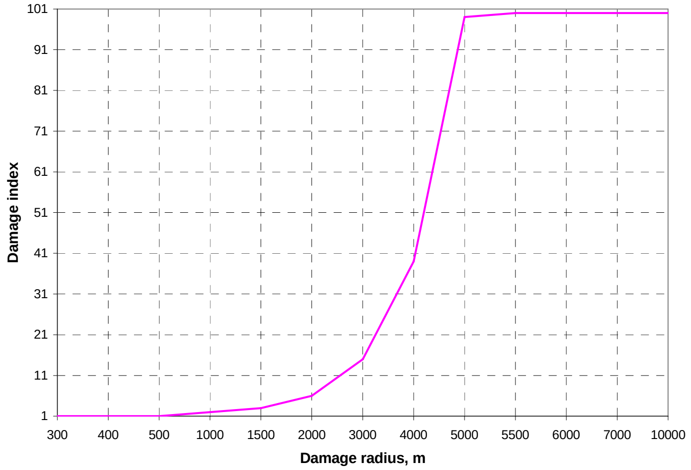


Figure 2.9c: Damage index (DI) graph for chronic toxicity.

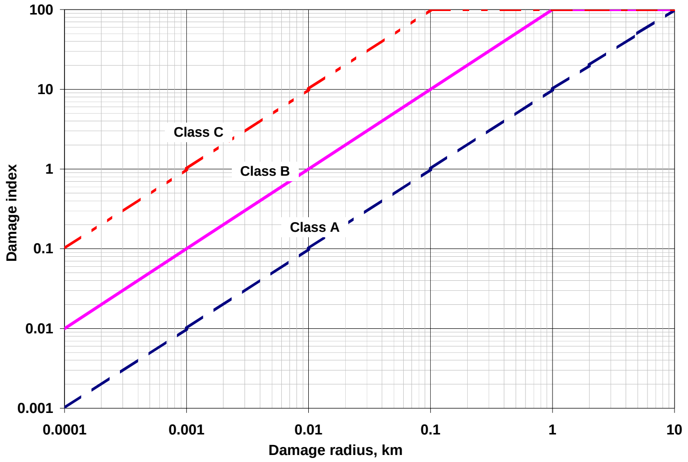


Figure 2.10a: Damage index (DI) graph for air pollution

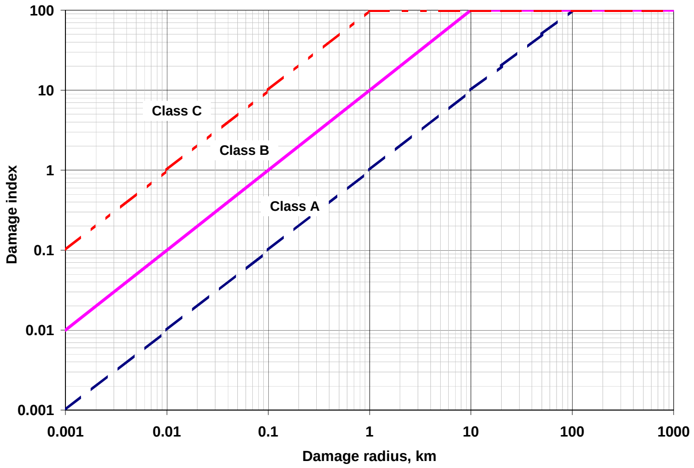


Figure 2.10b: Damage index (DI) graph for water pollution

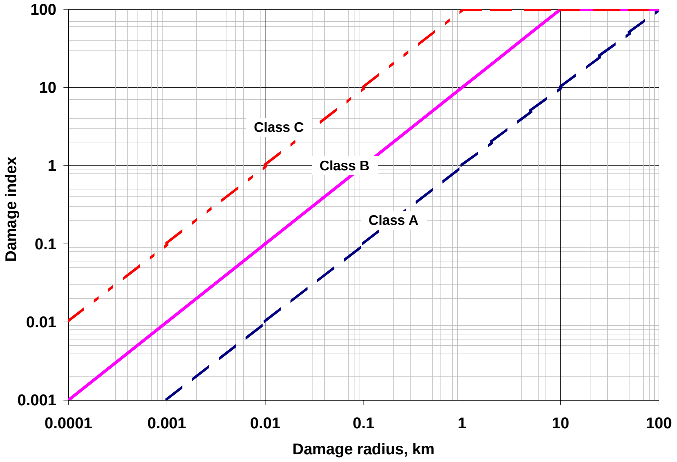


Figure 2.10c: Damage index (DI) graph for soil pollution.

The impact of temperatures is measured as pn_1 by considering the flash point, the fire point and the operating temperature of the unit. This penalty is derived by comparing the operating temperature with the limiting condition proposed by API-RP750M (API, 1990) and National Fire Protection Agency (NFPA) (Identification of Hazardous Material, 1989; Industrial Fire Hazards Handbook, 1990; Hazardous Materials Response Handbook 1992). The impact of pressure is quantified in terms of two energy factors F_2 and F_3 and one penalty, pn_2 to represent the operating pressure of the unit. The penalties for other criteria such as the quantity of chemical stored is pn_3, characteristics of the chemical is pn_4, location of the nearest hazardous unit is determined by pn_5, penalty due to the degree of congestion of the unit at the site is

pn_6, the effect of external factors such as earthquake and hurricane is pn_7, vulnerability is pn_8, type of reaction is pn_9 and potential of decomposition or side reaction is pn_{10}. The detail formulation of each penalty is available elsewhere (Khan et al., 2001).

2.4.4 Risk-based Methodology

As mentioned earlier, one common tool to assess risk in lifecycle of chemical process is QRA, which requires highly extensive information and suitable to be used during detailed design stage. Moreover, the element in probability occurrence of consequences in QRA required substantial information on frequency of failure based on previous history and statistical database of the equipment. This information is barely available for new design or new technology such as reactive distillation and intensified reactor.

For this reason, there were few attempts made at developing risk analysis tool specifically to evaluate inherently safer design alternatives during early design stage such as Rapid Risk Analysis Based Design (RRABD) proposed by Khan and Abbasi (1998). This tool utilised accident scenario generation, consequence analysis to estimate potential damage, estimation of domino effects and risk factors in asset loss and fatalities. The risk obtained from this tool is based on the conventional risk of QRA concept by determining the risk of fatalities using the principle of As Low As Reasonably Practicable (ALARP). The same principle is applied by Shariff and Leong (2009) in developing the Inherent Risk Assessment (IRA) method. Thus, the same difficulties are observed in the above tools when QRA is implemented at early design stage. There is also a study on assessment method using risk-based approach to assess thermal risk of chemical reaction developed by Stoessel (2002). The focus of this method is to provide guidance by using checklist questions and criticality of the thermal risk in order to determine the choice of safety measures. However, the method does not entirely concentrate on the evaluation of ISD concept and potential of conflict in the alternatives.

2.5 Limitations of the conventional safety analysis tools

According to studies done by Tixier et. al. (2002), currently, there are more than 62 methodologies developed to undertake safety analysis. These large numbers of methodologies implies that there are safety problems that cannot be analysed completely by the present available methodologies (Gentile, 2004). They classified the methods into qualitative and quantitative ones and analysed the relationships between the methodologies, input data and the results delivered. They concluded that there is not a single general method to deal with the problems of industrial risks. Tixier et al. (2002) also find that the analysts need to apply several methods to get better understanding of the risk. In order to get meaningful risk reduction strategies, the user needs experience, expert knowledge and high commitment from multi-background of expertises. The complex requirement in the present tools could cause an ineffective cost-saving and time consuming. Thus, this becomes obstacle for the management to conduct a thorough safety studies on their processes instead, the analysis is performed for the sake of meeting the minimum regulations requirement.

Among the obvious limitations in the conventional safety tools is the identified design solution always lead to the addition of passive, active or procedural strategies such as safety protection systems rather than eliminating the hazards at source. The inherent strategies are often not been captured due to the missing link with the ISD concept in the conventional tools, hence, separate review is required. For example, HAZOP is a systematic method that best applied during detail engineering design when process flow and instrumentation design has been completed. At this point, majority of the identified control measures are focusing on operational problems to mitigate the identified hazards. Thus, the hazard may still be present and safety depends on the reliability of the protective barriers, which cause other disadvantages such as high installation and maintenance costs (Lutz, 1997).

Another obvious restriction of the conventional tools especially QRA tools is the element in estimating the occurrence of consequences by probability models which requires substantial information to estimate frequency of failure based from previous history and statistical database. This requirement sometimes creates uncertainty especially for new equipment. The probability of failure for new design or new technology such as reactive distillation, intensified reactor or ionic liquids could not be estimated since they are yet to be commercialised and not in operating phase. Moreover, some failure frequency data are difficult to obtain especially for multi-purpose batch process plants such as pharmaceutical process due to the varying operating of the equipment from one process to another. QRA tools are also not suitable to be applied during process development due to lack of detailed information and knowledge of control instruments (Stoessel, 2008). Although the hazards and design solutions can sometimes be identified, QRA tools also required subjective judgement and can only provide partial idea on safety present in a facility (Leong, 2008). The identified options are still appended to end-users' knowledge and expertise judgement thus, the inherent strategies may not be fully considered in the decision. The outcomes from QRA can result in process design modifications, which may not reasonably economical to be executed due to project time constraints and cost factors. This is the reason why most of the resulting risk is to accept the hazards by adding safety mitigation devices and other barriers to manage those hazards, where these safety measures itself are prone to failure through time and due to human errors. This approach alone, as stated by Zwetsloot and Ashford (1999), is unable to avoid or reduce the risk of serious chemical accidents.

In conclusion, the present conventional safety analysis tools are effective to analyse safety if they are applied appropriately following to the main objective of their development. Furthermore, some of the tools would be able to analyse safety better than the others. However, the obvious loop holes in most of the tools are their capabilities in analysing inherent safety and evaluating the inherent risk reduction strategies particularly the safety conflicts are restricted. The constraints are mainly due to the substantial data requirement and not integrated with the ISD concept in a single tool. A separate tool is commonly required to achieve the above objective. This becomes the main motivation for the present research to develop a systematic safety analysis that is able to suggest design solutions that could eliminate or minimise the hazards rather than control it such as ISD concept. Although there are also many researches currently in progress towards the above objectives as reviewed in section 2.2, ISD concept is still not a routine in CPI. The limiting factors of the present Inherent Safety tools are discussed in the following section.

2.6 Limitations of the present Inherent Safety tools

There are tremendous efforts being made to inculcate ISD concept in CPI through development of useable Inherent Safety tools and techniques. From the observation made as in section 2.4, the evaluation of inherent safety by quantitative indexing approach has been widely explored in finding the suitable approach to assess inherent safety of a process. However, some of the tools are highly relied on subjective judgements such as previous experience and expert knowledge in the development of scoring process. The reason is commonly due to insufficient information available at the early stage of process design. In spite of this, the quantitative methods developed were still at their research stage and have not been used routinely in industry. There is, as yet, little data that relates the application of these indices to CPI (CCPS, 2008) due to several factors that restrict the application of the quantitative tools. Therefore, qualitative guidelines or procedures are still one of the substantial alternatives to CPI which would be sufficient to prevent and reduce the hazards at early stage of process design. However, the current qualitative tools that integrate ISD concept as discussed in section 2.4.1 are not yet mature and applied infrequently in the process design. Thus, in the next section, the factors that limiting the utilisation of the qualitative tools are discussed which indirectly lead to the development of new methodology that integrate ISD concept to enhance decision making during design process.

2.6.1 Constraint factors in Qualitative Inherent Safety tools

The presented checklists and tools which implement the ISD concept as a guidance to prevent and minimise the hazards in section 2.4.1 are too generic and highly dependent to end-users' experience and judgement. The inherent safety checklists may not allow for innovation and the analysis could be incomplete because the checklists itself is developed based on past experience (Palaniappan et al., 2002). The checklist questions must be developed and covered every detail area of the process in order to consider ISD concept and inherent strategies. In addition, the checklists have to be developed specifically for each design stage since different stage involves different set of process and criteria of hazards. The available qualitative tools for inherent safety are also not supported with decision making process to unravel any conflicts existence in design alternatives. The restriction in these qualitative methods which require tedious and time consuming manual work is not welcomed by end-users, who usually work under project time and cost constraints. Due to that matter, improvement of the current qualitative methods to incorporate ISD concept in simple and step-wise manner should be continued.

2.6.2 Constraint factors in Quantitative Inherent Safety Tools

It is obvious from the literatures that many Inherent Safety tools are focused on quantitative method to evaluate inherent safety characteristics in the studied process by applying indexing based approach. Some of the Inherent Safety tools are developed to achieve different set of objectives and use diverse methods. The designers need to understand the objectives, strengths and weaknesses of the method employed. Most of the attempts made are focused on the evaluation of Inherent Safety characteristics during process route and process design synthesis in identifying the inherently safer process chemistry. Thus, the main purpose of the available tools is to rank the existing route alternatives without having the opportunities to innovate better ISD options. Although the present Inherent Safety tools could be used to reduce the potential risk of accidents and is economically attractive to CPI to some extents, for example the Inherent Safety tools that utilised consequence-based approach, they also suffered from trade-offs on the resulted design alternatives. The design which identified to be inherently safer from one hazard could change the magnitude of other hazards that was not previously at critical level. The available tools were not able to evaluate the conflicts of hazards in the design alternatives effectively. This issue is related to the problems mentioned in Chapter 1 on the constraints of application of Inherent Safety principles in CPI.

Therefore, the existing inherent safety tools are not apparent to measure the above conflicts or trade-offs which are essential to assist in decision making. However, there are efforts to develop decision making tools to resolve some of the conflicts in particularly the conflicts in between inherent safety and environment. Several literatures such as Palaniappan et al. (2002) have developed a decision making tool to evaluate design alternative for synergies and trade-offs between inherently safer options and waste minimisation options. Allen and Rosselot (1997) also proposed a method to analyse waste minimisation alternatives that could have impacts on safety and health using weighing-based. Preston and Hawksley (1997) proposed a ‘target diagram’ that analyse conflict between safety, health and environment. Although the above tools could help in analysing the conflicts between inherent safety and environment, the other trade-offs associated with design modification as mentioned in Chapter 1 are also equally important to be analysed through understanding the process design features and problems related to decision variables in order to avoid inconsistencies across the projects (Cano Ruiz and McRae, 1998). It is also to ensure hazards are identified and prevented as early as possible in order to avoid and reduce risk of potential accidents throughout the chemical process lifecycle.

2.7 Concluding remarks

Despite of the above efforts, there remains the need to develop a design evaluation that is able to identify and assess inherent hazards associated with ISD options at early stage of design since this is the ideal time to minimise hazards with less cost and time. Besides, this study is aimed at developing a method which combines these two different activities i.e. generating inherently safer design alternatives and undertaking risk analysis as a part of the risk management procedure at early lifecycle of process plant. Apart from that, the present research also attempts to integrate qualitative and quantitative techniques to allow comprehensive safety analysis to be performed in a single framework. In the next section, several aspects considered in developing the new methodology are explained which takes into accounts some points and findings from literatures to further enhance the Inherent Safety analysis.

2.7.1 Aspects to consider in developing a Qualitative Methodology

Several researchers highlighted the importance of incorporating ISD concept at hazard review stage as one way to produce the inherent strategies. Moore (1999) pointed out the lack of standardised approaches to commonly applied process hazard studies and a failure to include Inherent Safety during process hazard review. He also suggested a hierarchy of Inherent Safety that could be suitable to be used during process hazard review. Kletz (1999) also stated that there is a lack of investigative tool, similar to HAZOP, for examining designs and uncovering ways of introducing intensified and other ISD options. He also discussed a possibility of modifying HAZOP method to be applied at early stage of process design for the purpose of generating potential ISD options. Bollinger et al. (1996) described in detail the Inherent Safety review method including the preparation to review, methods and tools and also the Inherent Safety strategies for the lifecycle of process. Preston and Hawskley (1997) suggested the application of checklists and guidewords for systematic consideration of health, safety and environment aspects during process design. Mansfield and Cassidy (1994) also suggested the use of structured brainstorming, guideword based HAZOP style examination of process at the early design stages, checklists and Inherent Safety index for performing safety, health and environment analysis. One example on the modification of HAZOP concept is illustrated by Mosley et al. (2000) to identify reactive chemical hazards during process development stage because HAZOP and its thought process are proven to be generalised enough to be applied at any design stage. Thus, based on the above literatures, it is shown that inherent strategies can be generated qualitatively by maximising the ISD concept during hazard review stage. In this way, one not only be able to understand the hazards involved in the process but also enable the identification of possible inherent solutions to eliminate or reduce the hazards.

By taking into account of the several limitations to incorporate ISD concept at early stage of design such as constraints in getting technical details, process information and time restriction, the present research attempts to develop an ISD methodology based on qualitative approach as this approach is far more easily accepted and it is proven through the success of HAZOP method. Thus, the qualitative method is developed in step-wise procedure which integrates the hazard analysis with the heuristics of ISD concept with the objective specifically to identify inherent hazards in the process as early as possible. In addition, the qualitative tool also should be able to generate ISD alternatives to resolve the hazards including capable in choosing the best ISD alternatives using several guidelines and guidewords to provide a simple and systematic technique in the methodology.

2.7.2 Approach and conflicts analysis in a Quantitative Methodology

The constraints on the available quantitative Inherent Safety tools in the literature merely focused on “single” or one-way evaluation of Inherent Safety characteristics and hazard magnitude within the process unit only and less focus on the “interaction” of potential hazards being transferred to the surrounding of the process unit when changes are made in the design. The “single framework” also denotes that the evaluation made is to compare between design options that could only minimise one hazard, which indirectly influenced the selection of dominance parameters in the overall score of the design option. While the “interaction framework” proposed a comparison between design options through evaluating the possibility of occurrence of other hazards from design modification to the surrounding of the studied process unit. It can be further explained through example given by Hendershot (2006) that a plant might reduce the size of a hazardous material storage tank, thereby reducing inventory and site risk. Use of smaller tanks, however, may require a change in how material is shipped to the plant from railroad tank cars (typically about 300,000 pound shipments for many materials) to trucks (typically about 30,000 pound shipments) because the smaller tank cannot contain more than a truck load of material. Now, the plant will receive 10 times as many shipments, and they will come by road rather than by rail. Depending on the particular location, road shipments may be inherently more hazardous. Even though the site risk is reduced, the overall risk to society may actually be increased.

As mentioned above, most of the previous works used a hazard-based approach to evaluate the Inherent Safety characteristics of different process options. This approach can generally indicate which option is relatively inherently safer, however, it may ignore the possibility of hazard transferred to other processes and its surroundings and new hazard could be difficult to control. Often when design is modified, there are possibilities of other hazards being introduced and increased the magnitude of the present hazards, which earlier are less critical. Therefore, a hazard-based method may not be the ultimate decision making tool to select the best ISD options as the likelihood of hazard being transferred due to design modification not fully captured in this approach. To overcome this limitation, a risk-based approach is proposed in this thesis to evaluate inherently safer process design alternatives. This approach is more sensible to facilitate the designers for realistic and effective decision-making in diverse likelihood of design scenarios. The proposed risk-based method is not fully following the conventional QRA approach but to expand the probability concept by evaluating the likelihood of hazard being transferred within the process rather than to put focused only on the failure of the associated equipment which perceptibly impractical to be done at preliminary design stage.

CHAPTER 3

INTEGRATED INHERENTLY SAFER DESIGN EVALUATION TOOL (IISDET) FRAMEWORK

3.1 Chapter Overview

In this chapter, related theories and methods used as the platform to support development of the framework are described. The discussion includes the modification made to suit the developed framework. Next, introduction to IISDET framework will be provided. The description includes the mechanism used, advantages and outputs expected from each developed sub-tool in IISDET.

3.2 TRIZ Theory

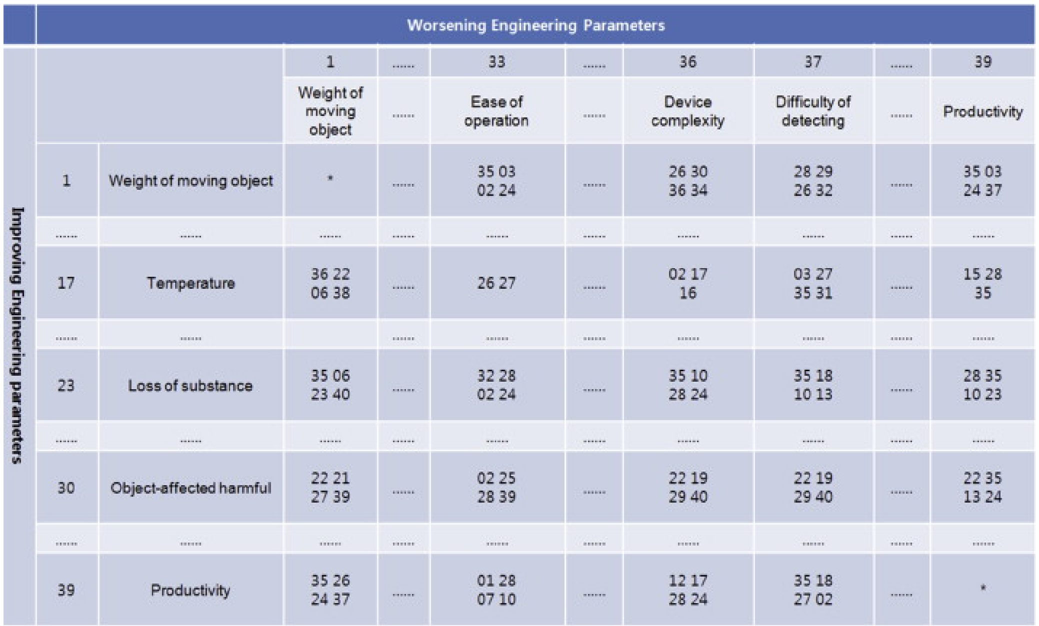
Common creative tools have been limited to brainstorming and other related methods such as HAZOP, What If Checklist, FMEA etc. which depend on intuition and the knowledge of the members of the team in order to identify the solution to problem in any kind of projects. These methods are typically described as psychologically based and having unpredictable and unrepeatable results. Thus, TRIZ, a Russian acronym for "The Theory of Inventive Problem Solving" has been introduced by Genrich Altshuller and his colleagues between 1964 and 1985 to generate innovative ideas and solutions for problem solving which at present, this tool has been expanded and applied to engineering field including the chemical engineering discipline. Many Fortune 500 companies such as BAE Systems, CSC, Procter & Gamble, Ford Motor Company, Boeing, Philips Semiconductors, Samsung, LG Electronics, and many others have used TRIZ concepts to systematically solve complex technical and organizational problems (Kim et al., 2009). There were several research efforts utilising TRIZ concept to analyse safety such as Srinivasan and Kraslawski (2006) who illustrated TRIZ by modifying the concept to solve problems related to safetyaspects specifically for inherently safer chemical processes. Kim et al. (2009) also proposed a modified TRIZ for the purpose of evaluating safety for retrofit design of chemical process.

According to Van Scyoc (2008), the origin of TRIZ theory is based on the study of the patterns of problems and solutions. There are more than three million patents analysed to discover the patterns that predict the breakthrough solutions to problems. The fundamental concept of TRIZ adopted from studying the patterns is that contradictions should be eliminated as the solutions. TRIZ recognised two type of contradictions, firstly, technical contradictions as the classical engineering trade-offs, for example, the product gets stronger (good) but the weight increases (bad). The second type of contradiction is physical contradictions, for example, software should be complex to have many features but should be simple to be easy to learn. For this reason, the Altshuller's study has found 40 principles that have been repeatedly used as the solutions to many general contradictions across many fields. These principles are then mapped in a contradiction matrix as shown in Table 3.1 by pairing the principles to analyse potential characteristics that are worsening and improving. Then, a list of possible inventive principles is identified based on the pattern analysis made earlier to solve this matrix. This concept shows that TRIZ is a method to solve problems based on logic and data to accelerate the ability to solve problems creatively rather than relying on intuition as commonly done through other conventional creativity tools.

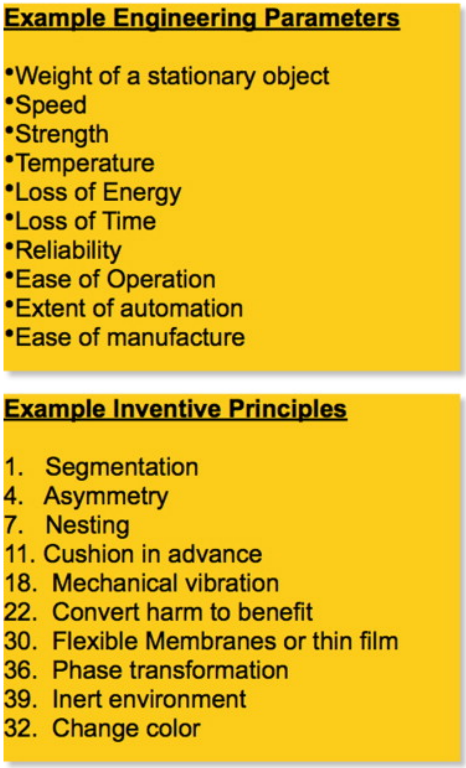
Van Scyoc (2008) summarised the general steps to apply TRIZ as the following (as shown in Figure 3.2):

- Capability to define a problem in technical terms recognising that resolution of one problem may introduce another (e.g. higher operating temperature/pressure may increase production but also may affect the potential for corrosion or cracking in pressure equipment)

Table 3.1: Excerpt of the TRIZ contradiction matrix (Kim et al., 2009)



			Worsening Engineering Parameters							
Improving Engineering parameters			1	......	33	......	36	37	......	39
			Weight of moving object	......	Ease of operation	......	Device complexity	Difficulty of detecting	......	Productivity
	1	Weight of moving object	*	......	35 03 02 24	......	26 30 36 34	28 29 26 32	......	35 03 24 37
	......	......	......	......	......	......	......	......	......	......
	17	Temperature	36 22 06 38	......	26 27	......	02 17 16	03 27 35 31	......	15 28 35
	......	......		......	......	......	......	......	......	......
	23	Loss of substance	35 06 23 40	......	32 28 02 24	......	35 10 28 24	35 18 10 13	......	28 35 10 23
	......	......	......	......	......	......	......	......	......	......
	30	Object-affected harmful	22 21 27 39	......	02 25 28 39	......	22 19 29 40	22 19 29 40	......	22 35 13 24
	......	......	......	......	......	......	......	......	......	......
	39	Productivity	35 26 24 37	......	01 28 07 10	......	12 17 28 24	35 18 27 02	......	*



Example Engineering Parameters

- Weight of a stationary object
- Speed
- Strength
- Temperature
- Loss of Energy
- Loss of Time
- Reliability
- Ease of Operation
- Extent of automation
- Ease of manufacture

Example Inventive Principles

1. Segmentation
4. Asymmetry
7. Nesting
11. Cushion in advance
18. Mechanical vibration
22. Convert harm to benefit
30. Flexible Membranes or thin film
36. Phase transformation
39. Inert environment
32. Change color

Figure 3.1: Examples of 39 engineering parameters and 40 inventive principles developed by Altshuller (Van Scyoc, 2008)

- Once the problem is defined, technical attributes of the problem and the possible secondary effects are represented in terms of the 39 engineering parameters. This important step is crucial for successful TRIZ application. It requires some knowledge of cause and effect to correctly pair the "improving" feature to the "worsening" feature

- The contradictions table then provides a link to a selection of inventive principles (by number) that might be considered in the solution. By thoughtful consideration of the inventive principles shown the ideal solution may be discovered.

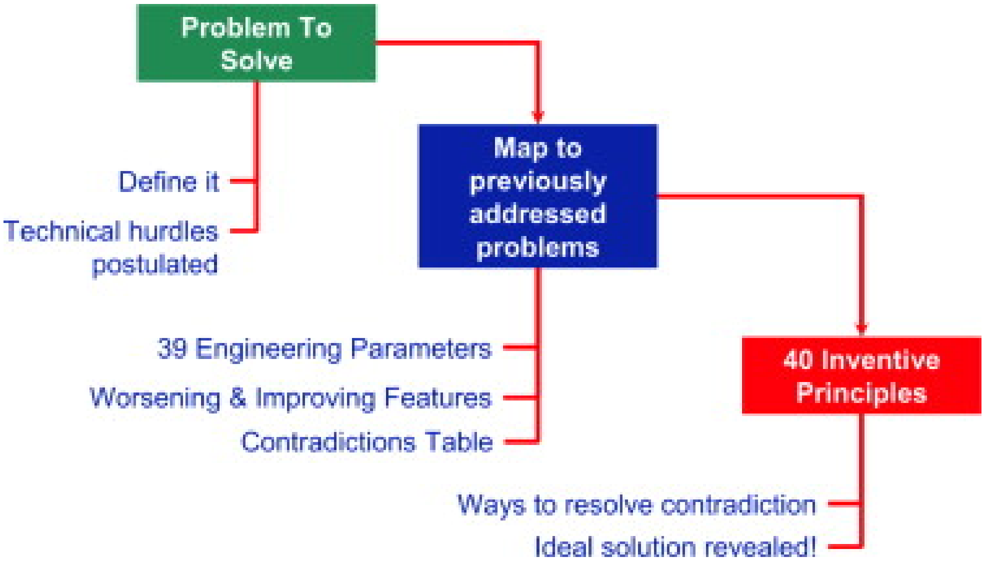


Figure 3.2: TRIZ process summary (Van Scyoc, 2008)

However, this classical TRIZ method is difficult to assess safety aspects due to the inapplicability and ambiguity of the terminology in classification of its parameters (Kim et al., 2009). TRIZ concept is thus modified to suit with the objective of this research to evaluate inherent safety conflicts of design alternatives in order to achieve process design that is AiSAP. This method is applied particularly during the evaluation stage as described in the section 4.4.4 to identify potential conflicts from the ISD options either positive (i.e. improving) or negative (i.e. worsening) through the application of the Inherent Safety principles. In addition, this modified TRIZ would assist in determining the alternative that has minimum potential of hazard and risk transfer due to hazard conflicts.

3.3 Predictive Failure Analysis (PFA)

PFA earlier known as Anticipatory Failure Determination is the inverse of TRIZ concept introduced by Zlotin in early 1970’s which is useful for failure analysis and prediction. The method utilised the traditional TRIZ problem solving algorithm in an inverted fashion. The missing link in the traditional TRIZ is the capability to identify all possible root causes to the problem. Therefore, PFA is another inventive thinking way of using TRIZ theory to identify root cause of the failure in reverse mode. The concept applied is entirely different from the conventional preliminary hazard review such as HAZOP and What-if Analysis because the latter methods commonly applied problem solving that focused on the problem itself without venturing its possibility outside of the box. However, PFA differs from the conventional analysis in perspective from which potential failures are determined. PFA is achieved via a core 3-step model to provide extraordinary effectiveness without any presumptions Hipple, J. (2002):

Step I: Invert the Problem
For Failure Analysis: Instead of asking “Why did the failure happen?” ask instead: “How can I make it happen?”
For Failure Prediction: Instead of asking “What failures might happen?” ask instead: “How can I make all possible dangerous or harmful failures happen?”

Step II: Identify Failure Hypotheses
Find a method by which the known or potential failures can be intentionally produced

Step III: Utilise Resources
Determine if all the components necessary to realise each hypothesis are available in the system or it can be derived from what is available, for example, are the required substances and materials present?, is the necessary energy available or produce?, etc.

The innovative questioning technique allows meticulously pro-active questions in different quadrant of human brains to trigger the source of hazards rather than putting high energy to what is already known and anticipated. Thus, PFA concept is used in the present research to facilitate the identification of inherent hazards from a process unit rather than cause of failure as described in Chapter 4. The PFA is renamed as the Predictive Inherent Hazard Analysis (PIHA) to suit the above objective. Table 3.2 shows an example of PIHA algorithm to interrogate the inherent hazards that would cause thermal runaway in a batch reactor.

Table 3.2: Example of PIHA Algorithm

Step i: Ideal State	We want no thermal runaway reaction in the nitration of toluene
Step ii: Inverse Ideal State	We want a thermal runaway reaction to occur in the nitration of toluene
Step iii: Exaggerate	We want to generate the reaction heat and release it in the process and cause severe injury, fatality and damage
Step iv: Find resources	How to accomplish this? What intrinsic resources are required?

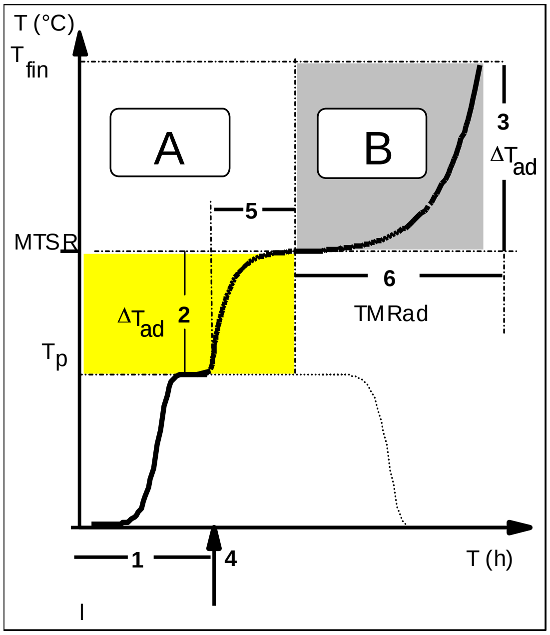
3.4 Theories and methods for fire and explosion hazards

Fire or combustion is a chemical reaction in which a substance reacts with oxygen and release significant amount of heat. Usually fire occurs when a source of heat comes into contact with a combustible material. There are three conditions essential for a fire; namely fuel, oxygen and heat. If one of the conditions is missing, fire will not occur and if one of them is removed, fire will be extinguished (Lees, 1996). The major difference between fire and explosion, according to Crowl and Louvar (2001), is the rate of energy release. Thus, an explosion is defined as a release of energy that causes a blast which then causes a transient change in the gas density, pressure and velocity of the air surrounding the explosion point (CCPS, 1994). The material that is involved in explosion is converted into high-pressure gas at high temperatures and a rapidly expanding shock front. In general, fire releases energy slowly whereas explosion releases energy rapidly typically on the order of microseconds. Fire can results from explosion and explosion can also results from fire. Regardless of the above variation, it is important to recognise fire and explosion hazards as early as possible to ensure the risk of accidents to occur could be minimise as low as possible.

Flammable, toxic and vapour clouds could be formed via release from process unit by any means. Some of the common causes of release from the process unit are leakage, overpressure, uncontrolled reactions, corrosion, human failure, auxiliary failure etc. One important way to eliminate or minimise hazard is through changing process design using the Inherent Safety principles where required which then lead to a more ISD option. Although the ISD option could be inherently safer in reducing the target hazard, it could also introduce new hazard in the process unit or other related process units. Thus, it is essential to evaluate the likelihood of conflicts in the design and it is inherently safer enough from these fire and explosion hazards by analysing the inherent properties of the substances and process unit conditions in very early development stage particularly during design stage. The evaluation can be achieved by better understanding of the fundamentals in fire and explosion hazards. One of the potential fire and explosion hazards considered in this research is the inherent hazards to cause thermal runaway. For that matter, the analysis to predict the likelihood of conflict in fire and explosion hazards in this research is done by examining potential hazards from two major causes of fire and explosion; potential hazards transfer from uncontrolled chemical reaction or better known as runaway reaction and the next category is potential hazard transfer by other than chemical reaction hazards such as overpressure due to physical hazards. Thus, in this research, several theories are applied to assess potential of hazards in the context of conflicts that could arise in the design which is triggered through Inherent Safety Principles. This is represented in the estimation of Likelihood Index of Hazard Migrate (LIHM) as described in subsection 3.7.3.2 of this chapter.

3.4.1 Methods to estimate thermal runaway characteristics

An exothermic reaction can leads to a thermal runaway situation which begins when the heat produced by the reaction exceeds the rate of heat removal from the system. The surplus heat raises the temperature of the reaction mass which causes the rate of reaction to increase. This in turn accelerates the rate of heat production. Thermal runaway can occur because when the temperature increases, the rate at which heat is removed (increases linearly) is insufficient compared to the rate at which it is produced (increases exponentially). Once control of the reaction is lost, temperature can rise rapidly leaving little time for correction. The reaction vessel may be at risk from over-pressurisation due to violent boiling or rapid gas generation. The escalating temperatures may initiate a secondary but more hazardous thermal runaways or decompositions. Figure 3.3 provides the graphical illustration of thermal runaway as functions of heat, temperature and time that commonly occurred in an exothermic batch reactor (Stoessel, 2008). This figure shows the potential of runaway when a cooling failure occurs (point 4) while the reactor is at the reaction temperature. If at this instant, the unconverted material is still present in the reactor, the temperature will continue to increase due to the completion of the reaction. The increment of temperature will be proportional to the amount of the non reacted material. As the temperature reached at the end of period 5, a secondary decomposition reaction may be initiated. The heat produced by this reaction may lead to a further increase in temperature (period 6). The runaway scenario is further explained in this section.



A	desired reaction
B	decomposition reaction
1	normal process
2	ΔT_{ad} (desired reaction)
3	ΔT_{ad} (decomposition reaction)
4	cooling failure
5	time taken to reach the Maximal Temperature of the Synthesis Reaction (MTSR)
6	Time to Maximum Rate at adiabatic condition (TMR_{ad})

Figure 3.3: Runaway scenario (Stoessel, 2008)

A study conducted by the Chemical Safety Hazard Investigation Board (CSB) found that over a 20-year period, US chemical companies had 167 serious reactive accidents killing 108 workers and injuring hundreds of people. They concluded that reactive chemicals present a significant safety problem for the CPI (Melhem, 2004). These accidents are not only happening in reactors but also in other type of process units such as storages, pressure vessels etc. Figure 3.4 shows the incident statistics involving reactive hazards.

Therefore, it is crucial to assess the potential of runaway reactions as early as possible during the development of a process where the assessment should be sufficient to identify the potential hazards and to investigate their causes. It is well known that detail evaluation of thermal reactivity requires substantial information of all the thermodynamic and kinetic parameters including onset temperature, adiabatic time to maximum rate etc. This detail analysis is time consuming and therefore, preliminary screening method is essential at early design stage since the above information may not be available. For thermal runaway, the present research applied several process factors that are related to temperature and pressure effects as described below.

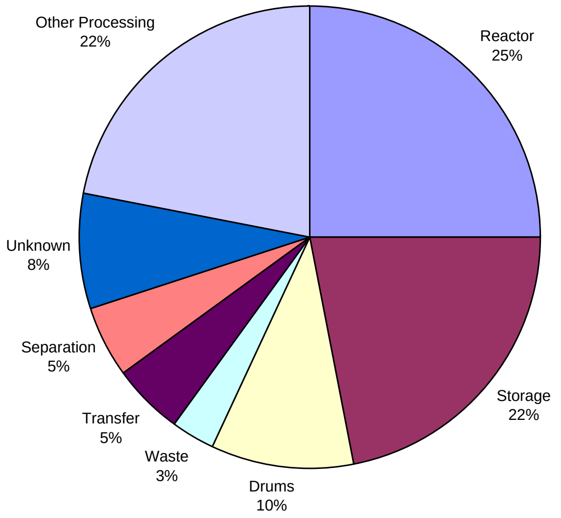


Figure 3.4: Recent incident statistics involving reactive chemicals based on CSB study from 1980-2001 (Murphy, 2002)

For temperature effects, Stoessel (2008) described that the energy of a reaction or decomposition is directly linked with severity that is the potential of destruction of a runaway. Where a reactive system cannot exchange energy with its surroundings, adiabatic conditions prevail. In such as case, the whole energy released by the reaction is used to increase the system's temperature. Thus, the temperature rise is proportional to the energy released and the adiabatic temperature rise is a more commonly used criteria to assess the severity of a runaway reaction. It can be calculated by dividing the energy of reaction by the specific heat capacity as shown in Equation 3.1:

$$\Delta T_{ad} = \frac{(-\Delta H_r)C_{A0}}{\rho c_p^{'}} = \frac{Q_r^{'}}{c_p^{'}} \tag{3.1}$$

where ΔT_{ad} is adiabatic temperature rise; ΔH_r is molar enthalpy; C_{A0} is reactant concentration; ρ is density; $c^{'}_{p}$ is specific heat capacity and $Q^{'}_{r}$ is specific heat reaction.

The adiabatic temperature rise is important in determination of the temperature levels. As a rule, high energy result in fast runaway or thermal explosion while lower energy (adiabatic rise less than 50K) result in slower temperature increase rates as shown in Figure 3.5, given in the same activation energy, the same initial heat release rate and starting temperature.

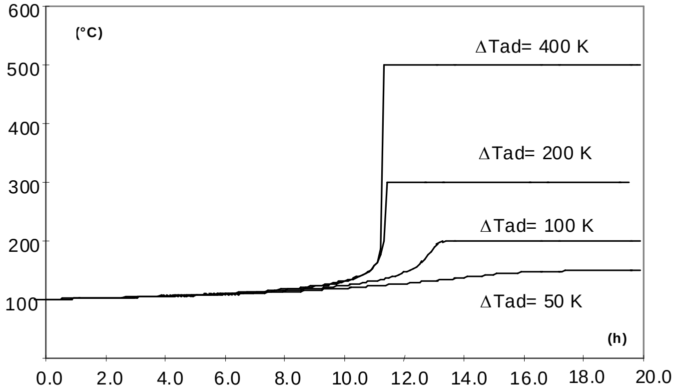


Figure 3.5: Adiabatic runaway curves with different adiabatic temperature rise (Stoessel, 2008)

Another process factor considered as temperature effect to indicate likelihood of hazard conflictss for thermal runaway is the time to maximum rate (TMR_{ad}) under adiabatic conditions. TMR_{ad} can be measured as the probability of triggering the runaway in terms of time-scale. Figure 3.6 illustrated the difference in runaway curves for two cases to represent the significant of TMR_{ad}. In case 1, after the temperature increase due to the main reaction, there is enough time left to take measures to regain control or recover a safe situation in comparable with case 2. Thus, Keller (1997) presented a screening procedure to estimate this parameter for a start temperature T_0 by assuming zeroth-order model reactions as shown in Equation 3.2:

$$TMR_{ad} = \frac{c'_p R T_0^2}{q(T_0) E_a} \tag{3.2}$$

where R is general gas constant, Jmol/K; q is heat release rate, W; T_0 is initial temperature, K and E_a is activation energy, J/mol.

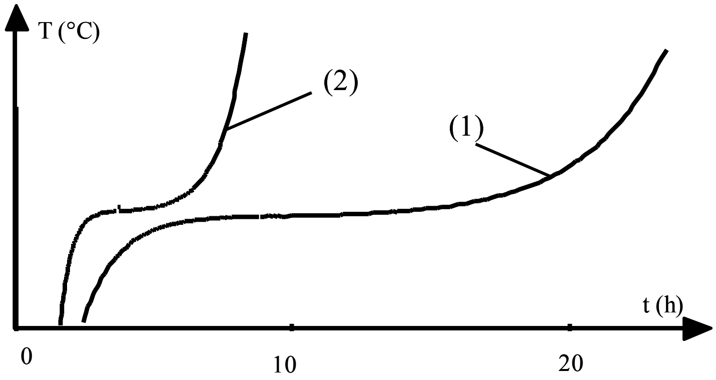


Figure 3.6: Time scale represents the TMR_{ad} (Keller, 1997)

In the case of unknown activation energy (E_a), as a rule of thumb, an activation energy as low as 50 kJ/mol can be taken for conservative screening purposes since the range of E_a is commonly in between 60 to 140 kJ/mol. The above estimation might be useful especially at the early stage of design however, when TMR_{ad} achieved is less than 8 hours, an experimental works could be done to obtain further results (Keller, 1997).

The destructive effect of a runaway reaction is always due to pressure. Pressure increases when the decomposition reaction occurred which often result in the production of small molecules which are gases or present of high vapour pressure. Thus, to assess the pressure effects, the process factors related to vapour pressure of the reaction mass can be estimated by the Clausius-Clapeyron law, which links the pressure to the temperature and the latent enthalpy of evaporation as illustrated in Equation 3.3:

$$\ln \frac{P}{P_0} = \frac{-\Delta H_v}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{3.3}$$

where P is pressure; P_0 is initial pressure; R is universal gas constant (8.314J/mol/K); ΔH_v is molar enthalpy of vaporisation (J/mol); T is process temperature; T_0 is initial temperature

Since vapour pressure increases exponentially with temperature, the effects of a temperature increase, for example due to uncontrolled reaction may be significant. As a rule of thumb, the vapour pressure doubles for every 20K increase in temperature.

The second process factor considered for pressure effects is the amount of solvent evaporated as this effect could form an explosive vapour cloud which in turn can lead to a severe explosion if ignited. Thus, the less amount of solvent evaporated would lead to an inherently safer design and this can be achieved when inherently safer condition is in place. Stoessel (2008) described, the amount of solvent evaporated can be estimated using the energy of reaction and/or decomposition as shown in Equation 3.4. In addition, the process factors could also be estimated from the “distance” to the boiling point since if this condition is reached, a fraction of the energy released is used to heat the reaction mass to the boiling point and the remaining fraction of the energy results in evaporation. Equation 3.4 provides the calculation as follows:

$$M_v = \frac{Q_r}{\Delta H_v^{'}} = \frac{M_r Q_r^{'}}{\Delta H_v^{'}} = \left(1 - \frac{T_b - T_0}{\Delta T_{ad}}\right)\frac{Q_r}{\Delta H_v^{'}} \tag{3.4}$$

where M_v is the amount of solvent evaporated; Q_r is the heat of reaction; ΔH_v is the specific enthalpy of evaporation; M_r is mass of reactant; T_b is the boiling point; T_0 is the initial temperature and ΔT_{ad} is the adiabatic temperature rise.

3.4.2 Methods to estimate flammable and explosive scenario

In the present research, the likelihood of design conflicts from fire and explosion due to flammability and explosive conditions is further supported by understanding the relationship of the effects of temperature in various flammability properties as shown in Figure 3.7. Among the important process safety factors that had been taken into account are the flash point and the limits of flammability.

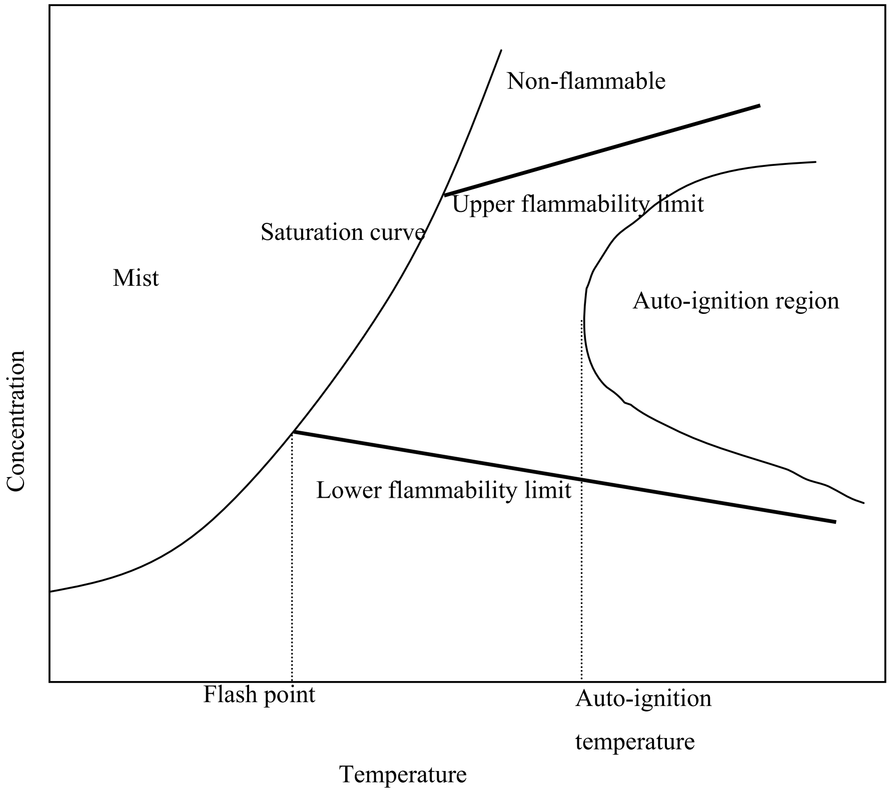


Figure 3.7: Relationships between various flammability properties (Crowl and Louvar, 2001)

Flash point is defined as the minimum temperature at which the vapour present over a liquid forms a flammable mixture when mixed with air. The flash point temperature is reached when a flame propagates from an ignition source through the vapour-air mixture (Gmehling and Rasmussen, 1982). Experimental flash point data of pure components are usually can be obtained from Material Safety Data Sheets (MSDS), the Society of Fire Protection Engineers (SPFE, 1995) and the Merc Index (1996). However, flash point data of liquid mixtures are scarce in the literatures although in reality, most of the chemicals handled in CPI are mixtures. Similar case is applied in the ISD option which would have to deal with mixtures and the potential conflicts that could arise in flash point value when the solvent is change. The behaviour of mixtures can be extremely different compared to the behaviour of the individual component and using the available methodologies for pure compounds to evaluate the risks can create uncertainty (Vidal et al., 2006). Therefore, a theoretical prediction method developed by Wickey and Chittenden (1963) is applied to estimate the flash point of the mixture. This method is selected due to its suitability as early screening tool in comparison with other methods which are more complex and require extensive data and information. The methodology is as follows:

- Calculate the flash point index:

$$\log_{10}(\mathrm{I}) = -6.1188 + \frac{2414}{\mathrm{T_f} + 230.56} \tag{3.5}$$

where T_f is the flash point of the pure component in °C.

- Determine the flash point index of the mixture:

$$\mathrm{I_{mix}} = \sum \phi_i \mathrm{I_i} \tag{3.6}$$

where I_{mix} is the index for the mixture and ϕ is the volume fraction of the components in the mixture.

- Determine the flash point temperature:

$$\mathrm{T_F} = \frac{2414}{6.1188 + \log_{10}(\mathrm{I_{mix}})} - 230.56 \tag{3.7}$$

where T_F is the flash point of mixture.

Flammability limit refers to the upper and lower concentrations which are normally expressed in volume% of a vapour in air that can be ignited by an ignition source. No ignition will take place when the concentration is above the upper limit or below the lower limit. The critical point between these two limits is the lower flammability limit because the temperature at this flammability limit would determine the possibility or likelihood of one process has reached its flammability condition. However, the lower flammability limit is different from flash point where flash point is reached when a flame propagates from ignition source such as external flame through the vapour-air mixture but lower flammability limit is essentially independent of the ignition source strength (Vidal et al., 2004 and Brandes et al., 2007). As a result, it can be concluded that the lower flammable limit always has lower value in comparison with the flash point. This result has been experimentally confirmed and therefore, operating at temperatures below the lower flammable limit gives sufficient safety (Brandes et al., 2007). Given the flammability limits of each of the components in a mixture, the estimation of the lower flammability limit of a mixture can be calculated by LeChatelier's rule (Le Chatelier, 1891). This method is well established and effective as screening tool. Equation 3.8 shows the method of calculation:

$$\mathrm{MLFL} = \frac{100}{\sum\left(\frac{\mathrm{C_i}}{\mathrm{LFL_i}}\right)} \tag{3.8}$$

where MLFL is the mixture lower flammability limit; C_i is the concentration of component i in the gas mixture on an air-free basis (vol%) and LFL_i is the lower flammability limit for component in the mixture (vol%).

Flammability range increases with temperature. In order to facilitate the estimation of the lower flammability limit of each component which depends on temperature, the following established empirical derived equation by Zabetakis et al. (1959) for vapours could be applied:

$$\mathrm{LFL_T} = \mathrm{LFL_{25}} - \frac{0.75}{\Delta \mathrm{H_c}}(\mathrm{T} - 25) \tag{3.9}$$

where LFL_T is the lower flammability limit at operating temperature of T; ΔH_c is the net heat of combustion (kcal/mole); LFL_{25} is the lower flammability limit at $25^{o}C$ and T is the operating temperature of the process.

Lower flammability limit at ambient temperature could be obtained from the standard references such as the MSDS or experimental data.

3.5 Integrated Inherently Safer Design Evaluation Tool (IISDET)

Resolving safety problems is a paramount task in CPI due to large variety of potential hazards from volatile materials and high-risk equipment that could lead to catastrophic disasters if the risk is not managed appropriately. Hence, it is crucial to apply a comprehensive safety analysis tool that not only enables the designers to identify and understand clearly the hazards in their developed processes but also able to recognise potential solutions to avoid the hazards. This could be done through design modification and the designers need to be aware of any trade offs from the changes made as early as possible. IISDET is developed to tailor the above requirements which aimed to incorporate ISD concept at the earliest possible of chemical process development particularly at preliminary design stage.

Therefore, IISDET framework is composed of all major safety analysis elements which are structured in a hierarchical manner. It begins with a method to identify inherent hazards, then several methods to generate and evaluate ISD alternatives based on consequence approach and finally a method to evaluate each risk reduction measure based on their trade-offs or conflicts due to process design and inherent safety. In addition, IISDET consists of two main frameworks which used two different methodologies. The first sub-framework applies qualitative approach, namely, Qualitative Evaluation of Inherently Safer Design (QEISD) while the second sub-framework uses a quantitative approach known as Quantitative Index of Inherently Safer Design (QIISD) as shown in Figure 3.8. The IISDET algorithm begins with QEISD that supported with four sub-tools for identification and evaluation of the ISD options. Then, QIISD is used when the decision to determine the best ISD option becomes difficult and highly complex through qualitative approach. Thus, IISDET framework offers flexibility in performing the safety analysis which could secure valuable time of the project to a minimum level as possible. Details of the two sub-frameworks are described in the following Section 3.6 and 3.7, respectively.

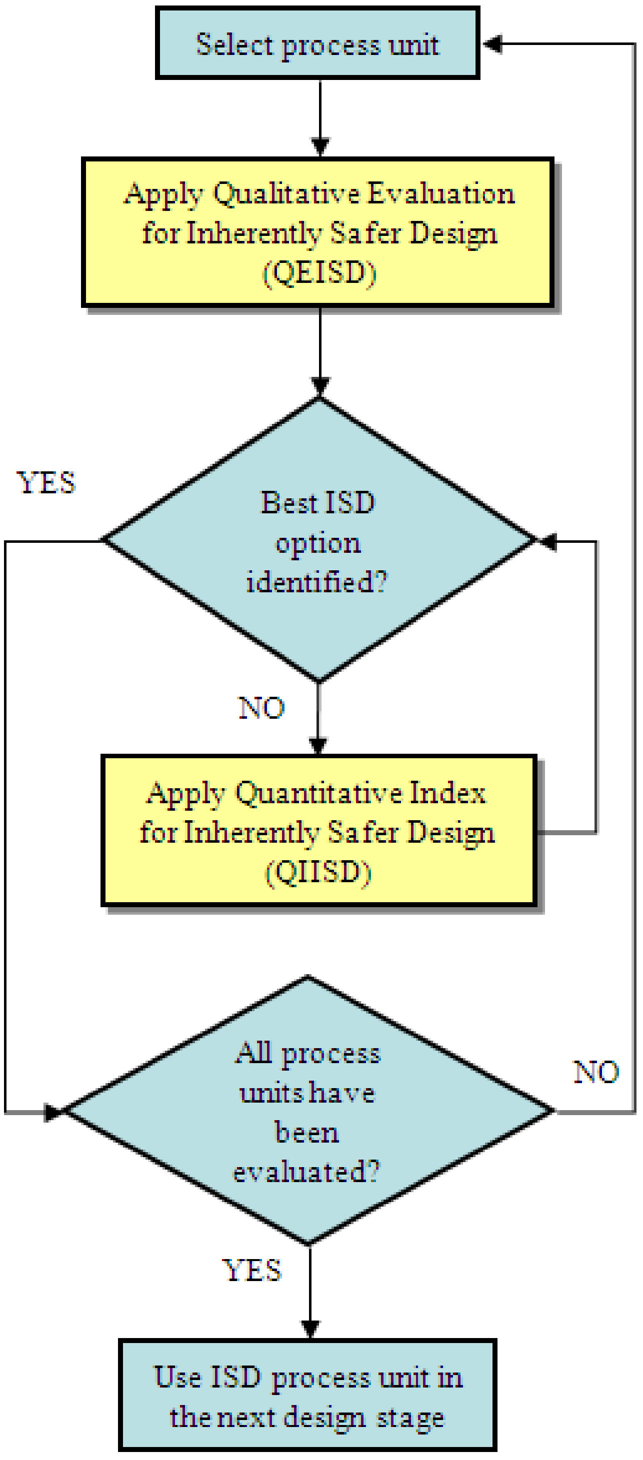


Figure 3.8: IISDET Framework

3.6 Qualitative Evaluation of Inherently Safer Design (QEISD)

The main objective of QEISD is to provide a systematic qualitative methodology as a platform to identify hazards, generate design alternatives that are inherently safer and evaluate each ISD option that is less time consuming, reliable and highly effective to be used during preliminary design stage. In order to materialise the above objective, the integration of ISD concept with process hazard analysis technique is executed through the development of qualitative guidelines that are supported with generic guidewords and fundamental factors in design conditions using heuristic structure. This unique structure is developed to allow the hazard evaluation to be performed although minimum data and information about the process is available. In addition, the methodology developed in this research is focused on the study of chemical process at preliminary design stage in view of the fact that at this design stage, the ISD concept is best to be implemented with maximum benefit for safer plant operation and minimum impact on the design costs. At this design stage, the information such as the potential process routes and the simplified process flow diagram (PFD) could be used to support the analysis. QEISD is expected to be the initial platform to understand the process hazards, predict any potential consequences from the process unit and finally to propose the best ISD option. Most importantly, QEISD is developed to provide guidance on how to eliminate or reduce those hazards qualitatively as proactive measures while the design is still at early stage.

QEISD is developed based on “gate-to-gate” process flow where the scope of assessment is carried out by analysing a process unit such as reactor, separator, heat exchanger etc. to allow better understanding and detail analysis of the hazards and possible ISD solutions. QEISD may not require the common brainstorming session since systematic guidelines or procedures are available for each sub-tool. However, user experiences and understanding of ISD concept will be an advantage for effective utilisation of QEISD.

Figure 3.9 shows the QEISD framework which consists of four main stages. The first stage is developed to identify inherent hazards using a sub-tool named as Register, Investigate and Prioritise (RIP). The second stage is to assist the creation of ISD options in order to reduce the inherent hazards using Inherent Design Heuristic

(IDH) as the sub-tool. Detail descriptions of these sub-tools are available in Section 3.6.1 and 3.6.2, respectively. The next two stages are developed with the aim to enhance the capability of this qualitative methodology with support tools that able to evaluate design options extensively to determine the design option that is As Inherently Safer As Practicable (AiSAP). A new sub-tool namely, the Inherently Feasible Matrix (IFM) is developed to rank the generated ISD options based on the practicability to implement the design option at conventional design stages. Finally, the identified ISD options are evaluated qualitatively on the potential of conflicts based on hazard transfer by applying Inherently Safer Matrix (ISM) as the sub-tool. Section 3.6.3 and 3.6.4 provide the detailed explanation of these tools. Table 3.3 provides the summary of techniques used in each sub-tool developed in QEISD.

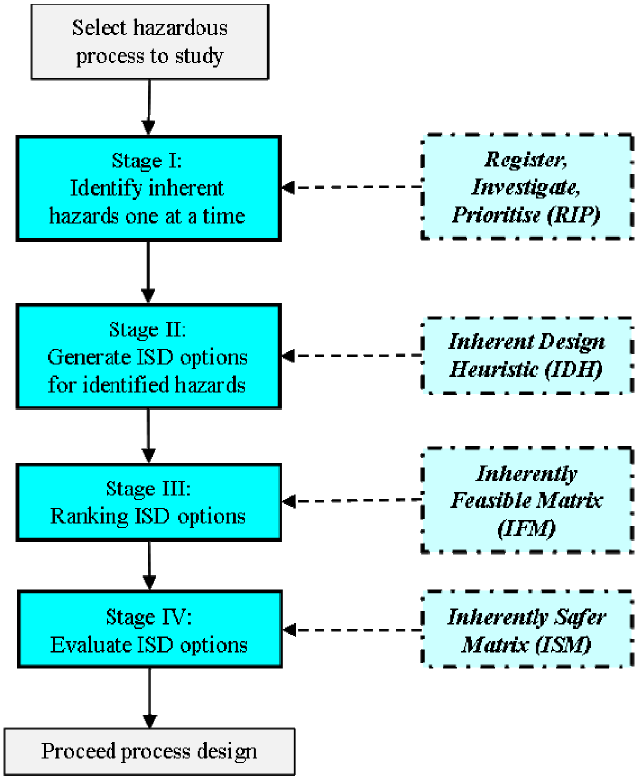


Figure 3.9: QEISD framework

Table 3.3: Sub-tools developed in QEISD

Stage	Sub-Tool	Technique
Stage I: Identification of Inherent Hazards	Register, Investigate, Prioritise (RIP)	Process Heuristics TRIZ-Predictive Failure Analysis Process Safety Databases
Stage II: Generation of ISD options	Inherent Design Heuristics (IDH)	Heuristic of ISD concept IS guidewords
Stage III: Ranking of ISD options	Inherently Feasible Matrix (IFM)	Conventional Process Design Stages
Stage IV: Evaluation of ISD options	Inherently Safer Matrix (ISM)	ISD Heuristic IS Guidewords Interaction Matrix

3.6.1 Stage I: Identification of inherent hazards in a process unit

It is believed that through the right and effective approach of identifying intrinsic hazards would lead to the best process of generating ISD options if suitable mechanism is used to find the hazards. Therefore, the purpose of this stage is to detect potential inherent hazards within a process unit through the application of Register, Investigate, and Prioritise (RIP) as the sub-tool for this stage. This is to allow a simple and systematic generation of potential source of hazards in the process in a single tool.

RIP represents three simple steps: i) Register, ii) Investigate and iii) Prioritise. For illustration, Figure 3.10 demonstrates the RIP tool in a single diagram for a reactor to identify the inherent hazards. For the first step, Register, is developed based on process heuristics which is supported by three criteria; *design factor*, *process attribute* and *hazard indicator*. *Design factor* represents the common design elements in a process unit such as chemical substances, process routes, process conditions, type of process unit etc. which significantly need to be explored because the existence of intrinsic hazards mostly contributed by the above design elements. *Process attribute* captures the characteristics available in the design factor, for example, reactant, solvent, and catalyst are the characteristics for chemical substances. *Hazard indicator* denotes the unsafe behaviour of the process attribute. For instance, flammable,

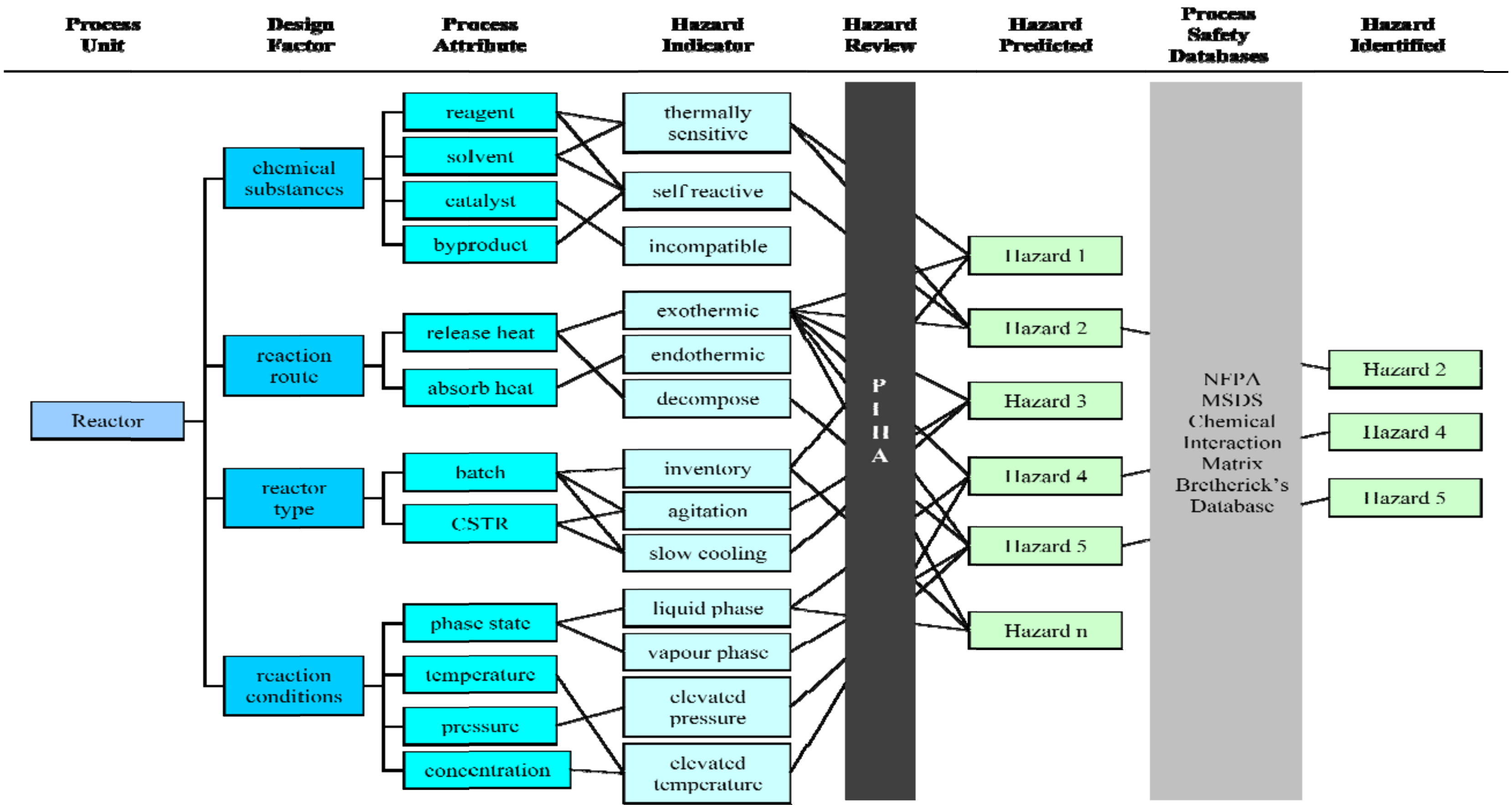


Figure 3.10: Process flow to identify hazards using the RIP tool for a reactor

reactive and toxic indicate the potential inherent hazards for a reagent. By following this process heuristic, the designer is required to record the above criteria for the studied process unit before proceed to the next step. Figure 3.11 shows the process heuristics that connecting the above criteria for a reactor as an example.

For the second step, Investigate, is a step to review all the registered hazards using the Predictive Failure Analysis (PFA) as described in section 3.3. The application of this hazard review is solely to identify source of hazards focusing on inherent hazards rather than external hazards. Thus, the method's name is changed to Predictive Inherent Hazard Analysis (PIHA) to suit the present study. The modification is consistent with ISD philosophy that when inherent hazards are fully understood and can be minimised inherently, the probability of external failure events would be less. As an illustrative example, the PIHA checklist questions for potential thermal runaway reaction for a process of nitration of toluene are shown in Table 3.4. These predictive questions enable human brain to creatively explore, think and identify all possible sources of hazards to accomplish thermal runaway in a reactor by tracing the internal factors such as process chemistry and physical properties without any restrictions.

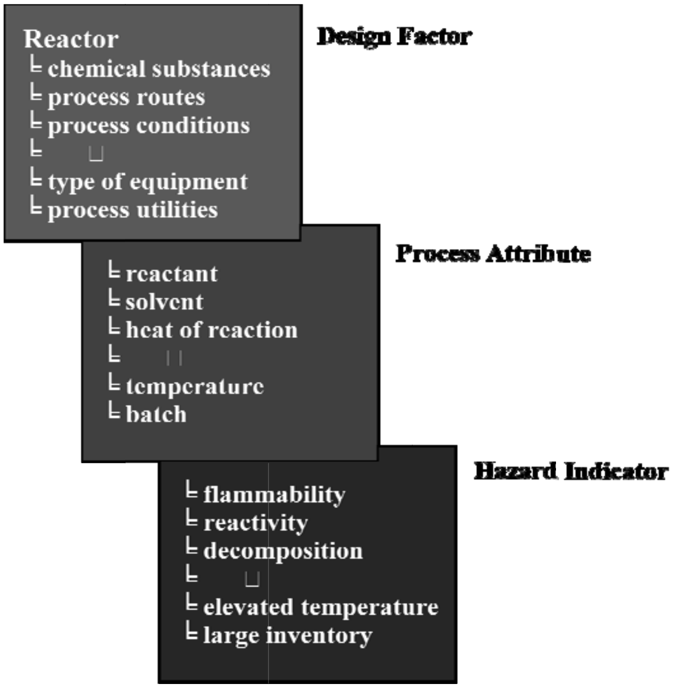


Figure 3.11: Process heuristics for a reactor

Table 3.4: Predictive Inherent Hazard Analysis (PIHA) for chemical reaction

Step i: Ideal State	We want no thermal runaway reaction in the nitration of toluene
Step ii: Inverse Ideal State	We want a thermal runaway reaction to happen in the nitration of toluene
Step iii: Exaggerate	We want to generate the reaction heat and release in the process and cause severe injury, fatality and damage
Step iv: Find resources	How to accomplish this? What intrinsic resources are required?

The third step, Prioritise, is to identify the dominant hazards because not all predicted hazards are necessarily hazardous. In addition, not all the listed hazards would cause accidents when the chosen materials or process conditions are not credible as hazardous or well below the safety threshold limit values. Therefore, some common process safety databases such as Bretherick's Handbook, National Fire Protection Association (NFPA) ranking, Incompatible Chemicals Database, Material Safety Data Sheets (MSDS), flammability limits, TCPA and any experimental results are used to prioritise the potential hazards in the studied process. For example, Table 3.5 shows the threshold quantities based on the ranges of heat reaction obtained from Toxic Catastrophe Prevention Act (TCPA, 2004) to provide guidance related to the limit of quantity of chemicals in terms of inventory. Appendix I listed several threshold limits of process safety criteria based on common references as a guideline to prioritise the predicted hazards.

Table 3.5: TCPA (2004) guidelines to show the threshold quantities based on heat of reaction

Heat of Reaction (cal/g)	**Threshold Quantity (lb)**
$100 \leq -\Delta H \leq 200$	13,100
$200 \leq -\Delta H \leq 300$	8,700
$300 \leq -\Delta H \leq 400$	6,500
$400 \leq -\Delta H \leq 500$	5,200
$500 \leq -\Delta H \leq 600$	4,400
$600 \leq -\Delta H \leq 700$	3,700
$700 \leq -\Delta H \leq 800$	3,300
$800 \leq -\Delta H \leq 900$	2,900
$900 \leq -\Delta H \leq 1000$	2,600
$-\Delta H \geq 1000$	2,400

The outcomes from RIP analysis must be documented by the analyst to ensure all identified hazards are communicated properly throughout the process lifecycle. The results shall be referred in every safety review or during management of change session. Table 3.6 shows the proposed RIP form for recording the inputs and findings for Stage I with brief descriptions on the functions of each column.

3.6.2 Stage II: Generation of ISD options for the identified hazards

The objective of this stage is to generate as many as possible ISD options based on ISD concept which could eliminate or minimise the inherent hazards. Figure 3.12 shows the hierarchy to analyse the selected inherent hazard using Inherent Design Heuristic (IDH) while Figure 3.13 shows the proposed work-flow to guide the generation of ISD options. IDH is an extended concept of Inherent Safety Heuristic (ISH) suggested by Moore (1999). The IDH demonstrates the way to investigate potential ISD options which is ranked into three categories; i) *Hazard Elimination*; options that eliminate hazards at source as first priority e.g. eliminate hazardous material, substitute with non hazardous material and eliminate intermediate storage, ii) *Consequence reduction*; options that reduce consequences if hazard is realised e.g. reduce inventory and substitute with less hazardous material and iii) *Likelihood reduction*; options that minimise chance of an error occurring or domino effects e.g. reduce potential for human error through simplicity of design and control ignition sources.

Each IDH category is supported with Inherent Safety Guidewords (ISG) as summarised in Table 3.7 that complies within the hierarchy given by Moore (1999). For example, *substitute* and *eliminate* is the ISG for Hazard Elimination category. Under ISG, a list of Inherently Safer Design Indicator (ISDI) is specified to show the type of process elements that can be applied to the selected ISG. As an example, *process route* and *hazardous substance* indicate the process elements that apply the ISG for *substitute* and *eliminate*.

Table 3.6: Guidelines to tabulate the RIP inputs and inherent hazards

<table>
<tr><th colspan="5">QUALITATIVE EVALUATION FOR INHERENTLY SAFER DESIGN (QEISD)</th></tr>
<tr><th colspan="5">Stage I: Identification of Inherent Hazards</th></tr>
<tr><td colspan="5">Process:</td></tr>
<tr><td colspan="3">Process Unit:</td><td colspan="2">Materials in Process Unit:</td></tr>
<tr><th colspan="3">Register</th><th>Investigate</th><th>Prioritise</th></tr>
<tr><th>Design Factor</th><th>Process Attribute (Base Case Data)</th><th>Hazard Indicator</th><th>Predicted Hazard</th><th>Prioritised Hazard</th></tr>
<tr><td>Identify Design Factors of the Process unit with inputs from the base case. Example: substances, reaction conditions, type of reactor etc.</td><td>Make a list of Process Attributes for the identfied Design Factor. Example: Substances - reactant, solvent, catalyst</td><td>Indicate the hazardous characteristics of the identified Process Attribute. Example: reactant - flammable and toxic.</td><td>Predicted hazards are investigated using TRIZ's brainstorm steps (as in Table 5) to enquire all potential intrinsic resources (inherent hazards) that would magnify the stated consequences and used the registered hazard indicators as guidance. The output of all predicted hazards are listed in this column, e.g. utilise the highest reactive reactant in the process, accumulate as large as possible volume of mixture</td><td>Prioritised hazards are recognised with the assistance of common Hazardous Materials and Process Safety References and listed in this column, e.g. highly reactive reactant is exist based on Bretherick's and NFPA, large inventory is exist because using batch reactor</td></tr>
</table>

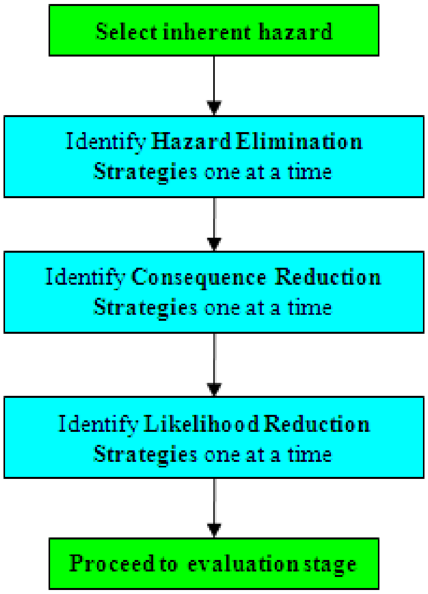


Figure 3.12: ISD Hierarchy model to analyse inherent hazard

The design solution is focused on the changes in process and design fundamentals through selected process variables. The process variable is classified as ISD Variable (ISDV). For instance, *new safer solvent* and *new safer reactant* are the potential ISDV for *hazardous substance*. The final step in this stage is to identify any immediate potential of new hazards that possibly occur when the identified ISD option is implemented. This instantaneous response is guided by checking potential deviation in the process conditions. For example, when the volume is minimised by changing the type of reactor to a smaller reactor, increased in operating temperature and pressure would happen in order to accommodate the main objective of the process such as to maintain the product final quality. Thus, these new hazards could lead to a new design solution which probably could be more inherently safer than the first option. Otherwise, the new hazards could also be analysed during the decision making stage where the best ISD option need to be evaluated.

The generated ISD options as suggested by the work-flow (Figure 3.13) allows the designer to focus the modification at fundamental design through application of basic engineering principles rather than directly focus on added safety control measures to eliminate and reduce the hazard. It should be noted that the application of

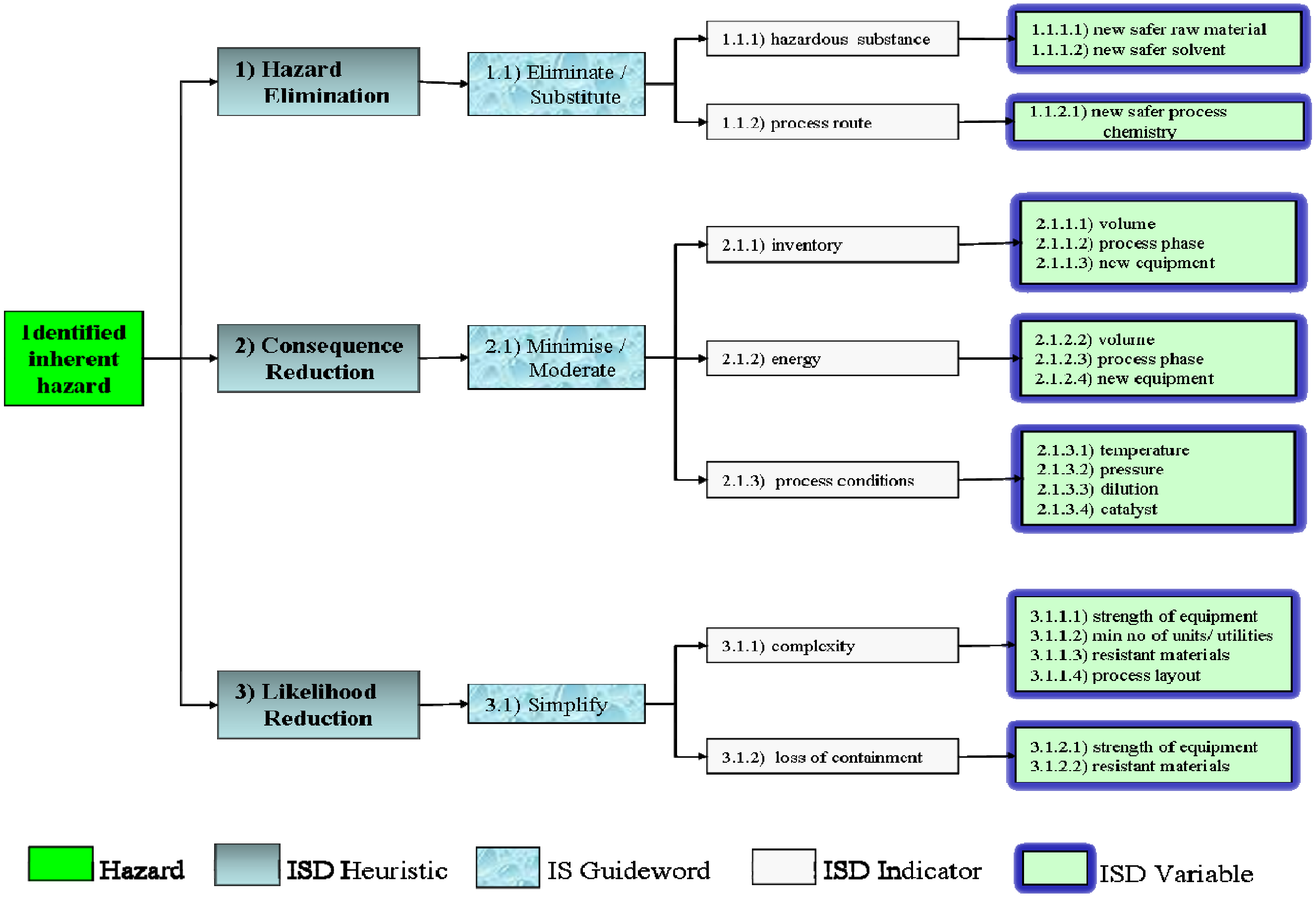


Figure 3.13: Work-flow diagram of IDH tool

Table 3.7: Potential ISG for each ISH

Inherent Safety Heuristics (ISH)	*Inherent Safety Guidewords (ISG)*
Hazard Elimination	Eliminate, Substitute
Consequence Reduction	Minimise, Moderate
Likelihood Reduction	Simplify

IDH tool to one identified hazard would possibly regenerate an identical ISD option for another hazard(s). This replication process is purposely developed in this tool in order to generate as many ISD options as possible before the best one is identified. If this does happen, it will bring significant impact towards the design because the identified ISD solution could reduce or resolve not only one hazard but possibly two or three hazards at a time. This indicates that if the identified ISD option is feasible and practical in meeting the process requirement, the implementation of the option could bring huge credits in the inherently safer design point of view. At this stage, QEISD is expected to provide a systematic guidance which opens up the avenues of thought and creative thinking in innovating potential design alternatives for inherently safer process. It is also desired to allow the designer to look for better solutions and not stopping at the first identified solution. The generated ISD options are documented using the proposed format in Table 3.8 for preparation in the next stage of QEISD.

3.6.3 Stage III: Evaluation of feasibility design to reduce hazards

The objective of this stage is to evaluate the generated ISD options with respect to its technicality and feasibility issues in reducing the identified hazards. The suitability to implement the ISD options is analysed qualitatively using a typical process design lifecycle stage. This procedure will allow the designer to filter the infeasible ISD options and able to identify the best ISD option that could reduce or eliminate most of the hazards. This stage will also assist the designer to prioritise which hazard is most important to be solved first based on the criteria or outputs required from each process design stage.

Table 3.8: Guidelines for IDH and tabulate all inputs including generating ISD options

QUALITATIVE EVALUATION FOR INHERENTLY SAFER DESIGN (QEISD)						
Stage II: Generation of Inherently Safer Design Options						
Process:						
Process Unit:			Materials in Process Unit:			
Inherent Design Heuristic						
Prioritised Hazard	**ISD Heuristic**	**Inherent Safety Guideword**	**ISD Indicator**	**ISD Variable**	**ISD Option**	**Prompts on potential of other hazards**
Each predicted hazard identified in Stage I is analysed using Inherent Invention Heuristic	The hierarchy of ISD is applied to identify potential inherent strtegies: Hazard Elimination, Consequence Reduction, Likelihood Reduction	Suitable Inherent Safety Guidewords for each ISD strategy to highlight potential inherent strategies, e.g. eliminate and substitute for Hazard Elimination strategy	Potential process elements which are suitable to apply the IS Guidewords, e.g. hazardous substance and process route is the indicator for eliminate and substitute	Potential process variables for ISD Indicator to be considered for design modification, e.g. new safer material is the variable to consider in hazardous substance	The output of all ISD options are listed in this column, e.g. substitute nitric acid with less energetic reactant	This column is to highlight any potential occurrence of new hazards if the option is applied, e.g. elevated operating conditions and increase complexity in control measures

This stage is supported by the Inherent Feasibility Matrix (IFM) tool which allows the designer to observe which options would give high impact in reducing the hazards since some of the ISD options are repeated and implied the same strategy in a number of hazards. Table 3.9 provides the common criteria or expected outcomes from each process design stage as the guidelines to determine the suitability of the ISD options. The proposed design stages are not all inclusive and it can be tailored to include other process stage such as for operation, retrofit and maintenance stages. This screening stage also allow the designer to consider all the identified ISD options and investigate its feasibility at every stage of process design with related experimental works through out the design development. This stage demonstrates that the IFM tool is concurrent with the ISD concept as an evolutionary approach where the process is made inherently safer by a number of incremental changes throughout the lifecycle of process (Overton and King, 2006).

For illustration purposes, the IFM tool concentrates at early research and development (R&D) up to the detailed design engineering stages. For example, the criteria used to screen the feasible ISD options at R&D stage would be the ISD options that will utilise the less hazardous raw materials to produce the targeted product. Other criteria could be the process that will produce no or less hazardous by-products, hence, minimum safety requirement will be required in handling the by-products. The designer could obtain the above information from the process or experimental databases and literatures that related to the studied process. Once all the generated ISD options have been classified according to the appropriate process design stage, the ISD option that could eliminate or reduce most of the hazards is determined using the simple matrix table as shown in Table 3.10. The final procedure is to implement the feasible ISD options according to the design stage as recommended by Overton and King (2006).

Table 3.9: Potential criteria and expected key decision/outputs from process design stage (Mannan, 2005; CCPS, 1996)

Preliminary process research and development	selection of basic process technology	raw materials	intermediate products	by-products and waste products	chemical synthesis routes	
Process research and development	selection of specific unit operations	type of reactors and other processing equipment	selection of operating conditions	recycle	product purification	waste treatment
Preliminary plant design	location of manufacturing facility	location of units on a selected site	size and number of production lines	size of raw material, intermediate and product storage facilities	selection of specific equipment types for the required unit operations	process control philosophies
Detailed plant design	size of all equipment	pressure rating and detailed design of all equipment and piping	inventory in processing equipment	location of specific equipment in the plant	layout of equipment	detailed control system design
Operation	identification of other opportunities to modify plant to enhance inherent safety (reduce inventory, upgrade with more modern equipment, identify opportunities for inherently safer operation based on improved process understanding), considerations of inherently safer design when making modifications and changes, user-friendly operating instructions and procedures					

3.6.4 Stage IV: Evaluation of potential hazard conflicts

The aim of this stage is to provide designer a qualitative evaluation platform in order to obtain the best risk reduction alternative when there is more than one ISD options that could eliminate or reduce the inherent hazards. The evaluation is done by analysing potential design conflicts in the form of positive or negative impact towards inherent safety that could be present if ISD option is implemented.

The Inherent Safety Matrix (ISM) is developed to support the evaluation using an interaction matrix technique which is first initiated by Leopold et al. in early 1970s (Hellawell et al., 2007). This interaction matrix technique is then combined with TRIZ technique as described in section 3.2 to identify the design conflict effectively. The mechanism used is through the interaction of Inherent Safety principles with the

Table 3.10: Guidelines to tabulate IFM for feasibility study of ISD options

QUALITATIVE EVALUATION FOR INHERENTLY SAFER DESIGN (QEISD)						
Stage III: Feasibility of Inherently Safer Design						
Process:						
Process Unit:			Materials in Process Unit:			
INHERENT FEASIBILITY MATRIX						
Inherently Safer Design (ISD) options	**Process Design Stages**					**Remarks on the List of the Identified Hazards**
	Chemical Route Synthesis	**Conceptual Process Design**	**Process Development**	**Process engineering**	**Detailed Engineering**	
Option 1	Hazard 1					Hazard 1, Hazard 2, Hazard 3, Hazard 4, Hazard m
Option 2	Hazard 1				Hazard m	
Option 3		Hazard 1	Hazard 1, Hazard 2, Hazard m			
Option 4		Hazard 4		Hazard 2, Hazard 3		
Option 5			Hazard 2			
Option n	Hazard 3, Hazard m					

Inherent Safety Factors (IS Factors) possess by the ISD option. For example, if the option has an Inherent Safety attribute of *Substitute* where the reactant need to be substituted with less reactive material (*Reactivity* as the IS Factors), this option is then interacted with all other IS Factors that correspond to the same Inherent Safety principle such as *Flammability*, *Toxicity* etc. Table 3.11 illustrates the interaction matrix between the ISD option and the IS Factors. The interaction between these IS Factors will create positive or negative impacts to the design and also conflicts towards the inherent safety. For example, although the substituted reactant has less reactive property to meet the first option, the reactant could contain higher toxicity level based on the NFPA or MSDS databases. This interaction is evaluated as a *negative impact* which would create another hazard. On the other hand, the *positive impact* is reported if the substituted reactant has lower flammability limit that could reduce potential of fire and explosion hazards. The above interaction procedure is also applied to other Inherent Safety principles until all ISD options have been evaluated. The designer could refer to the process safety references, literatures or may apply their expert judgements in determining the conflicts issues. The attempt to resolve this conflict issues may require an integral component of all engineering activities (Khan and Amyotte, 2003). However, this tool will systematically guide the designer in identifying potential Inherent Safety conflicts by providing suitable Inherent Safety principles and IS Factors for this evaluation stage as shown in Table 3.12. Hence, less experience designer would also be able to perform this decision making stage.

For this study, the scope of Inherent Safety principles is focused on the first four principles i.e. *eliminate*, *substitute*, *minimise*, *moderate* and *simplify* due to their suitability to be used during early design stage. As shown in Table 3.12, several Process Subsets that suit the Inherent Safety principle are proposed to assist the interaction process. For example, *Hazardous Properties* is the Process Subset for *eliminate and substitute* principles. The proposed IS Factors for the above Process Subset are the hazardous characteristics for materials including by-products. For *minimise* principle, the deviation in *inventory* of the hazardous chemicals are analysed such as end-product and by-product from the main process and site-process. Whereas the *moderate* principle considers the conflicts in operating conditions which include the physical and chemical conditions. In this study, the proposed IS Factors for *moderate* principle are temperature, pressure, reaction and decomposition. Finally, the conflict issues for *simplify* principle would be the complexity in safety control measures and difficulty in handling the process unit. Some of the proposed IS Factors for this principle are the requirement to meet specific technical and safety regulations and also possibility to increase or decrease unnecessary pipelines to the reactor.

Table 3.11: Illustrations of ISM tool for selected IS principles
P = Positive impact; N = Negative impact

			IS Principle>	**Eliminate/ Substitute**			**Minimise**		**Moderate**				**Total Index**
			Process Subset>	**Hazardous Properties**			**Inventory**		**Physical/Chemical Conditions**				
<ISD Option	**<IS Principle**	**<IS Factor**	**IS Factor >**	**Flammability**	**Reactivity**	**Toxicity**	**Main Process**	**Site Process**	**Temperature**	**Pressure**	**Reaction phase**	**Decomposition**	
Option 1	Substitute	Reactivity	Substitute nitric acid with acetyl nitrate	P	-	-	P	P	-	P	-	-	4
				-	N	N	-	N	N	-	N	N	6

The best ISD option is determined by ranking the options based on the total number of impacts for each ISD option. The ISD option that has the lowest negative impact and the highest positive impact is the design that As Inherently Safer As Practicable (AiSAP) because this option would has less Inherent Safety conflict issues although the design has been modified according to ISD concept. Table 3.13 shows the proposed ISM form to evaluate all ISD options that could be able to avoid the conflicts and hazard transfer.

This ISM tool is used to provide a basic qualitative screening of the available ISD alternatives before the design is continued to the advanced stage. However, when conflicts in the design becomes complicated which involved multi-criteria of process safety such as the magnitude of hazard severity and the cost of losses, a quantitative approach should be used to assist in the decision making. Therefore, the Inherent Safety assessment need to proceed to the second framework as described in the section 3.2. Regardless of this constraint, this tool would give significant impact to the design because the matrix enables the identification of other potential hazards qualitatively at early stage and also provide guidelines in prioritising the inherent safety conflicts to allow detail investigation and analysis to be made before the best ISD option is selected.

Table 3.12: Guidelines for selecting Inherent Safety Factors based on the Process Subsets in ISD Heuristics

ISD Heuristic	IS Principle	Process Subsets	IS Factors	ISM Code
Hazard Elimination	Eliminate	Hazardous Properties	Flammability	E1
			Explosive	E2
	Substitute		Reactivity	E3
			Toxicity	E4
Consequence Reduction	Minimise	Inventory	Process	C1
			Site-Process	C2
	Moderate	Physical Conditions	Temperature	C3
			Pressure	C4
		Chemical Conditions	Reaction	C5
			Decomposition	C6
Likelihood Reduction	Simplify	Control Measures	Requirement in technical and safety regulation measures	L1
		Equipment and Handling Measures	Frequency in maintenance of safety measures	L2
			Process extensions	L3
			Transportation and loading/ unloading activities	L4
			Site-storages	L5

Table 3.13: Guidelines to tabulate results after applying ISM tool

[redacted]

3.7 Quantitative Index of Inherently Safer Design (QIISD)

The main objective of QIISD is to evaluate the inherent safety performance of the process unit based on the initial design. A risk-based evaluation approach is developed by determining the likelihood of hazard magnitude through Inherent Safety conflicts. The overall QIISD flow diagram is shown in Figure 3.14, which comprised of the following three main stages: i) quantification of inherent hazards, ii) generation of ISD options and iii) evaluation of ISD options. Specific sub-tool is developed to achieve the objective in each stage and Table 3.14 provides summary of the approach used in the developed sub-tools. The detailed description is given in this section.

Fire and explosion hazards have been selected as the main hazard considered in QIISD because previous accident histories have shown that the chemical plant accidents are mostly due to this hazard which had resulted in high fatality and damage to equipment and building (Crowl and Louvar, 2002). The probability of occurrence of these accidents especially fire is also high and potential of economic loss is high for explosion accidents (Crowl and Louvar, 2002). Meanwhile, the accidents due to toxic exposure had caused high potential of fatalities to people and the environment but contribute very low impact to equipment and structures, hence lower potential of economic losses. The statistic of accidents due to fire and explosion had showed that these hazards contribute up to 85% from the total of 242 accidents of storage tanks from petroleum refineries, oil terminals and storages in between 1953 to 2004 (Chang and Lin, 2006).

3.7.1 Stage I: Quantification of hazards in a process unit

The main objective of this stage is to estimate the consequence or the degree of hazards based on the potential energy contained in the process unit under the worst case scenario. The analysis of hazards through consequences is helpful in understanding the relative inherent safety of process alternatives (Khan and Amyotte, 2003). This potential energy is correlated as the potential damage value in unit distance as damage radii (DR). Then, the DR is converted to index value which is ranked based on a proposed tolerability range. Index technique is used because the suitability of this approach for early design stage where most of the information is limited. This tolerable limit determines if new design options would be required to eliminate or minimise the estimated consequence. Otherwise, the designer can proceed to the next stage of process design with the proposed process unit.

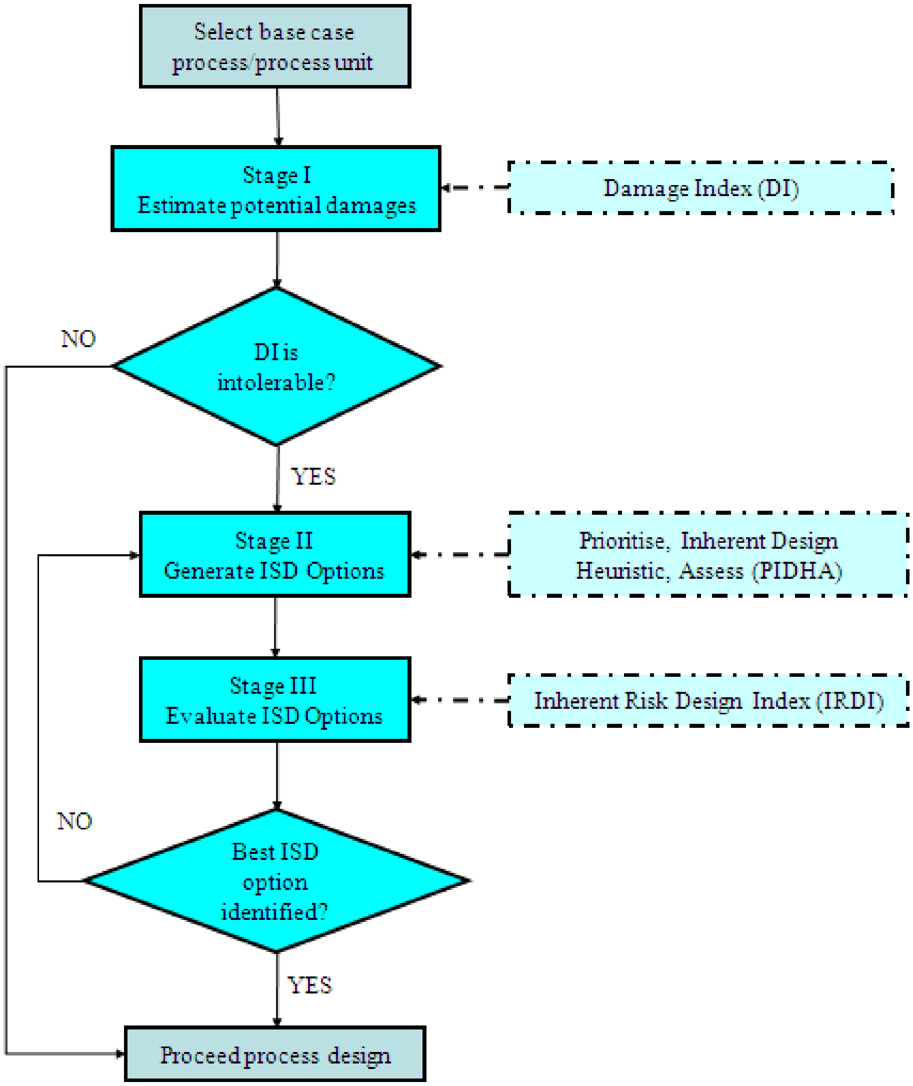


Figure 3.14: Framework and sub-tools of QIISD

Table 3.14: Summary of sub-tools developed for QIISD

Stage	Sub-Tool	Technique
Stage I: Quantify Hazards	Damage Index (DI)	Consequence-based of potential energy
Stage II: Generate ISD options	Prioritise, Inherent Design Heuristics, Assess (PIDHA)	Energy factors and penalties Inherent Design Heuristics
Stage III: Evaluate ISD options	Inherent Risk Design Index (IRDI)	Risk-based IS Guidewords Interaction Matrix

The quantification of hazards is based on the SWeHI and I2SI approaches. As described in Chapter 2, SWeHI and I2SI are chosen due to their robustness and its good technical judgement in quantifying potential hazards through consequence mode rather than individual ranking scales for the hazard properties. However, these two methods required review and revision of the sub indices of the original assessment procedure in order to suit with the objectives of the present study. The revised factors are as below:

- The potential hazard is estimated using Damage Radius (DR) instead of Damage Index (DI) to significantly represent the radii as the moderate hazard for 50% probability of fatality or damage that could readily occur.
- The estimation of DR is modified by estimating the individual potential energy factor and its related penalties that could contribute to the severity of fire and explosion. The DR is then computed as the summation of all energy factors and general penalties as Damage Potential (DP). The penalties are given in Table 3.15 and detail estimation for each penalty is given in Table 3.16.
- The strength of the reaction energy index is further enhanced by adopting the estimation of potential reaction energy using Marshall and Ruhemann (2001) as described in Equation (3.15).
- As shown in Table 3.15, several penalty factors for reactivity and decomposition hazards are also considered in the development of this tool. These penalties are referred as the safe limit parameters based on several standard database and references for process safety such as Bretherick's Handbooks for reactive materials or through results of related experiment. This modification is necessary to take into account the sensitivity of the index to runaway reaction hazards.

Detail background of the theory related to runaway reaction and its parameters can be obtained in the subsection 3.4.1 of this chapter.

The DR tolerability limit at 200 meters is retained in this study to show the significant distance that could cause 50% probability of fatality/damage especially to neighbouring plants and public/residential area as illustrated in Table 2.11 of Chapter 2. The distance limit of DR is used as the set point or guideline to conduct further analysis to the process unit by generating ISD options in the next stage of QIISD method. It is assumed that the population of people below than this distance is very small that could be affected from this moderate hazard. In addition, this tolerable limit is less conservative in comparison with the degree of hazard rating in DOW F&EI (Crowl and Louvar, 2002) as previously shown in Table 2.8 where the index value of 159 and above represents very severe hazard at the distance of 41 meters and above after all control measures have been considered. Furthermore, the tolerable limit is reasonable according to land-use planning criteria to determine safety distance using consequence-based approach for the control of major accident hazards which is widely used in European countries such as France and Belgium (Christou et al. 1999; Cozzani et al. 2006). This limit is only a guideline and can be substituted with the safety distance set by the relevant country. For instance, Malaysia required 500 meters as the safety buffer zone as stipulated in the Department of Environment regulations.

For this study, the estimation of DR for fire and explosion hazards used Equation 3.10 to represent 50% probability of fatality or damage and Equation 3.11 is the revised formulation to estimate the Damage Potential (DP) as follow:

$$\mathrm{DR}_{\mathrm{bc}} = 4.76(\mathrm{DP}_{\mathrm{fe}})^{\frac{1}{3}} \tag{3.10}$$

where

$$\mathrm{DP}_{\mathrm{fe}} = \left(\mathrm{EF}_{\mathrm{co}} + \mathrm{EF}_{\mathrm{ph}} + \mathrm{EF}_{\mathrm{re}}\right) \times \mathrm{pn}_3 \times \mathrm{pn}_4 \tag{3.11}$$

where bc is the base case unit; DR is the damage radii for base case unit; $\mathrm{DPI}_{\mathrm{fe}}$ is the damage potential for fire and explosion; $\mathrm{EF}_{\mathrm{co}}$ is the energy factor for combustion energy; $\mathrm{EF}_{\mathrm{ph}}$ is the energy factor for physical energy; $\mathrm{EF}_{\mathrm{re}}$ is the energy factor of reaction energy for base case unit; pn$_3$ is the quantity of chemical stored and pn$_4$ is the characteristics of the chemical.

Table 3.15: Energy factors and penalties to estimate DR (Khan et al., 2001)

Initial Energy Factors	**Process Variables**
F1 – Combustion energy	*f*(heat combustion, mass)
F2 – Physical energy	*f*(operating pressure, volume)
F3 – Physical energy	*f*(operating pressure, temperature)
F4 – Reaction energy	*f*(heat reaction, mass, reaction rate, volume)
Penalty Factors	**Safe Design Limit**
pn1 – Process temperature	*f*(flash point, fire point, autoignition)
pn2 – Process pressure	*f*(vapour pressure)
pn3 – Capacity of unit	*f*(hazardous criteria, inventory)
pn4 – Hazardous characteristics	*f*(NFPA ranking; flammability, reactivity)
pn7 – Type of reaction:	Penalty:
Oxidation	1.60
Electrolysis	1.20
Nitration	1.95
Polymerisation	1.50
Pyrolysis	1.45
Halogenation	1.45
Aminolysis	1.40
Esterification	1.25
Hydrogenation	1.35
Sulfonation	1.30
Alkylation	1.25
Reduction	1.10
pn8 – Side reaction:	Penalty:
Autocatalytic reaction	1.65
Non-autocatalytic reaction (above normal)	1.45
Non-autocatalytic reaction (below normal)	1.20

Table 3.16: Detailed formulation to estimate the penalties (Khan et al., 2001)

Penalty Factors	**Safe Design Limit**
pn1	=IF(OT>FP, IF(OT<FRP,1.45,IF(OT<0.75*AIT,1.75, 1.95)),1.1)
pn2	=IF(VP>AP,IF(VP<OP,1+0.6*(OP-VP)/OP,1+0.4*(VP-OP)/OP),1+0.2*(OP-VP)/OP)
pn3	=IF(MAX(NR,NF)=4,0.01*INV*1000+1,IF(MAX(NR,NF)=3,0.007*INV*1000 +1 ,IF(MAX(NR,NF)=2,0.005*INV*1000+1.05,0.002*INV*1000+1.02)))
pn4	=1+0.25*(NR+NF)

Detail formulation of the initial energy factor of F_1, F_2, F_3 and F_4 for combustion, physical and reaction energies respectively can be obtained in section 2.4.3.1. However, the mathematical relationship of EF in Equation (3.11) is restructured to combine the initial energy factors with the related penalties only. As an example, the revised equations given below are developed for chemical reaction based process units:

$$EF_{co} = F_1 \times pn_1 \tag{3.12}$$

$$EF_{ph} = f(F_2, F_3) \times pn_2 \tag{3.13}$$

$$EF_{re} = F_4 \times pn_7 \times pn_8 \tag{3.14}$$

where pn_1 is the penalty for temperature; pn_2 is the penalty for pressure; pn_7 is the penalty for type of reaction and pn_8 is the penalty for side reaction or decomposition.

In addition, the initial energy factor for reaction, F_4 is revised to take into account the sensitivity of reactivity hazards based on the volume and also concentration of the material used in the process unit as described by Marshall and Ruhemann (2001) in Equation 3.15:

$$F_4 = V \times C \times \frac{\Delta H_r}{K} \tag{3.15}$$

where F_{re} is the initial energy factor for reaction; V is the volume of reactant; C is the concentration of reactant; ΔH_r is the molar enthalpy of reaction and K is the constant 3.148.

This step is crucial to screen process units that potentially have high hazardous energy to cause fire and explosion. The identified process unit would require further analysis by generating other potential ISD options. It is presumed that for the process unit which produced DR of more than 200 meters from its total energy content would give significant severity in terms of fatality and structural damage. This is due to potential of exposure to large population of people including plant personnel and nearby society. In addition, the exposure would involve highly congested structure of equipment, pipelines and building which indirectly would contribute towards the total risk of the plant. Thus, the tolerable limit of 200 meters is only a guideline which subject to the size of the process plant and the number of people could be exposed during day and night. The distance of the process unit to the nearest residential or public area also has to be considered when determining the reference point of DR. The designer could modify this threshold limit depending on the above factors.

3.7.2 Stage II: Generation of new ISD options

At this stage, ISD options will be generated using a semi-quantitative approach if the estimated DR in the first stage is higher than the threshold limit. The guidelines to generate ISD options are described as PIDHA which refer to the following steps:

i. PRIORITISE - Prioritise the estimated energy factors, EF and penalties into high to low rank in order to identify the most influencing process parameters that highly contributed to the DR.
ii. IDH - Apply Inherent Design Heuristic (IDH) tool in QEISD module as described in subsection 3.6.2 to generate potential ISD options according to ISD heuristics.
iii. ASSESS – Assess the feasibility of all ISD options whether the target production can be achieved using basic design calculation or assisted by process design simulator.

The generation of design alternatives in this step is more systematic than in QEISD because the initial energy factors involved are known, thus, the contributed process variables in the energy factors can be used to assist the generation of options. For example, if the potential energy release from the reaction energy is higher than the physical and combustion energies, the possible ISD alternatives can be focused in the reducing the heat of reaction, volume and concentration of the reactants. Table 3.17 shows the potential ISD options to eliminate and minimise reaction energy after applying the above PIDHA guidelines.

Table 3.17: Examples of the generated ISD options using PIDHA

IS Principles	Design parameters used to quantify reaction energy		
	Concentration	**Volume**	**Enthalpy of reaction**
Substitute	Change feedstock/solvent	Change feedstock/solvent	Change reaction path
Minimise	Reduce charging	Decrease inventory	Reaction reactants
Moderate	Lower temperature Use dilution	moderate pressure	Lower temperature
Simplify	not applicable	Reduce number of reactor	Change type of reactor

3.7.3 Stage III: Evaluation of ISD options

This stage is aimed at evaluating performance of the identified ISD options in avoiding or reducing the estimated hazards. This evaluation stage is important because the implementation of the identified ISD options could reduce the target potential energy but the changes made may increase the other hazards or introduce a new hazard to the process or other system. Therefore, in this study, any possibility of conflicts after design modification is measured by a risk-based performance index known as Inherent Risk of Design Index (IRDI). IRDI is developed to alert process designer on the level of safety of the process after the inherent strategies are considered in the design. The ultimate result of IRDI is used to rank the safety performance associated in the ISD options with relation to the criticality of the hazards using risk-based approach.

The common procedure to quantify risk is to measure the hazard severity and likelihood of hazard to occur as in the following equation:

$$\text{Risk} = \text{Severity of accident} \times \text{Likelihood of accident to occur} \tag{3.16}$$

Therefore, IRDI is quantified using similar risk expression;

$$\text{IRDI}_{\text{op-i}} = \text{DI}_{\text{op-i}} \times \text{LIHM}_{\text{op-i}} \tag{3.17}$$

where

$$\text{LIHM}_{\text{op-i}} = (1 - \text{LIDIS}_{\text{op-i}}) \tag{3.18}$$

where op-i is the option i; DI is the estimated Damage Index for option-i; LIHM is the Likelihood Index of Hazard Migrate for option-i and LIDIS is the Likelihood Index of Design is Inherently Safer for option-i. Detail descriptions of DPI and LIHM are given in the next section.

For IRDI, the severity of the hazard is represented by DI and the likelihood of the hazard to occur is quantified by LIHM where this index can be obtained from LIDIS as the likelihood of the design is inherently safer after considering the ISD concept.

3.7.3.1 Damage Index (DI)

DI represents the damage created by the potential hazardous energy in the ISD option after design modifications have been made in line with the ISD concept. To facilitate the estimation of DI, the calculation procedures shown in Stage I are used and the DR value is correlated as an index value. The DI value of all ISD options are then compared with the base case design in order to observe the variation in the potential energy produced by each ISD option i.e. whether the hazard severity is reduced or increased after consideration of ISD principles.

The DI is obtained by computing the DR which is represented as the damage radii due to fire and explosion using a graphical index in the I2SI procedure. The DI can also be computed using Equation (3.19):

$$\mathrm{DI} = \mathrm{Max}\left(5, \mathrm{Min}\left(100, \frac{\mathrm{DR}}{2}\right)\right) \tag{3.19}$$

The graphical index represents the DI increment values for fire and explosion as shown in Figure 2.9a in Chapter 2. The damage radius is converted to an index value in order to obtain the value of IRDI. The higher the DI value means the less inherently safer the process unit. As the damage radius that could cause 50% probability of fatality or damage increases due to fire and explosion, it means more people and structures would be affected in the accident which will increase the overall risk of the plant. Therefore, for this study, when the DR reached 200 meters and above, the value of DI is established at the maximum value, 100 which shows that the ISD option is significantly not inherently safer and could contribute to the total risk of the plant.

3.7.3.2 Likelihood Index of Hazard Migration (LIHM)

The aimed of IRDI is to capture the potential of risk transfer and to inform the criticality of the hazards of the design options before a decision is made. Although the design option that applies Inherent Safety concept could dramatically reduce the severity from the identified hazards, there are also possibilities that the design option could introduce new hazards or causes some hazards to be conflicted to other related site processes or even to the external environment. Therefore, LIHM is developed to recognise the possibility of these hazards migration which could cause failure or uncontrollable hazard and resulted in the increase of the overall risk of accident in the final stage of design. LIHM is estimated using the Eq. (3.18) after quantifying the order of hazard magnitude due to changes in the targeted inherent safety parameters known as the Likelihood Index of Design is Inherently Safer (LIDIS). The LIDIS will be in positive and negative values depending on the changes in hazard magnitude of the Target Process Safety Factors (TPSF) as described in Table 3.18. If the LIDIS is positive, it shows that the ISD option has reduced the hazard contributed by the TPSF. Subsequently, when the LIDIS is at negative value, it shows that the ISD option has increased the hazard of the TPSF which indirectly reveals the potential of hazard conflicts introduced by the ISD option. In addition, the likelihood of risk is reduced or increased is captured not only within the main process unit but also the related site-process units such as auxiliary units, storages and transportations.

LIDIS represents the possibility of conflicts in the design options that would contain the inherent safety advantages and disadvantages regardless of the type of hazards. Hence, LIDIS objective is to select or screen the inherently safer process unit at preliminary design stage that would have less likelihood to migrate the hazards to the internal or external processes. In order to estimate LIDIS, a simple interaction matrix is developed as a tool to evaluate the above conflicts since this method can combine multi-criteria in a single form. The approach used is similar with the chemical compatibility chart method introduced by Hendershot (2003) to identify the incompatibility of a chemical when it mix with other materials, but, in this new developed tool, the degree of conflicts is quantified via semi-quantitative approach.

Table 3.18: Target Process Safety Factors (TPSF) in LIDIS

Inherent Safety Principles	**Target Characteristics**	**Target Process Safety Factors (TPSF)**	
Substitution	Quality of materials used or produced	Hazardous of substances = NFPA ranking on flammability, explosive, reactivity and toxicity for feed, product and by-product	
Minimisation	Quantity of process inventory	Volume = percent accumulated in vessel and intermediate storage, amount of gas release, concentration	
Moderation	Operating and safe limit conditions	Thermal Runaway	Temperature effect = adiabatic temperature rise, time to maximum rate of runaway Pressure effect = vapour pressure, amount of solvent evaporated
		Fire and Explosion	Temperature effect = flash point, flammability limits, Pressure effect = fraction liquid vaporised, pressure build-up
Simplification	Easiness in the design and operating	Controllability – basic requirement	Basic controls in flow, temperature, pressure, level etc.
		Controllability – technical requirement	Advance technical control measures such as emergency cooling, quenching and flooding, depressurisation etc.
		Complexity on overall process unit and plant	Number of vessels, auxiliary units, frequency of transportation, complexity in maintenance etc.

The assessment of LIDIS is developed by a combination of qualitative knowledge of Inherent Safety principles with the process factors and its safety hazard characteristics in order to obtain the group of potential conflicts as described in section 1.2.2 as follows:

- potential conflicts between Inherent Safety Principles
- potential conflicts or deficiencies between Hazards
- potential conflicts within inherent safety principle itself

The likelihood study is facilitated by the Inherent Safety guidewords to trigger potential conflicts among the principles. For example, one ISD option proposed a smaller type of continuous reactor (application of *minimisation* principle) instead of a batch reactor but may require high temperature and pressure (conflict in application of *moderation* principle). Furthermore, this option may require frequent transportation of the material due to constraints in the on-site inventory (conflict in application of *simplification* principle). The analysis is also assisted by the guidewords of process and safety factors which could be relevant to signify the Inherent Safety Principles in order to prompt the potential conflicts within the Inherent Safety Principle itself. This arrangement enables effective interaction of potential conflicts between hazards and conflicts on the complexities of safety for the overall plant. For example, one ISD option proposed to use a less toxic solvent (application of *substitution* principle for *toxicity* aspect) but may have a lower boiling point that could lead to the possibility of a pressure hazard due to boiling solvent in the event of a runaway reaction (conflict in application of *substitution* for *flammability* aspect).

For this study, the focus of IS guidewords is limited to four IS principles as shown in Table 1.2 since these are the most general and widely applicable (Khan and Amyotte, 2003) especially at early design stage. The selection of guidewords for process and safety factors is determined based on the definition of IS principle itself. The suitability of the above factors is also depends on the stage of design since each design stage has their specific objectives to achieve and could only contain minimum process information. For example, the research and development (R&D) stage is the stage to select a feasible and profitable process route to produce the targeted product. The information required at this stage would consist of, for example, the reaction chemistry, the chemical and physical properties of the raw materials and the historical or patented process conditions to achieve the targeted product. Since the study focused at preliminary design stage, the guidewords for process and safety factors are limited to chemical and physical properties of the substances, process conditions and preliminary design data of the process units. These inputs are typically available in the simplified process flow diagram (PFD) and the preliminary equipment design. Table 3.18 earlier shows the proposed IS guidewords and the suitable target process safety factors for LIDIS to assess the ISD options.

The computation of LIDIS for a specified option, LIDIS_{op} is calculated by dividing the actual Likelihood Score of Inherently Safer Design (LSISD_{act}) and the maximum $LSISD_{max}$ that the option should be achieved as shown in the following equation:

$$LIDIS_{op} = \frac{LSISD_{act}}{LSISD_{max}} \tag{3.20}$$

For an option, the actual score, $LSISD_{act}$, is derived from the summation of Total Likelihood Score (TLS) of all IS principles. The TLS for each principle is estimated by adding the Process Factor Score of each design factor in the individual IS principle as illustrated in Equation 3.21 and 3.22, respectively:

$$LSISD_{act} = TLS_{sub} + TLS_{min} + TLS_{mod} + TLS_{sim} \tag{3.21}$$

$$TLS_{j} = \sum_{i=m}^{n} PFS_{i} \tag{3.22}$$

where the subscripts j, i, n, sub, min, mod and sim refer to principle j, process factor score i, design factor m, design factor n, substitute, minimise, moderate and simplify, respectively.

Subsequently, Equation (3.23) is used to estimate the $LSISD_{max}$ as follow:

$$LSISD_{max} = N_{df} \times 10 \tag{3.23}$$

where N_{df} is the total number of design factor (df) considered for all IS principles in a specified option.

A guideline to determine the deviation of the hazard transfer is developed using an index range with increment of 1 is developed from +10 to -10 to indicate the likelihood of a hazard migrated. The difference in each process safety factor for the base case and the ISD option is estimated using Equation 3.24 and 3.25, respectively:

$$\mathrm{PFS_i} = \mathrm{Max}\left[-10, \left(1 - \frac{\mathrm{df_{op}}}{\mathrm{df_{bc}}}\right) \times (10)\right] \quad \text{if } \mathrm{df_{op}} > \mathrm{df_{bc}} \tag{3.24}$$

$$\mathrm{PFS_i} = \mathrm{Min}\left[10, \left(1 - \frac{\mathrm{df_{bc}}}{\mathrm{df_{op}}}\right) \times (-10)\right] \quad \text{if } \mathrm{df_{op}} < \mathrm{df_{bc}} \tag{3.25}$$

where the subscript i refers to Process Factor Score i; $\mathrm{df_{op}}$ is the design factor for the ISD option and $\mathrm{df_{bc}}$ is the design factor for the base case.

The Likelihood Score of TPSF for *substitute, minimise and moderate* in Table 3.18 is estimated using the actual value of the TPSF from each design option. However, the estimation of Likelihood Score for *simplify* principle ($\mathrm{LS_{sim}}$) which representing the complexity in process safety controls requirement, layout, handling and transportation need to refer to guidelines as shown in Table 3.19 and 3.20. This is required since some of the information may not be available at early stage of design. Therefore, the guidelines below are developed to assist subjective criteria. The first index table is to determine the degree of requirement for basic and add-on control requirements and the second table is for design complexity and frequency of handling. The indices are applied to the initial design and also the ISD options. This index is determined using fundamental basic design calculations, literatures and also expert judgements because the design factors considered in this principle are suffered from limited information at early design stage compare to other principles.

Table 3.19: Guidelines for $\mathrm{LS_{sim}}$ for requirement of basic and advance controls requirement

Description	**Index value**
Essential	10
Very important	9
Important	8
Not important but required	7
Required	6
Requirement is moderate	5
Good if available	4
Requirement does not affect process	3
Not required	1-2

Table 3.20: Guidelines for LS_{sim} for complexity and handling of process unit

Process Complexity	Description	Index value
Agitator Auxiliary unit; compressors, pumps Multi-unit, parallel, length of piping, Storages Frequency of handling Mode of transportation	Essential	10
	Very important	9
	Important	8
	Not important but required	7
	Required	6
	Requirement is moderate	5
	Good if available	4
	Requirement does not affect process	3
	Not required	1-2

3.7.3.3 Inherent Risk Matrix

In order to identify the best ISD option, a risk ranking is developed to illustrate the criticality of the hazards in each ISD option as a guideline in the decision making. A risk matrix concept is applied by categorising the DI and LIHM into several levels of criteria to demonstrate the degree of risk as shown in Table 3.21.

The DI scale represents the damage distance from the point source of release. The severity from the damage is scaled to 5 levels to show the severity from Highly High Severity (HHS) to Highly Low Severity (HLS). The DI value is equally distributed with the highest index is 100 to represent any damage distance 200 meters and above. Then, the lowest index is set at 5 to represent the damage distance of 10 meters and below as the HLS level.

The LIHM of ISD option that would cause hazard conflicts is reflected through 5 levels which are from Highly High Likelihood (HHL) to Highly Low Likelihood (HLL) level. As explained earlier, the LIHM of one ISD option is estimated based on the deviation created in the design factors in comparable to the base case design. The deviations could lead to the uncontrollable stage of the hazards either by creating new hazards or escalating the current existing ones. Therefore, the ISD option is considered as ideally inherently safer when it has attained the lowest LIHM at 0 because the possibility of hazard conflicts in this option is highly unlikely. Then, the ISD option that has LIHM less than 1 shows that ISD option would probably have fewer hazard conflicts. The ISD option with LIHM equivalent to 1 is expected to have the similar potential hazards as the base case design which could have been transferred to the other parts of the plant. Finally, the ISD option which is regard as not inherently safe is the ISD option that obtained the LIHM of more than 1 to the highest LIHM at 2. This index value demonstrates that the modification proposed by the ISD option would create substantial hazard conflicts by critically increasing the hazards in the process unit or the other parts of the plant.

Table 3.22 is developed to illustrate the criticality of the proposed ISD options based on IRDI. This guideline is to assist the designer to choose the design option that is sufficiently close to the ideal ISD. The risk index is categorised based on the lower to upper limit outputs attained from both DI and LIHM to inform the potential performance of the ISD options.

Table 3.21: Risk ranking for IRDI based on DI and LIHM

Inherent Risk Design Index (IRDI)			**Likelihood Index of Hazard Migrate (LIHM)**				
			HLL	**LL**	**ML**	**HL**	**HHL**
			0	**0.5**	**1**	**1.5**	**2**
Damage Index (DI)	**HLS**	**5**	0	2.5	5	7.5	10
	LS	**25**	0	12.5	25	37.5	50
	MS	**50**	0	25	50	75	100
	HS	**75**	0	37.5	75	112.5	150
	HHS	**100**	0	50	100	150	200

where;

DI	**LIHM**
HLS – Highly Low Severity	HLL – Highly Low Likelihood
LS – Low Severity	LL – Low Likelihood
MS – Medium Severity	ML – Medium Likelihood
HS – Highly Severity	HL – High Likelihood
HHL – Highly High Severity	HHL – Highly High Likelihood

The IRDI is developed based on several literatures and guidelines in order to determine the acceptable size of damage area impacted by fire and explosion at worst case scenario (Dow Fire & Explosion Index, 1997; Piang and Ahmad, 2002; CCPS, 1996; Lees, 1996). For instance, Dow F&E Index has considered the severe level at index of 159 and above which represent about 41 meters of exposure radius after taking into account the process control measures (Dow F&E Index, 1997). Therefore, as demonstrated in Table 3.22, the ISD option with IRDI value at 76 and above is determined as a design that has a combination of medium to high potential energy that would cause high severity of damage and potentially to create high hazard conflicts if the proposed ISD is implemented. As a result, it is recommended to perform detailed assessment and redesigns are highly required before implementing the ISD option. Apart from this HIGH category, the IRDI value in between 26 to 75 is considered as MEDIUM risk where the proposed ISD option would cause medium severity damage due to hazard conflicts. Thus, review of the design may require based on the hazard conflicts predicted from the LIHM stage. Otherwise, the designer could consider adding other safety measures based on active and passive control measures which could lower the hazard conflicts and the damage potential. Finally, the ISD option which falls under LOW risk is considered as inherently safer design and redesign may not required. However, the design should follow standard process safety management throughout the stage of design in order to sustain the safety of the process.

Table 3.22: Guidelines for criticality of IRDI risk level

IRDI	Risk Level	Design Criticality Description
76-200	**High**	Design option is highly critical Redesign is highly required Technical safety measures are highly required
26-75	**Medium**	Design option is critical Redesign may required Technical safety measures may required
0-25	**Low**	Design option is inherently safer Additional risk reduction may not required Proceed with standard process safety management

For a specific case when the designer make a decision to select an ISD option that has low DI but consider to be high LIHM, they could possibly conduct further investigation by re-observing the LIDIS assessment where the trade-off or conflict of hazards are assessed. For example, if the design is causing potential of transportation hazards as estimated by the *simplify* principle, the designer would have ample time to change the mode of transportation to the railway or pipeline mode. Moreover, the designer could consider other actions to be taken such as to redesign the option, to perform detail experiments or to develop the second stage of risk reduction measures as the final alternatives. This risk ranking is expected to alert the designer on any potential process safety issues at early stage of design.

By monitoring the IRDI ranking, this guideline will allow the designer to compare the risk in between ISD options as the indicator to evaluate the best inherently safer design after meticulous consideration on potential of new hazards and hazard migration beyond the studied process unit. After completing this final stage of analysis, the designer should be able to identify the best ISD option and may proceed to the next stage of the design process with the chosen ISD option that is expected to be AiSAP.

CHAPTER 4
VALIDATION AND CASE STUDIES

4.1 Chapter overview

This chapter presents the validation works, conducted for the tools that were developed through the application of qualitative and quantitative methods, within the proposed IISDET framework, using several case studies. Brief descriptions on the background of the chosen process and safety issues or problems, are highlighted prior to the validation. The results obtained are also supported through analysis and discussions on the effectiveness and usefulness of IISDET, in evaluating process design, with the aim of achieving a process that is inherently safer.

Validation of the proposed quantitative tool i.e., QIISD, is carried out in order to estimate the energy factors i.e., F_1 for combustion energy, F_2 and F_3 for physical energy, and F_4 for reaction energy, against published case studies used in journals written by previous researchers. The objective of the validation works (as in Case I) is to ensure that the present study has applied similar formulations with no discrepancies in the results, after the comparisons have been made with the published results.

Application of the qualitative and quantitative tools, developed within the IISDET, is demonstrated in this chapter using several case studies, in accordance with the stages developed in the framework. The second case study (i.e., Case II) illustrates the application of the qualitative tool, which is referred to as QEISD, in order to identify the inherent hazards of using a RIP tool for the batch reactor, which is widely utilised in a nitration process plant. Then, the IDH tool is applied to the same case study, to illustrate the generation of potential ISD options, in eliminating or reducing the identified hazards, according to the ISD concept. The third case study (i.e., Case III) demonstrates the ISM method, which is applied for the purpose of identifying a suitable solvent for a selective catalytic reactor. This tool allows evaluation using the qualitative method to select the best option that has least conflict or trade-offs, to the overall process design. The fourth case study (i.e., Case IV) represents the application of both qualitative and quantitative tools, in evaluating the Inherent Safety conflicts, in order to determine the best ISD option, for the reactor unit of the nitration process. Finally, the fifth case study (i.e., Case V) is solely used to demonstrate the capability of the IRDI tool to evaluate the inherently safer design in hydrogen storage systems, and hence, to discover the criticality of each design option via an IRDI risk level. In order to facilitate an understanding of the developed methodologies, where appropriate, some examples have been given throughout the results and discussions for each case study, and explanations are provided accordingly.

4.2 Case I: Validation of energy factors using sulfonation reaction unit

The energy factors used to predict the potential damage of fire and explosion in the QIISD method are the combustion, reaction, and physical energies, developed by Khan et al., (2001) as described in Section 2.4.3.1. Some examples of physical energy are hazardous energy developed through overpressure, mechanical failure, over-temperature, etc., of the pressure system. However, the reaction energy (F_4) used in this study was modified, as described in Section 3.7.3.1. Thus, this validation is performed for the above energy factors, prior to the modification of the reaction energy.

The case study used is taken from Khan et al., (2001) involving a reactor unit from a sulfolane manufacturing plant. Butadiene and sulphur dioxide are stored in a liquid state under high pressure. The process involves a reaction of the two compounds under controlled temperature and pressure conditions, in a stirred tank reactor (CSTR), to produce sulfolene. The temperature of the CSTR is maintained at approximately 75°C using a cooling liquid (water mixed with methanol). The ratio of butadiene to sulphur dioxide in the reactor is 1:1.2. The final output product of the reactor is sulfolene, with 99% purity. The reaction between butadiene and sulphur dioxide is exothermic under normal operating conditions. Moreover, the operating condition of the reactor is a high pressure of 5atm and a temperature of 75°C. The reaction is highly susceptible to undesirable side reactions of high temperature and low pressure conditions. The addition of approximately 200ppm of solvent (tert-butyl cethchol) inhibits these side reactions. It is important to note, that butadiene and sulfolene are highly flammable and that sulphur dioxide is toxic. A slight increase in temperature of the sulfonation reactor could cause a runaway reaction to occur, generating excessive heat, which leads to a sudden rise in temperature and pressure. If the pressure escalates too high, it may cause the reactor to burst (BLEVE/CVCE) and/or release chemicals. Any reduction in the butadiene to sulphur dioxide ratio below 1:1 may also cause a side reaction (i.e., the formation of polymer butadiene sulfone; an undesirable hazardous chemical). A summary of information and data used for the validation of the energy factors is shown in Table 4.1.

Table 4.1: Input data for validation of energy factors

Input data available based on Khan et al., (2001)	
Process Unit	CSTR – 3 stages
Chemical	butadiene, sulphur dioxide, butadiene-sulfone (sulfolene)
Reaction temperature	75°C
Reaction pressure	5atm
Capacity of unit	5tonnes
Characteristics of chemical	NFPA rating - 2 (Flammability), 3 (Reactivity)
Other input data used in this study	
Heat of combustion	46966kJ/kg (Perry's Handbook, 2007)
Vapour pressure	10 bar (Air Liquide, 2009)
Flash point – butadiene	-76°C (NIST, 2008)
Fire point – butadiene	-66°C (NIST, 2008)
Heat of reaction	944.86kJ/kg (McKetta, 1977)

4.2.1 Results of validation and discussions

The energy factors for combustion (F_1), physical (F_2 and F_3), and reaction (F_4) for the sulfonator unit, are estimated according to Equations (3.2) – (3.5), as described in Chapter 3. All results are compared to the estimated energy factors published by Khan et al., (2001). Table 4.2 illustrates the results of the energy factors, calculated for the present study, in comparison to the published results. The results show that the present study has agreement with the published data, with a minor percentage of differences. These differences could be due to several factors, such as the estimation of heat combustion for butadiene, the estimation of vapour pressure at the given process temperature, and the heat reaction for reaction energy, which could be different based on the references used (McKetta, 1977; Perry's Handbook, 2007; NIST, 2008; Air Liquide, 2009), could contribute to the difference in the results since these values were not published by Khan et al., (2001). However, the trend results of the present study are in the same range as Khan et al., (2001). Based on the above results, the formulation of energy factors, and penalties, QIISD will be further developed based on these validation works.

Table 4.2: Calculated energy factors for the sulfonator unit

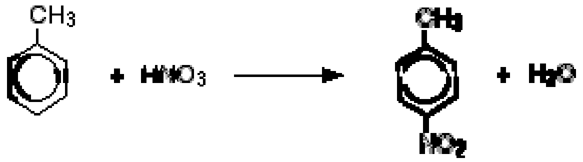
Energy Factors	Khan et al., (2001)	QIISD	Differences (%)
Combustion – F_1	4.89E+04	3.53E+04	27.8
Physical – F_2 and F_3	5.90E+03 22.067	4.62E+03 33.69	21.7 52.7
Reaction – F_4	1213.91	1255.57	3.4

4.3 Case II: Identification of inherent hazards and generation of ISD options for nitration of toluene using the RIP and IDH tools

The nitration of toluene process in a batch reactor is used to illustrate the application of qualitative tools in IISDET methodology. Nitration of aromatics is one of the oldest and most important industrial reactions for the formation of intermediates of many compounds, including pharmaceuticals, dyes, explosives, pesticides, etc. In spite of that, the nitration reaction is the second most hazardous reaction after polymerisation, which caused approximately 15 serious incidents in the UK involving thermal runaway chemical reactions in a batch/semi-batch reactor (Barton and Rogers, 1997). Moreover, the US Chemical Safety and Hazard Investigation Board (USCSB) reported that 167 serious chemical incidents in the US, involved uncontrolled chemical reactions. For this reason, the nitration reaction was selected to illustrate the applicability of QAISD since the initial design of the nitration process is based on a batch system, where the reaction is generally fast and highly exothermic, involving flammable organics and a toxic mixture of acids. In addition, reactors represent a large portion of the chemical process, where most of the inherent dangers are present and with the thoughts that if inherent safety could be incorporated early in the reactor process, then the remaining of hazards in the downstream process would be preventable and an inherently safer process as a whole could be achieved.

Industrially, the production of nitrotoluenes is achieved by mixing nitric acid and sulphuric acid in a two-phase liquid-liquid reaction, in which toluene diffuses into the aqueous acid phase and the reaction takes place in the acid phase. The stoichiometric of this reaction is given by:

$$\text{toluene} + \text{nitric acid} \xrightarrow{\text{sulphuric acid}} \text{nitrotoluene} + \text{water}$$



Sulphuric acid is used to donate a proton to the nitric acid, thus forming a nitronium ion, which then reacts with toluene to form the three isomers of nitrotoluene in the mononitration process (Halder et al., 2007). Table 4.3 is a summary of a typical database for a batch reactor process to produce mono-nitrotoluene based on several references (Othmer, 2004; Ullmans, 2003; Bretherick's, 1995) as the base case design.

Table 4.3: Typical properties of toluene nitration in a batch reactor (Othmer, 2004; Ullman's, 2003; Bretherick's, 1995)

Process and Safety Parameters	Typical Values
Chemicals	Toluene, 28-32wt% nitric acid, 52-56wt% sulphuric acid, 12-20wt% water
Products	55-60wt% *o*-nitrotoluene, 3-4wt% *m*-nitrotoluene, 35-40wt%*p*-nitrotoluene
Reactors	Liquid phase Batch
Capacity	6000-L
Reaction time	2-4h
Heat of reaction	-216kJ/kg (Exothermic)
Reaction temperature	35 – 40^{o}C
Reaction pressure	1atm
Decomposition temperature	160^{o}C
Heat of decomposition	-162kJ/mol
Flammability, reactivity	Toluene, Nitric acid, Sulphuric acid
Hazardous by-products	NO_x, SO_x, 4-nitrotoluene-2-sulfonic acid

4.3.1 Results analysis and discussions

The potential of inherent hazards in the toluene nitration process is explored in this study using the RIP tool. Table 4.4 shows the predicted hazards after applying the RIP tool in Stage I of QEISD. Based on the information given in Table 4.3, there are eleven potential inherent hazards i.e., the inherent hazards of H1 to H11, such as highly-reactive reagent, excessive heat of reaction, thermally decomposed chemical, large inventory, etc. After assessing the hazards with process safety references and nitration process literatures, nine out of the eleven inherent hazards have been screened as being prioritised hazards. These prioritised hazards have been identified as the inherent hazards that could lead to fire and explosion, due to thermal runaway. The prioritised hazards for H1 and H3 are in agreement with several other publications, e.g., Chen and Wu (1996) and Chen et al., (1998). Their experiments showed that the desired reaction has a high potential to trigger a thermal explosion, which is caused by the decomposition of mononitrotoluene and nitric acid.

The prioritised hazards of H1, H2, H6, and H10, are selected in order to illustrate the application of the IDH tool. As described in Chapter 2, each hazard is required to go through ISD Heuristics i.e., Hazard Elimination, Consequence Reduction, and Likelihood Reduction, in order to generate all possible ISD options. Tables 4.5a and 4.5b provide the summary of the generated ISD options, to eliminate or minimise the above hazards. As described earlier, every single hazard will be examined through ISD heuristics and the related IS principles, in order to generate suitable ISD options. For example, when the identified hazard, such as the highly exothermic reaction of toluene nitration in liquid phase (H6) is assessed using the IDH work-flow diagram, five potential ISD options are generated. For example, the substitution to vapour phase reaction (OP8), minimisation of volume by replacing the batch reactor with a continuous or intensified reactor (OP3), moderation of current reaction energy by using diluted nitric acid (OP5), etc. Several options are also repeated in other hazards during this process,in order to meet the objective of this stage, which is to create all possible ISD options and not to conclude at the first identified solution. In addition, this IDH tool also allows the identification of potential conflicts, due to the implementation of IS principles, as shown in both tables.

Some of the identified ISD options are found to be feasible to eliminate the hazard, such as the option to nitrate toluene via a vapour phase reaction (OP8) (Dagade et al., 2002; Sawant et al., 2007; Pirngruber et al.; 2007). The vapour phase nitration of toluene is found to be a very fast reaction of less than 1-hour reaction time that will not allow the accumulation of reactive reagents. The possibility of decomposition, due to excessive heat of the reaction when there is a failure in the cooling system, could be minimised or eliminated through this ISD option. This option could also minimise the inventory of reaction mixture, as it is repeated as an option to minimise the large liquid phase inventory (H10).

In addition, OP3 proposed to reduce the volume by replacing the batch reactor with a continuous mode or intensified reactor, such as a micro reactor, which is also possible to minimise the consequence of thermal runaway, due to the high heat of the reaction as the minimum volume of the reaction mixture available in the vessel during the process. This was proven possible through recent findings by Halder et al., (2007) that micro reactors have been shown to have a very high heat transfer rate, due to their high surface area to volume ratio, which enables the micro reactors to control highly exothermic reactions efficiently. One of the identified new hazards, if the design is modified according to OP3, is the potential of complexity in controlling the intensified reactor, which is in agreement with Luyben and Hendershot's (2004) findings, that the fast dynamics of the reactor could endanger the stability of the process against disturbances, and hence, could lead to a thermal explosion.

Based on the above results, the designer would have many ISD options to consider during the early design stage, and thus, be able to conduct necessary investigations and experiments prior to choosing the best design option that is inherently safer. The identified solutions are also in contrast with the conventional safety measures to manage hazards of the toluene nitration process, which commonly focuses more on controlling the cooling system, installation of pressure relief devices, and classification of explosion zones (Shah, 2004). The identified ISD options (in Stage II) may need to proceed to the evaluation stage for selection of the most appropriate design solution; which is not only inherently safer, but also could reduce the lifecycle cost of the process. Thus, the evaluation stage could be done using the

Table 4.4: Results from the application of RIP to identify inherent hazards in toluene nitration

QUALITATIVE EVALUATION OF INHERENTLY SAFER DESIGN (QEISD)

Stage I: Identification of Inherent Hazards using the RIP method

Process: *Production of Mononitrotoluene using mixed acid*

Process Unit: *Batch reactor* | Materials in Process Unit: *Toluene, Nitric acid, and Sulphuric acid*

Register			**Investigate**	**Prioritise**
Design Factor	**Process Attributed with Base Case data**	**Hazard Indicator**	**Predicted Hazard**	**Prioritised Hazard**
Chemicals	reactant: toluene, nitric acid, sulphuric acid	reactive, incompatibility, flammability, toxic, stability, etc.	H1: use a highly reactive reagent	H1: highly reactive reagent (nitric acid)
			H2: use a highly concentrated reagent	H2: high concentration reagent (sulphuric acid)
	end-product: mononitrotoluene		H3: use a chemical that easily decomposes	H3: decompose chemical (mononitrotoluene)
	by-product: NO2, SOx, H2O		H4: create incompatibility of reagent and products	H4: incompatible reaction (nitric/sulphuric acid with H2O)
			H5: use a high energy molecular group	H5: high energy molecular group (nitro compounds)
Reaction conditions	heat of reaction: -216kJ/kg	exothermic, hazardous inventory, elevated temperature or pressure, high concentration, liquid or vapour phase, etc.	H6: use reaction route that produces high heat of reaction	H6: high heat of reaction route (mixed acid)
	volume: 6000L liquid inventory		H7: operate at a high temperature to activate decomposition	
	temperature: max 25degC, due to highly exothermic		H8: operate at low temperature to accumulate high reagent	
	pressure: 1atm		H9: create high pressure, due to gas evolution	H9: create high pressure, due to gas evolution (by-products, such as NO2)
	concentration: 98% sulphuric acid, 60% nitric acid		H10: accumulate large inventory of liquid-phase mixture	H10: large inventory (liquid phase)
	reaction phase: liquid-phase			

<table>
<tr><th colspan="5">QUALITATIVE EVALUATION OF INHERENTLY SAFER DESIGN (QEISD)</th></tr>
<tr><th colspan="5">Stage I: Identification of Inherent Hazards using the RIP method</th></tr>
<tr><td colspan="5">Process: <i>Production of Mononitrotoluene using mixed acid</i></td></tr>
<tr><td colspan="3">Process Unit: <i>Batch reactor</i></td><td colspan="2">Materials in Process Unit: <i>Toluene, Nitric acid, and Sulphuric acid</i></td></tr>
<tr><th colspan="3">Register</th><th>Investigate</th><th>Prioritise</th></tr>
<tr><th>Design Factor</th><th>Process Attributed with Base Case data</th><th>Hazard Indicator</th><th>Predicted Hazard</th><th>Prioritised Hazard</th></tr>
<tr><td rowspan="3">Type of reactor</td><td>batch: large inventory</td><td rowspan="3">high inventory,
agitator speed,
hot spot,
etc.</td><td>H10: accumulate large inventory of liquid-phase mixture</td><td>H10: large inventory (batch reactor)</td></tr>
<tr><td>controls in agitation</td><td rowspan="2">H11: generate hot spot in a reactor</td><td rowspan="2">H11: hot spot generated in a reactor (speed of mixer)</td></tr>
<tr><td>controls of cooling system</td></tr>
</table>

Table 4.5a: Results of ISD options from the application of IDH (Stage II) to generate ISD options for toluene nitration process

QUALITATIVE EVALUATION OF INHERENTLY SAFER DESIGN (QEISD)

Stage II: Generation of Inherently Safer Design Options using the IDH method

Process: *Production of Mononitrotoluene using mixed acid*

Process Unit: *Batch reactor* | Materials in Process Unit: *Toluene, Nitric acid, and Sulphuric acid*

Prioritised Hazard	**ISD Heuristic**	**IS Guideword**	**ISD Indicator**	**ISD Variable**	**ISD Option**	**Prompts on potential of other hazards**
H1: highly reactive reagent (nitric acid)	Hazard Elimination	Substitute	hazardous substance	new or safer substances	OP1: substitute with less energetic nitrating reagent	decomposition due to batch reaction time
		Substitute	process route	new or safer process chemistry	OP2: substitute with energetic nitrating reagent such as acetyl nitrate	incompatibility with other reactants
	Consequence Reduction	Minimise	inventory	volume, process phase, new equipment	OP3: minimise volume use with CSTR/smaller reactor/intensified reactor	elevated operating conditions, increase complexity in control
		Minimise	energy	volume , reaction phase, new equipment	OP4:minimise volume use by changing reaction phase to gas	elevated operating conditions, increase complexity in control
		Moderate	reaction condition	temperature, pressure, dilution, catalyst	OP5: moderate reaction condition with dilute nitric acid	increase inventory of reactant
H2: high concentration reagent (sulphuric acid)	Hazard Elimination	Eliminate	hazardous substance	new or safer substances	OP6: eliminate with solid acid catalyst	toxic release
		Eliminate	process route	new or safer process chemistry	OP7: eliminate with green ionic liquid	toxic release
	Consequence Reduction	Minimise	inventory	volume, process phase, new equipment	OP3: minimise volume use with CSTR/smaller reactor/intensified reactor	elevated operating conditions, increase complexity in control
		Minimise	energy	volume , reaction phase, new equipment		
		Moderate	reaction condition	temperature, pressure, dilution, catalyst	OP5: moderate reaction condition with dilute sulphuric acid	

Table 4.5b: ISD options for inherent hazards H6 and H10 after application of IDH (Stage II) for toluene nitration process

QUALITATIVE EVALUATION OF INHERENTLY SAFER DESIGN (QEISD)						
Stage II: Generation of Inherently Safer Design Option using the IDH method						
Process: *Production of Mononitrotoluene using mixed acid*						
Process Unit: *Batch reactor*				Materials in Process Unit: *Toluene, Nitric acid, Sulphuric acid*		
Prioritised Hazard	**ISD Heuristic**	**IS Guideword**	**ISD Indicator**	**ISD Variable**	**ISD Option**	**Prompts on potential of other hazards**
H6: highly heat of reaction route (mixed acid)	Hazard Elimination	Substitute	hazardous substance	new or safer substances	OP8: substitute with vapour phase reaction route	elevated operating conditions, increase complexity in control
			process route	new or safer process chemistry		
	Consequence Reduction	Minimise	inventory	volume, process phase, new equipment	OP3: minimise volume use with CSTR/smaller reactor/intensified reactor	elevated operating conditions, increase complexity in control
		Minimise	energy	volume, reaction phase, new equipment	OP9: minimise volume with increase in mixing speed	
		Moderate	reaction condition	temperature, pressure, dilution, catalyst	OP5: moderate reaction energy with dilute nitric acid	toxic release
		Moderate			OP10: moderate reaction energy with catalyst	autocatalysis
	Likelihood Reduction	Simplify	complexity	strength of equipment, min no of units/utilities, resistant materials, process layout	OP11: simplify vessel by designing withstand high pressure vessel	
			loss of containment	strength of equipment, resistant materials		

QUALITATIVE EVALUATION OF INHERENTLY SAFER DESIGN (QEISD)

Stage II: Generation of Inherently Safer Design Option using the IDH method

Process: *Production of Mononitrotoluene using mixed acid*

Process Unit: *Batch reactor*

Materials in Process Unit: *Toluene, Nitric acid, Sulphuric acid*

Prioritised Hazard	**ISD Heuristic**	**IS Guideword**	**ISD Indicator**	**ISD Variable**	**ISD Option**	**Prompts on potential of other hazards**
H10: large liquid phase inventory (batch reactor)	Hazard Elimination	Substitute	hazardous substance	new or safer substances	OP8: substitute with vapour phase reaction route	elevated operating conditions, increase complexity in control
			process route	new or safer process chemistry		
	Consequence Reduction	Minimise	inventory	volume, process phase, new equipment	OP3: minimise volume use with CSTR/smaller reactor/intensified reactor	elevated operating conditions, increase complexity in control
		Moderate	energy	volume , reaction phase, new equipment	OP9: moderate energy with increase in mixing speed	autocatalysis
			reaction condition	temperature, pressure, dilution, catalyst		
	Likelihood Reduction	Simplify	complexity	strength of equipment, min no of units/utilities, resistant materials, process layout	OP12: simplify vessel with gravity liquid transfer to avoid leakage	
			loss of containment	strength of equipment, resistant materials		

end-user's expert judgement. Selection could be based on the feasibility of the design option, preliminary design costs, safety impacts, etc.

4.4 Case III: Qualitative evaluation of ammonia for selective catalytic reactor in controlling NO_x emissions using the ISM tool

This case study is based on a journal published by Study (2007), which describes the actual practice of identifying an inherently safer solvent for Selective Catalytic Reduction (SCR). With the objective to find a suitable ammonia feedstock, to be supplied to SCR at the preliminary design stage, the ISM tool is used to evaluate the identified ISD options qualitatively.

A steam production unit is required by new environmental regulations, to reduce nitrogen oxide (NO_x) emissions. Thus, a design team is formed to assess different NO_x reduction options and the team chose to install a SCR, which is aimed at reducing NO_x in the boiler flue gas, to nitrogen and water. This is done by a reaction process between NO_x and ammonia in the SCR catalyst bed. However, ammonia is well known for its hazardous toxic characteristics. Exposure to ammonia vapours or liquid has a potential for serious injury or fatality, in terms of its toxicity, and there are major regulatory requirements, which are specifically USEPA and US OSHA; which classify anhydrous ammonia as a hazardous material. Ammonia, in a concentration of above 20%, will present a significant danger to human health. Therefore, the transportation, storage, and handling of this chemical, triggers stringent safety and environmental regulatory requirements, in terms of risk management plans, accident prevention programmes, emergency response plans, and release analysis (Mahalik et al., 2010). Thus, it is crucial to understand the hazards and risks associated with the processing and handling of ammonia-based processes. The hazardous characteristics and regulatory requirements of ammonia are shown in Table 4.6.

The initial design, proposed by the design team, is to use existing liquid anhydrous ammonia supplied by a nearby processing unit. A vaporizer skid, using steam to vaporise the liquid ammonia prior to injecting it into the SCR, is proposed to be installed near to the boiler. The operating temperature of SCR is 150-500°C and the piping is to be minimised as much as possible to 600ft. of 2inch pipe. Figure 4.1 shows the illustrated Process Flow Diagram (PFD) for the supply of liquid anhydrous ammonia. The other two design proposals are aqueous ammonia (Figure 4.2) and anhydrous ammonia vapour (Figure 4.3) that is based on the design team's proposals. The final potential ISD option that is considered based on the findings from the present research works, is to substitute the initial proposal with urea.

Table 4.6: Physical and hazardous properties of ammonia and regulatory requirements (Cameo Chemicals, 2010)

Colour	Colourless
State	Gas
Relative density, gas	0.6 (air = 1)
Relative density, liquid	0.7 (water = 1)
Vapour pressure	124 psi at 20°C (68°F)
Boiling point	-33°C (-27°F)
Solubility in water	Completely soluble
Percent volatility (%)	100
Lower explosive limit (%)	15
Upper explosive limit (%)	30
Immediately dangerous to life and health (IDLH)	300ppm (NIOSH, 2003)
Emergency Response Planning Guidelines (ERPG) up to 1 hour exposure durations (AIHA, 2008)	
ERPG 1	25ppm
ERPG 2	150ppm
ERPG 3	750ppm
Process Safety Management (PSM)	Threshold quantities of 3732 kg (10,000 lbs.)
Risk Management Plan (RMP)	

Aqueous ammonia is suggested as one of the ISD alternatives, due to its low vapour pressure, which significantly reduces the hazard distance in case of a leak or spill. For aqueous ammonia, the process team proposed to deliver the solvent to the boiler facility via a connection downstream from the storage tank. A 2000ft.2 inchpipeline is required to connect the tank to the boiler. In addition, the tank requires new positive displacement pumps to supply the aqueous ammonia. Furthermore, a temporary supply alternative had to be built into the design, since temporary shutdowns are required of the aqueous ammonia tank. To accommodate these supply requirements, additional connections and provisions are made for tanker truck deliveries of aqueous ammonia. Figure 4.2 shows the proposed supply of aqueous ammonia to the SCR process.

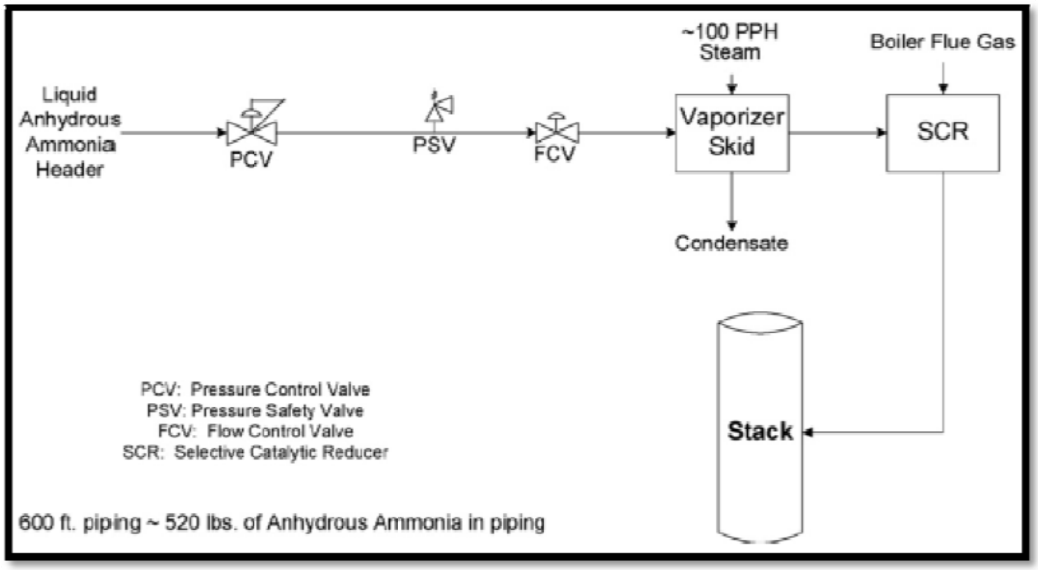


Figure 4.1: Initial ammonia proposal: Liquid anhydrous ammonia supply (Study, 2007)

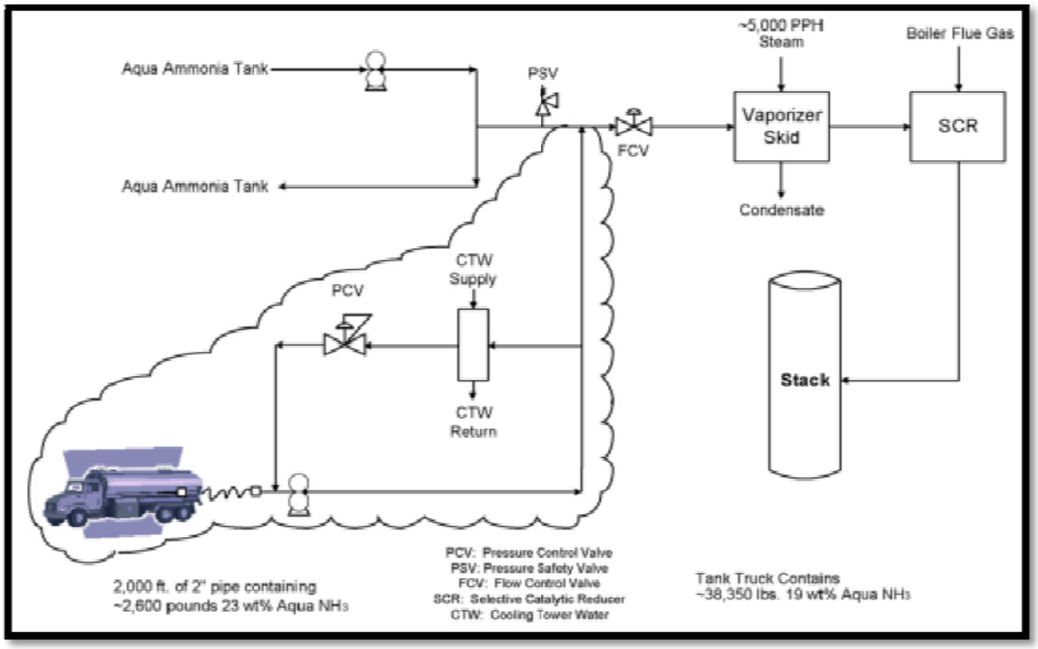


Figure 4.2: Aqueous ammonia supply proposal (Study, 2007)

The third option is the anhydrous ammonia in vapour phase, which is available from a nearby process unit via 2000 ft. pipeline. A redundant instrument is proposed to solve the flow control issues. The ammonia pressure is suggested to be at 25 psi, in order to avoid condensation in the transfer piping. Moreover, low-pressure steam is added to the ammonia, prior to its injection into SCR, as a diluent to more evenly disperse the ammonia in the catalyst bed. Figure 4.3 shows the proposed flow of the anhydrous ammonia vapour option.

The final option is to replace the initial design with urea-based ammonia, after applying the 'substitution' principle, in the Stage II analysis. Since this option is not included as one of the potential ISD options by Study (2007), a simplified PFD (shown in Figure 4.4), which is described by Salib and Keeth (2003) for an Ammonia-On-Demand system, is proposed to be attached to the SCR. The extension of the plant consists of dry urea unloading equipment, a storage silo, a dissolving tank using de-ionised water, a feed tank and pump, a solution heater, and a hydrolysing reactor to convert urea to ammonia, before it is transferred to the SCR. Table 4.7 shows the properties of the urea used in this case study, which is collected from reference.

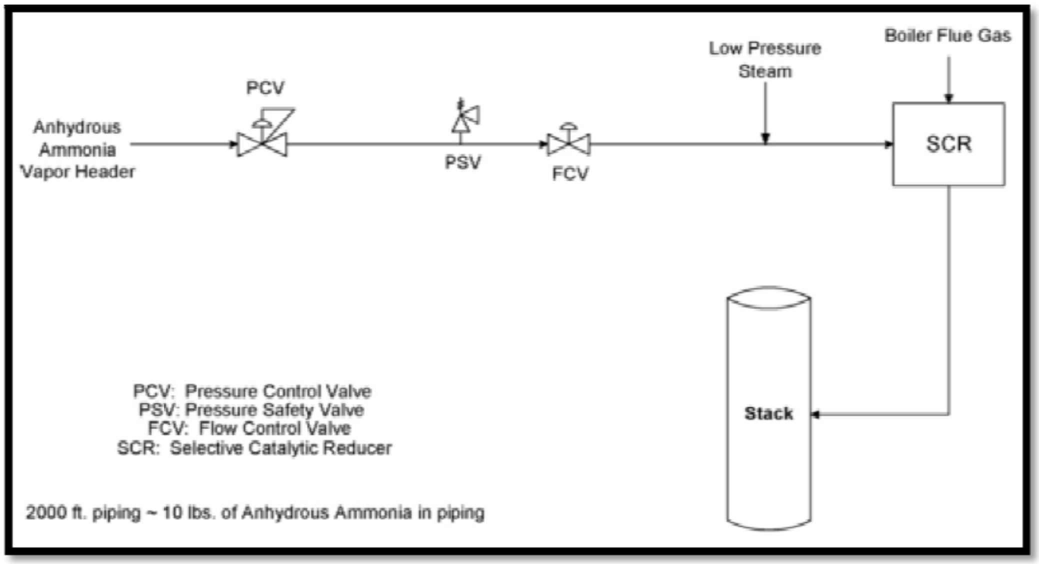


Figure 4.3: Anhydrous ammonia vapour supply (Study, 2007)

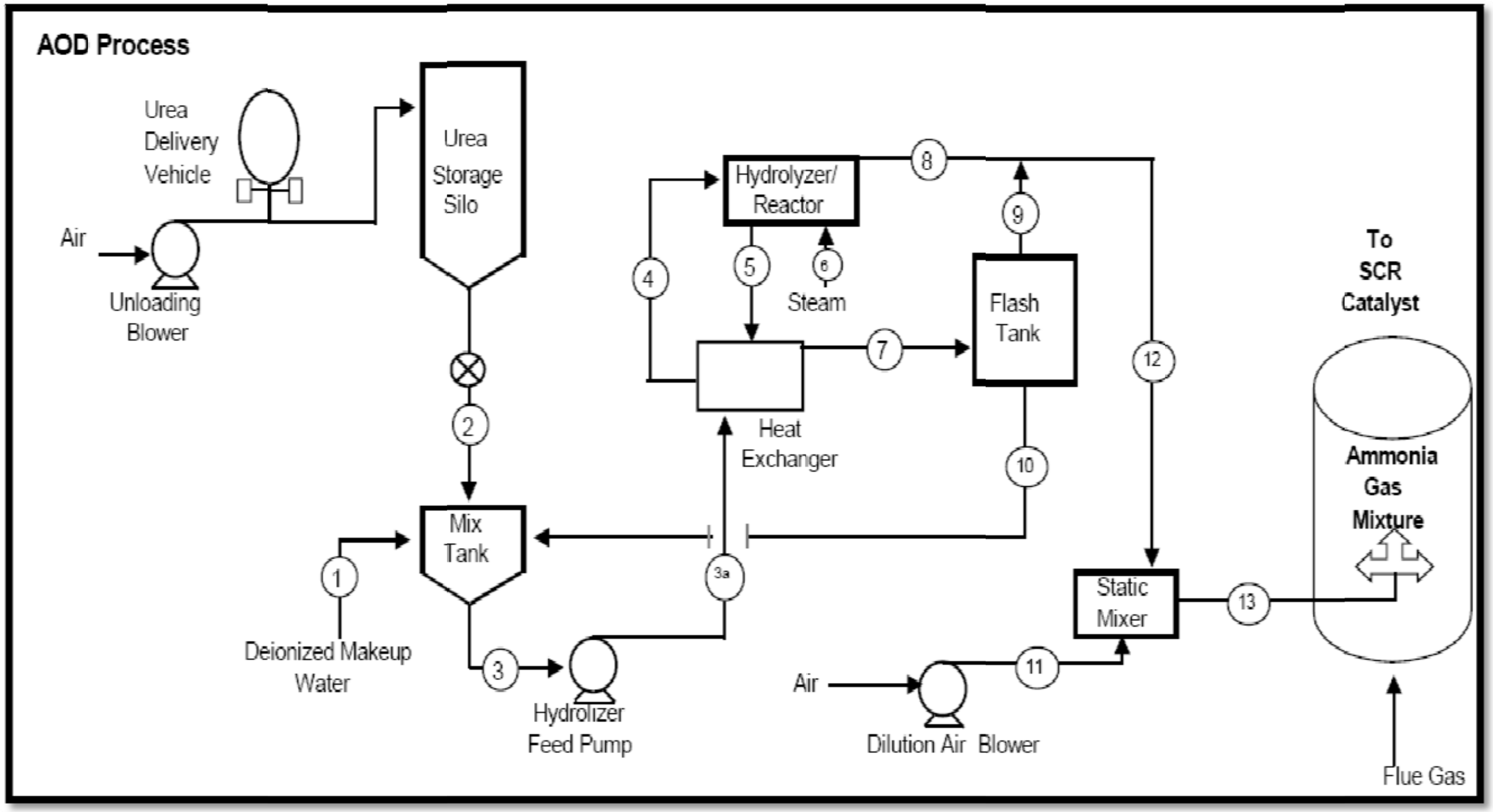


Figure 4.4: Urea-based ammonia using an Ammonia-On-Demand (AOD) system (Salib and Keeth, 2003)

Table 4.7: Properties of urea (Cameo Chemicals, 2010)

Odourless or slight ammonia odour
pH: 7.2 (10% water solution)
Decomposes at 132.7°C; into ammonia and carbon dioxide. If burned, emits small amounts of nitrogen oxide
Solubility in water is 119g per 100g water at 25°C
Specific gravity: 1.34 at 20°C, heavier than water (1)
Molecular weight: 60.06

4.4.1 Results analysis and discussions

Relevant data and information have been extracted from selected references (CCPS, 2008; Salib and Keeth, 2003) to assist in the application of the ISM tool, in order to identify the suitable ISD option, which has less conflict or trade-off, qualitatively. Table 4.8 summarises the inventory of ammonia from each ISD option supplied to the SCR process. The estimated amount of ammonia is based on the mass of ammonia inside the transfer piping and associated equipment, using the density of ammonia and water at 27°C, which is 593kg/m^3 and 993kg/m^3, respectively.

Table 4.8: Comparison of inventory for the ammonia based process (Study, 2007)

Option	**Piping length (ft.)**	**Volume (ft^3)**	**NH_3 Mass (lbs.)**
Option 1: Anhydrous liquid ammonia – base case	600 (183m)	14 (0.4m^3)	520 (194kg)
Option 2: Aqueous ammonia (23wt% NH_3)	2,000 (610m)	47 (1.3m^3)	600 (224kg)
Option 2:Aqueous ammonia tanker truck (19wt%NH_3)	n/a	652 (18.5m^3)	7,300 (2725kg)
Option 3: Anhydrous ammonia vapour	2,000 (610m)	47 (1.3m^3)	10 (4kg)
Option 4: Urea-based ammonia	Extension of plant is required (Salib and Keeth, 2003)	n/a	n/a

n/a: not applicable

Table 4.9 shows the results from the application of the ISM tool, which demonstrates that there are potential conflicts in the ISD options. The ISM tool revealed possibilities of conflict in the hazards between the principles and within the principle itself, which could specifically affect process safety performance and

Table 4.9: ISM results of the inherently safer reactant for Selective Catalytic Reduction (SCR) System

QUALITATIVE EVALUATION OF INHERENTLY SAFER DESIGN (QEISD)								
Stage IV: Evaluation of Inherently Safer Design Options								
Process: Reducing NO$_x$ Emissions								
Process Unit: Selective Catalytic Reduction (SCR)				Materials in Process Unit: Flue gas and reductant				
INHERENT SAFETY MATRIX (ISM)								
Identified Hazard	**ISD options**	**Interaction Indicator**	**Inherent Safety Guideword**					**Total Interaction Indicators**
			Hazard Elimination		**Consequence Reduction**		**Likelihood Reduction**	
			Elimination	**Substitution**	**Minimisation**	**Moderation**	**Simplification**	
Hazard: Hazardous Reductant used in SCR	Option 1(base case): Substitute with Anhydrous Liquid Ammonia	**Positive**			**C1,C2**		**L4,L5**	**4**
		Negative		E4			L1,L2	3
	Option 2: Substitute with Aqueous Ammonia	**Positive**		**E4**				**1**
		Negative			C1,C2		L1,L2,L4,L5	6
	Option 3: Substitute with Anhydrous Vapour Ammonia	**Positive**			**C1**		**L4,L5**	**3**
		Negative		E4	C2		L1,L2	4
	Option 4: Substitute with Urea-based Ammonia	**Positive**	**E4**		**C1,C2**		**L4,L5**	**5**
		Negative					L2,L3	2

generally, the design and technical safety measures. These conflicts are obtained through the interaction between the principle behind the option and the IS principle in the ISD Heuristics. Then, under each IS principle, selected IS factors have been classified and are described in Table 3.12. The interaction is made by analysing potential deviation, by either an increase or decrease in the value of the IS factor. For example, the inventory (C1) of the second option (aqueous ammonia) has increased due to the actual concentration of ammonia supplied in the piping for option 2 at 23wt%, and in the tanker truck at 19wt%, as shown in Table 4.8. The increase in inventory reflects a negative impact on the ISD option, because large amounts of hazardous inventory means a higher potential for damage if an accident occurs. Furthermore, the utilisation of aqueous ammonia, which was initially thought to be inherently safer for this process, would actually create additional hazards, due to transport delivery and unloading activities (L4). This negative impact is evaluated under the *simplify* principle, as shown in Table 4.9. Thus, this ISD option was no different from the initial proposal i.e., anhydrous liquid ammonia. However, this second option could be a suitable ISD option compared to anhydrous ammonia, if this option required a high frequency of delivery (L4) and storage activities (L5). In addition, the regulatory requirements (L1) permitting storage tanks for anhydrous ammonia are more stringent compared to that of aqueous ammonia or urea, due to its high potential in causing a heavy toxic cloud (Salib and Keeth, 2003).

When anhydrous ammonia is compared to urea-based ammonia, the ISM tool shows that the latter is more desirable, due to its inherently safer characteristics and that it creates less conflict to the process, in terms of transportation, regulatory, and process issues. One of the main advantages of urea is its toxic properties (E4), which are inherently safer, and do not require a permit for transportation, since it is not listed as a hazardous material. Urea is commonly supplied in a solid form as prills or granulated material. Solid urea is normally delivered by rail or truck, depending on consumption rates or size of the plants. Therefore, the potential for ammonia spills is eliminated and overall, accumulated ammonia is much less when compared to other options. However, the plant would require an extension of process (L3) to cater for the urea conversion process. In this case, the use of urea-based ammonia could increase the conflict of the plant system, since it requires de-mineralised water for the hydrolysis reaction, in order to convert ammonia on-site. Therefore, the extended plant may heavily consume steam, electricity, and water, which could increase the frequency of maintenance (L2) in the plant. Thus, the analysis of lifecycle costs for all design alternatives could be used to assists in making the decision. Comparisons of costs should include the costs of losses, evacuation planning, permitting, and risk management; the costs of capital and the operating of the process are not within the scope of this research.

Based on the above analysis, the best ISD option is determined through observing the positive and negative impacts that potentially may occur. An option that has the lowest number of negative impacts and the highest number of positive impacts is considered to be the design that is AiSAP. For this ammonia case study, the substitution with urea-based ammonia is the AiSAP option (Option 4), since this option meets the above criteria.

In conclusion, the ISM tool (Table 4.9) is able to identify hazard conflicts qualitatively and assist the designer in achieving a design that is AiSAP. For this case study, the evaluation using the ISM tool is sufficient to evaluate and screen the inherently safer options, without extending the evaluation to the quantitative stage. Further detailed quantification of the actual degree of hazards and the likelihood of the hazard transfer or trade-offs(depending on the evaluation criteria required by the end-user, such as by estimating the distances affected by a release and the frequency of the release), which involves or requires extensive data, is mostly not available during the early stage of design.

4.5 Case IV: Identification of the ISD reactor for the nitration of toluene using the ISM and IRDI tools

Case II, involving the toluene nitration process, is revisited in order to illustrate the integration of the ISM and IRDI tools. The objective is to resolve conflicts during the selection of an inherently safer reactor, not only to minimise runaway reaction, but also for less trade-offs or hazard migration, due to ISD modifications. The ISM tool is initially applied to the case study in order to rank qualitatively the ISD options based on their positive and negative interactions. Later, the IRDI tool is applied to quantify potential conflicts from the ISD options and to compare them to the base case.

In this case study, a batch reactor (described in Table 4.3) is used as the base case. The design option 'through minimising the volume of reactants using continuous intensified reactor' (OP3) and the design option 'by substituting the process route to vapour phase reaction' (OP8) have been selected. This selection was performed through the screening step, based on the feasibility study of the generated options, according to the process design stage. From several literatures (Othmer, 2004; Ullman's, 2003; Halder et al., 2007; Kuba et al., 2007), there are many potential routes for the nitration of toluene. However, in this study, the selection of options is based on the ISD concept as the highest priority, which is to avoid or reduce runaway reactions. Therefore, the nitration process based on Halder et al., (2007) is selected to represent OP3, because the researcher applies an intensified reactor to react the nitric acid and toluene in liquid phase. Using this process, the volume of reactants is significantly reduced compared to the nitration process in a batch reactor. OP8 is based on the study by Kuba et al., (2007) where the gas phase nitration of toluene with catalyst, since the reaction only required nitric acid as the nitrating agent. This process is considered to be inherently safer, due to the elimination of sulphuric acid, which is a corrosive chemical. Table 4.10 shows the data summary used to evaluate OP3 and OP8, based on the above literatures.

Table 4.10: Input data for the ISM tool, to evaluate OP3 and OP8 (Halder et al., 2007 and Kuba et al., 2007)

Input data	OP3: liquid phase nitration	OP8: gas phase nitration
Type of reactor	Intensified continuous reactor	Continuous plug flow reactor
Chemicals	Toluene and nitric acid	Toluene, nitric acid, nitrogen, and zeolite beta catalyst
Potential by-products	Not available	α-nitrotoluene and oxidation products, like benzaldehyde
Operating conditions	80°C	80 – 180°C
Reaction time	For 1.3 molar ratio of feed concentration toluene to nitric acid 2500s for batch reactor 160s for intensified reactor	Estimated at 4hrs for toluene to nitric acid feed ratio of 1.4:1

4.5.1 Results analysis and discussions for the ISM tool

The ISM code for IS factors is applied to the base case and to OP3 and OP8. Table 4.11 shows the results from the interaction between IS factors for each option. The selection of IS factors and codes for this case study is based on published information. The most apparent IS factor in this case study is the inventory (C1) of chemicals in each process unit. In contrast with the batch reactor that used large amounts of reactants, the intensified reactor and gas phase reactor contained smaller amounts of inventory, since the reaction time (C5) is faster, as was claimed by Halder et al., (2007) and Kuba et al., (2007). Halder et al., (2007) also demonstrated that the common by-products (E4) of this reaction are eliminated in the intensified reactor of the liquid phase nitration. However, the temperature of reaction (C3) is higher than the batch reactor. A similar interaction was also applied in the gas phase nitration, where Kuba et al., (2007) reported that a higher reaction temperature is used to achieve the gas reaction process. As can be seen in Table 4.3, the decomposition temperature (C6) of nitrotoluene is 160^{o}C, which shows that there is potential for a runaway reaction to occur in the event of failure to control the temperature. Therefore, the complexity of safety control measures (L1) could be higher in both options,as both processes are operating in extreme conditions. Another IS factor that needs to be considered, is the transportation issue (L4); as both options attempt to minimise the volume and size of the process unit, which could therefore affect the overall inventory of the plant.

The results from the application of the ISM tool show that OP3 and OP8 have similar total scores of potential conflicts of both positive and negative impacts. Both options also have insignificantly different positive impacts i.e., 2 and 3 for OP3 and OP8, respectively. Therefore, the IRDI tool needs to be applied to the case study, because the qualitative method is unable to identify the options that are AiSAP. The degree of conflicts can be estimated using the IRDI tool, by applying a risk based approach. The applications and results of the IRDI tool are explained in the following section.

Table 4.11: Results obtained after the application of ISM tool

QUALITATIVE EVALUATION OF INHERENTLY SAFER DESIGN (QEISD)								
Stage IV: Evaluation of Inherently Safer Design Options								
Process: Nitration of Toluene to produce Mononitrotoluenes								
Process Unit: Batch Reactor				Materials: Toluene and Mixed acids (Nitric Acid, Sulphuric Acid)				
INHERENT SAFETY MATRIX								
Identified Hazard	**ISD Option**	**Interaction Indicator**	**Inherent Safety Guideword**					**Total Credit Interaction**
			Hazard Elimination		**Consequence Reduction**		**Likelihood Reduction**	
			Elimination	**Substitution**	**Minimisation**	**Moderation**	**Simplification**	
Hazard 4: large inventory	Base Case: high volume in batch reactor	Positive Interaction				C3	L1,L4	3
		Negative Interaction	E4		C1	C5,C6		4
	OP3: minimise volume use with CSTR/smaller reactor/intensified reactor (minimise)	Positive Interaction	E4		C1	C5		3
		Negative Interaction				C3,C6	L1,L4	4
	OP8: substitute with vapour phase reaction route	Positive Interaction			C1	C5		2
		Negative Interaction	E4			C3,C6	L1,L4	5

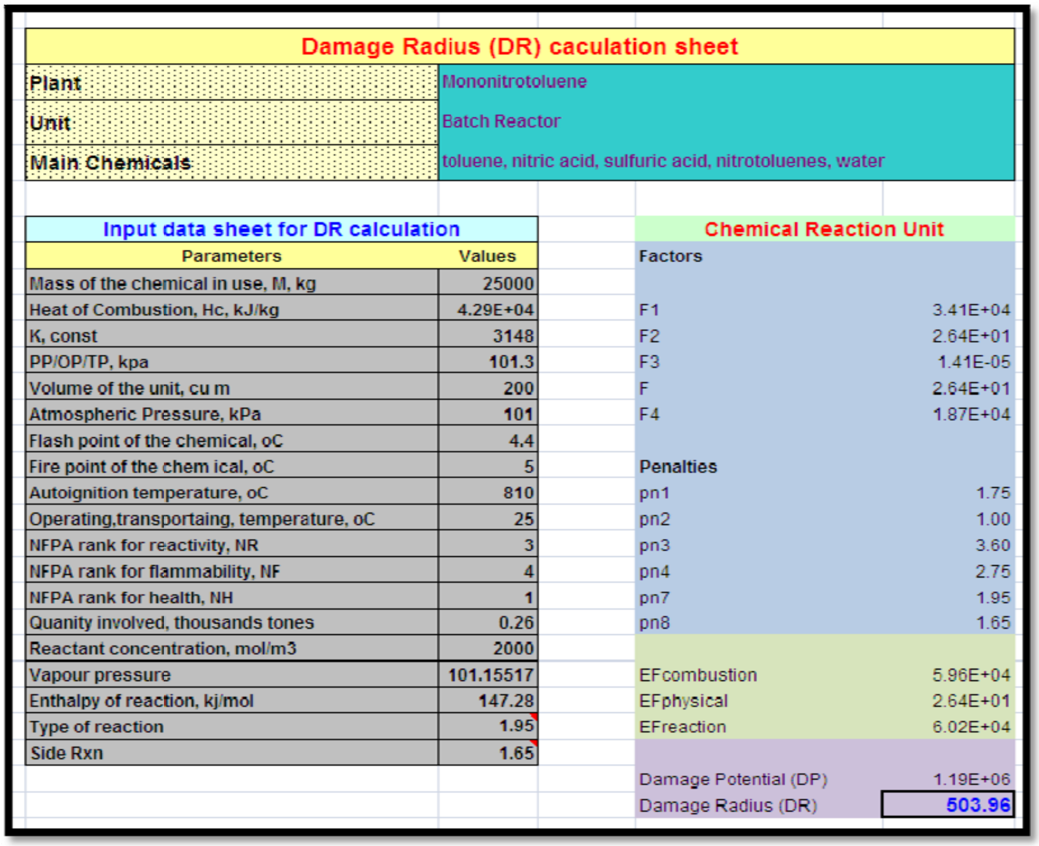
4.5.2 Results analysis and discussions for the IRDI tool

In this case study, a toluene nitration reaction, with a production capacity of 25 tons/day of mixed mononitrotoluenes (MNT), is used in demonstrating the quantitative index tool. In addition, other information from literature, basic design calculations, rules-of-thumb, assumptions, and results from IDH and IFM tools, are applied within this section. Examples of calculation are attached where appropriate; to further illustrate the application of IRDI. For this case study, a typical set-up for a batch reactor (Luyben and Hendershot, 2004) is used as the base case, as shown in Figure 4.5.

The evaluation is performed by quantifying the damage potential of the base case i.e., the batch reactor, by estimating the DR as described in Chapter 3. Figure 4.6 shows the DR calculation for the batch reactor, and Table 4.12 summarises the estimated DR for the batch reactor, which is found to be at an unacceptable potential damage level, where the radii exceeds the tolerable limit of 200 meters. The estimated energy factors, contained in the batch reactor, is huge; especially the thermal energy from the reaction itself. If any failure scenario occurs, such as failure of the temperature control system, the reaction would easily runaway and if there is any delay in mitigation measures, the scenario would lead to a leak or a rupture, due to the overpressure developed in the reactor; hence, causing fire and possible explosion. Therefore, new inherently safer design options are required, in order to reduce the potential energy in the reactor, to eliminate or reduce the potential runaway reaction from the process.

By following the ISD heuristic-rule (proposed by QEISD tools), the reduction of inventory by changing the type of reactor is further evaluated in this study, since it could minimise the reaction energy in the process, as shown in Table 4.12. The options considered in the ISM tool are further refined by extending the ISD options to three types of reactor i.e., semi-batch, intensified and vapour phase. An example of a schematic flow sheet used for intensified reactor is shown in Figure 4.7.

Figure 4.5: Schematic diagram of batch and semi-batch nitration processes (Luyben and Hendershot, 2004)



Damage Radius (DR) caculation sheet

Plant	Mononitrotoluene
Unit	Batch Reactor
Main Chemicals	toluene, nitric acid, sulfuric acid, nitrotoluenes, water

Input data sheet for DR calculation

Parameters	Values
Mass of the chemical in use, M, kg	25000
Heat of Combustion, Hc, kJ/kg	4.29E+04
K, const	3148
PP/OP/TP, kpa	101.3
Volume of the unit, cu m	200
Atmospheric Pressure, kPa	101
Flash point of the chemical, oC	4.4
Fire point of the chem ical, oC	5
Autoignition temperature, oC	810
Operating,transportaing, temperature, oC	25
NFPA rank for reactivity, NR	3
NFPA rank for flammability, NF	4
NFPA rank for health, NH	1
Quanity involved, thousands tones	0.26
Reactant concentration, mol/m3	2000
Vapour pressure	101.15517
Enthalpy of reaction, kj/mol	147.28
Type of reaction	1.95
Side Rxn	1.65

Chemical Reaction Unit

Factors	
F1	3.41E+04
F2	2.64E+01
F3	1.41E-05
F	2.64E+01
F4	1.87E+04
Penalties	
pn1	1.75
pn2	1.00
pn3	3.60
pn4	2.75
pn7	1.95
pn8	1.65
EFcombustion	5.96E+04
EFphysical	2.64E+01
EFreaction	6.02E+04
Damage Potential (DP)	1.19E+06
Damage Radius (DR)	503.96

Figure 4.6: Input data and calculations of DR for the base case (batch reactor)

Table 4.12: Results summary for DR of the base case (batch reactor)

Energy Factors	**Values**
EF_{ce}: Combustion energy	5.96×10^4
EF_{ph}: Physical energy	2.64×10^1
EF_{re}: Reaction energy	6.02×10^4
Damage Radius, DR	**503.96 > 200m**

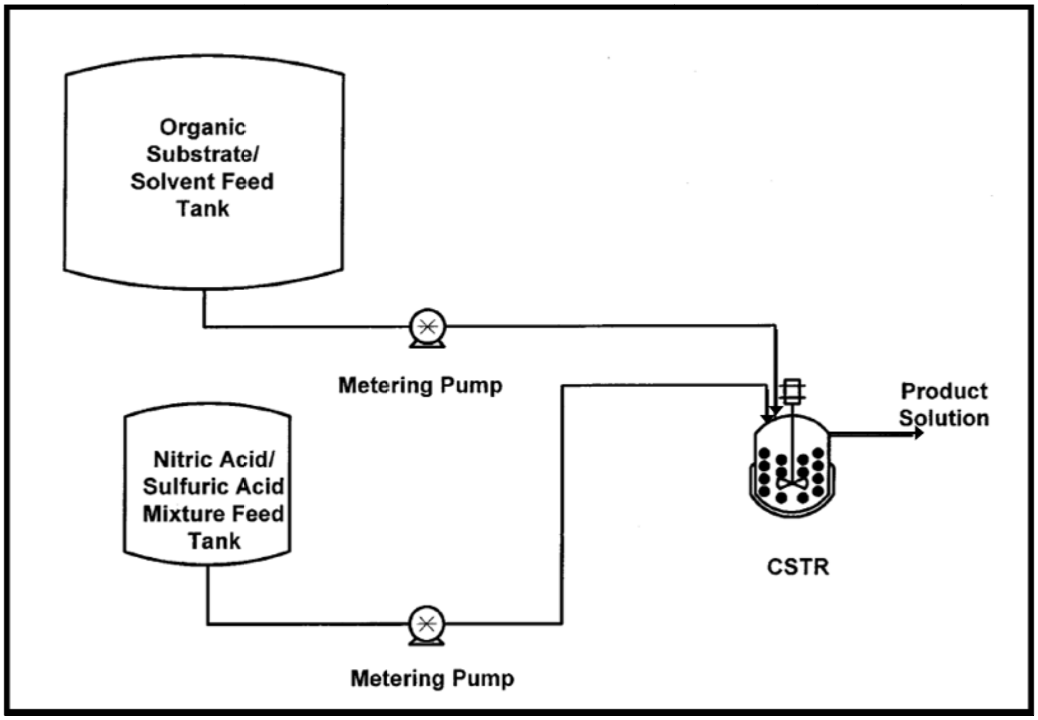


Figure 4.7: Schematic diagram for the intensified reactor (Luyben and Hendershot, 2004)

In order to evaluate the inherent safeness of each reactor, preliminary design calculations, based on the above production rates and a compilation of related literatures, such as Stoessel (2008), Kuba et al., (2007), Chaubal et al., (2007), D'Angelo et al., (2003), Keller et al., (1997), Duh et al., (1997), and Chen and Wu (1996), are used to estimate the amount of reactants, operating conditions, and related safety information. The energy factors contained in all ISD options are estimated by following the procedures in the batch reactor and the energy values are further applied to estimate the DI for fire and explosion, as given in Equation 3.19. As shown in Table 4.13, the DI is estimated for all design options; the intensified reactor and vapour phase reactor shows a marked reduction of DI. This result is expected, since the mass of reactants and size of the reactor is 10 times smaller than the batch reactor. However, the energy factors in the semi-batch reactor still exceed the tolerable criterion, which indicates that the ISD option was unable to reduce the severity of fire and explosion. The DI results for all options are also in agreement with the trend results of Dow F&EI; although this tool has a different definition of its risk level. In spite of the differences, the Dow F&E Index has a similar objective with DI to estimate the hazard based on consequences, as described in Chapter 3.

Table 4.13: Results of DI for the base case and all ISD options

Design Options	**Damage Index, DI**		**Dow F&EI**	
	Score	**Rank**	**Score**	**Rank**
Batch	100	High	165	Severe
Semi-Batch	100	High	154	Heavy
Intensified reactor	48.16	Low	98	Intermediate
Vapour phase	72.71	Medium	112	Intermediate

The damage potential from the process units is significantly reduced due to the minimisation in the chemical inventory in the reactor. However, the DI is estimated based on changes or modifications made to one process unit only, without considering the hidden deviation or instability that could occur due to the minimisation of the inventory. In addition, the estimated severity does not take into account the hazardous changes that could happen to other process units or process areas. Therefore, IRDI is developed to include the above factors, which are significantly different compared to other conventional consequence methods. The above issues are further evaluated through the application of the LIHM method.

For this case study, the estimation of LIHM is supported by Equations 3.18 to 3.25, as described in Chapter 3. Table 4.14 shows a sample of the estimation results of LIDIS for the vapour phase reactor against the base case, to illustrate the deviation or

Table 4.14: Sample of input data and LIDIS estimation for the vapour phase reactor

LIHM caculation sheet			
Plant	Mononitrotoluene		
Unit	Batch Reactor		
Main Chemicals	toluene, nitric acid, sulfuric acid, nitrotoluenes, water		
Inherent Safety Principles	Base Case	ISD Option	LDS
Process Safety Factors	Batch Reactor	VapPhase Reactor	
Substitution			
Flammable	4.0	3.0	2.5
Explosive			
Reactive	3.0	4.0	-3.3
Toxicity	1.0	4.0	-10.0
			-10.8
Minimisation			
Process vessel	100.0	20.0	8.0
Feed and product vessels	25.0	50.0	-10.0
			-2.0
Moderation			
Temperature (Runaway)			
Adiabatic temperature rise,oC	163.6	81.8	5.0
Time to max rate (hr)	83.1	119.7	4.4
Temperature (Fire and Explosion)			
Boiling point - 111oC	25.0	180.0	-6.2
Flash point - 4.4oC	4.4	0.4	-9.1
LFL(%) 1.27vol%	1.4	0.5	-6.4
Pressure	1.0	2.0	-10.0
Vapour pressure (kPa)	101.2	200.1	-9.8
Amount of solvent evaporate	0.4	8.0	-10.0
			-42.1
Simplification			
Complexity I:			
Temperature	6.0	10.0	-2.5
Pressure	3.0	6.0	-10.0
Flow	4.0	6.0	-5.0
Level	8.0	4.0	5.0
			-12.5
Complexity II:			
Secondary containment	8.0	7.0	1.3
Forced dilution system	3.0	6.0	-10.0
Blast wall	4.0	6.0	-5.0
Depressurisation	8.0	8.0	0.0
Quenching and flooding	6.0	8.0	-3.3
			-17.1
Complexity II:			
Auxillary units; compressor, pumps	5.0	8.0	-6.0
Multi-unit;parallel, lengthy, agitators	5.0	6.0	-2.0
Site-Storages	5.0	8.0	-6.0
Frequency of transportation activities	5.0	8.0	-6.0
			-20.0
Total LSISD			-104.5
Max LSISD			260.0
LIDIS			-0.402
LIHM			1.402

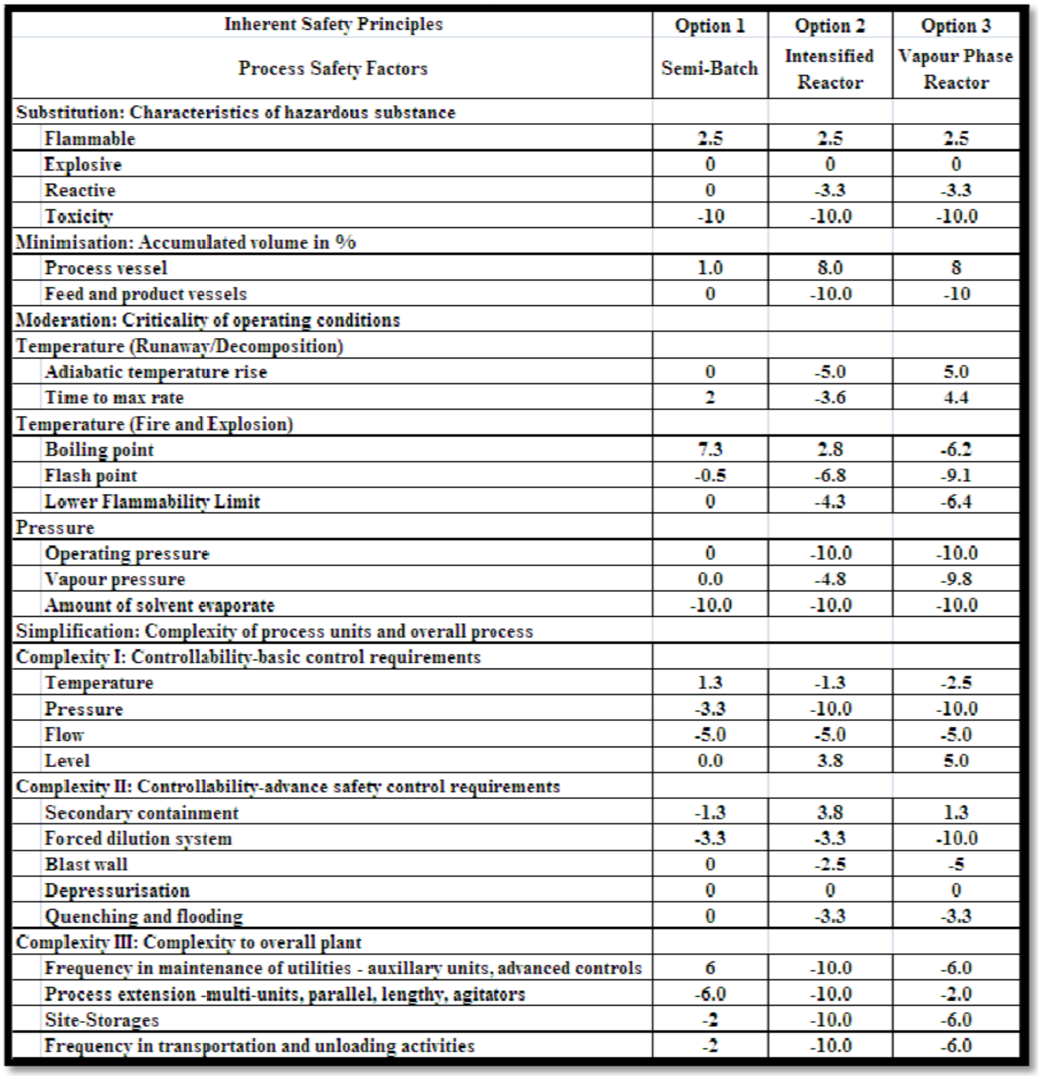
hazard migration between the target process safety factors (as described in Table 3.15) when IS principles are considered in the design. The complete LIDIS results for all ISD options are shown in Table 4.15, where the intensified reactor and the vapour phase reactor demonstrate a significant likelihood of the hazard being migrated to other process factors.

As shown in Table 4.15, the LIHM for the *minimisation* principle is determined by the percentage volume accumulated in the plant. The intensified and vapour phase reactors would have increased in their inventory, especially the feed tank, since a continuous process would require a larger feed tank to ensure that the process would run smoothly and continuously for 24 hours a day. In addition, the larger feed tank is also necessary to avoid frequent transportation activities, such as loading and unloading, which could create other hazards, such as flammable releases and spillage. As such, this could alert the designer about the requirement to assess the potential damage of fire and explosion from the feed tanks that hold these hazardous substances. Thus, the LIHM for semi-batch has the same degree of conflicts as the batch reactor, while the intensified and vapour phase reactors show a higher degree of conflicts compared to the base case, due to the above factors.

Furthermore, the likelihood of hazard in the *moderation* principle is also increased, due to operating in explosive conditions that could increase the uncontrolled release of solvent vapour, as estimated in this case study. The potential for thermal runaway is higher in the intensified and vapour phase reactors. MNT products would easily decompose through the gas phase reaction (Kuba et al., 2007). This finding is in agreement with the statement by Anxionnaz et al., (2008), on the potential of reaction propagation out of an intensified reactor. This ISD option would require a design consideration to remove the heat of the reaction. This could alert the designer to pay special attention to the design of the protection systems. However, history of previous accidents show that technical safety measures do fail and absolute reliability can never be guaranteed (Stoessel, 2008).

The *simplification* principle illustrates that the intensified reactor required frequent transportation and unloading activities, in order to make up for the reduction of plant inventories. These activities could lead to the hazard of spillage and leaks of the hazardous materials. This would alert the designer to consider on-site processes in their design, rather than being highly dependent on conventional delivery activities. In addition to the high frequency of transportation, increasing the number of intensified reactors is also required, in order to achieve the same amount of product, as the batch system. This configuration requirement could increase the complexity of the plant, including the auxiliary reaction control systems.

Table 4.15: Results of LIDIS for all ISD options



Inherent Safety Principles	Option 1	Option 2	Option 3
Process Safety Factors	Semi-Batch	Intensified Reactor	Vapour Phase Reactor
Substitution: Characteristics of hazardous substance			
Flammable	2.5	2.5	2.5
Explosive	0	0	0
Reactive	0	-3.3	-3.3
Toxicity	-10	-10.0	-10.0
Minimisation: Accumulated volume in %			
Process vessel	1.0	8.0	8
Feed and product vessels	0	-10.0	-10
Moderation: Criticality of operating conditions			
Temperature (Runaway/Decomposition)			
Adiabatic temperature rise	0	-5.0	5.0
Time to max rate	2	-3.6	4.4
Temperature (Fire and Explosion)			
Boiling point	7.3	2.8	-6.2
Flash point	-0.5	-6.8	-9.1
Lower Flammability Limit	0	-4.3	-6.4
Pressure			
Operating pressure	0	-10.0	-10.0
Vapour pressure	0.0	-4.8	-9.8
Amount of solvent evaporate	-10.0	-10.0	-10.0
Simplification: Complexity of process units and overall process			
Complexity I: Controllability-basic control requirements			
Temperature	1.3	-1.3	-2.5
Pressure	-3.3	-10.0	-10.0
Flow	-5.0	-5.0	-5.0
Level	0.0	3.8	5.0
Complexity II: Controllability-advance safety control requirements			
Secondary containment	-1.3	3.8	1.3
Forced dilution system	-3.3	-3.3	-10.0
Blast wall	0	-2.5	-5
Depressurisation	0	0	0
Quenching and flooding	0	-3.3	-3.3
Complexity III: Complexity to overall plant			
Frequency in maintenance of utilities - auxillary units, advanced controls	6	-10.0	-6.0
Process extension -multi-units, parallel, lengthy, agitators	-6.0	-10.0	-2.0
Site-Storages	-2	-10.0	-6.0
Frequency in transportation and unloading activities	-2	-10.0	-6.0

These findings are in agreement with the conclusions made by Anxionnaz et al., (2008) on the potential problems in deviation detection by process control for an intensified reactor. As explained in Case I, Luyben and Hendershot (2004) also felt that the intensified continuous reactor process is highly dependent on instruments that could fail and lead to explosion. They conducted four cases, where the smaller volumes of the intensified process unit, put stability in jeopardy. For the vapour phase reactor, the decisive requirements to provide advanced safety technical measures are high, due to the process of dealing with vapour phase conditions (Kogelbauer et al., 2000). The estimated LIHM for all options are compared to the base case value, where the LIHM of base case is 1 is as shown in Figure 4.8. Interestingly, the LIHM of all options are more than the base case value. These values demonstrate that all ISD options, considered in this case study, produced conflicts of hazards and could contribute to the overall risk of the process.

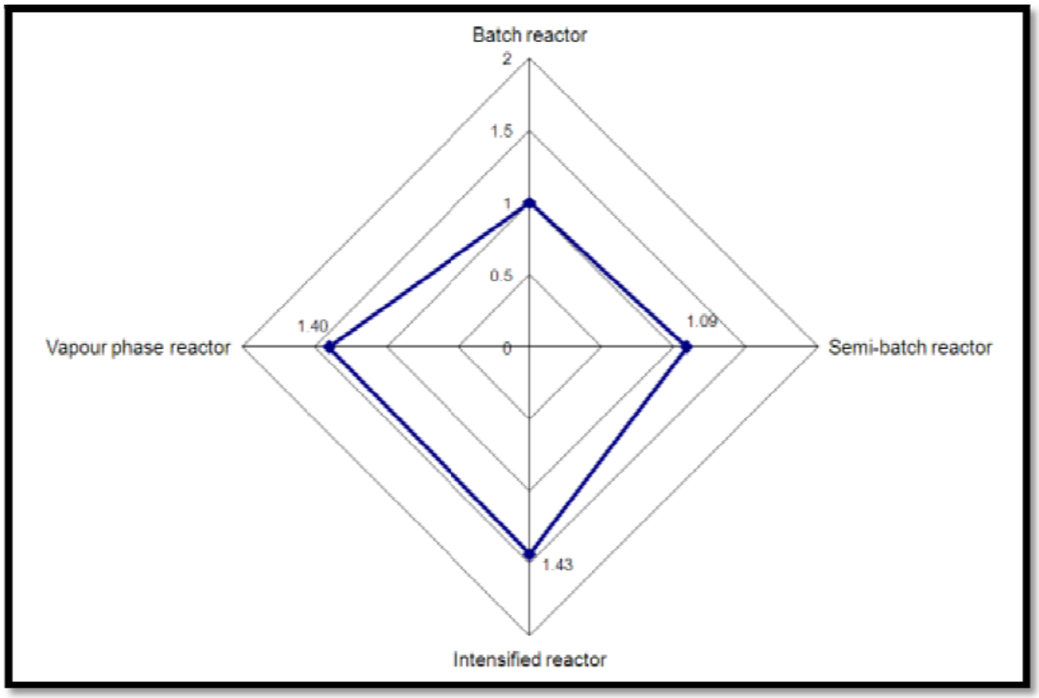


Figure 4.8: LIHM results for the base case and all ISD options

This case study has demonstrated that all options produced hazard trade-offs in their design, especially for the *moderation* and *simplification* guidewords, as shown in Figure 4.9. The LIDIS shows that consequence reduction could be achieved from the intensified reactor design option, since the volume used in the individual process unit is very small and the process conditions are slightly less hazardous than the vapour phase reactor. This is in agreement with several literatures on the vapour phase nitration of toluene that required a process temperature of 100-200^{o}C (Chaubal and Sawant, 2006; Dagade et al., 2001; Kuba et al., 2007). However, the intensified reactor could have a high likelihood of the hazard being transferred through the requirement of handling the extreme process, via an advanced control system, transportation, numbering-up the reactors, and frequency of maintaining the reliability of the auxiliary units. Moulijn et al., (2008) also highlighted that a process intensification, which is aimed at the better utilization of physical resources and an associated reduction in sizes of process equipment, is not risk free. While reduced storage of dangerous materials will greatly improve safety, the fast dynamics of the process (unit) can endanger the resilience or stability of the process against disturbances. For that reason, the designer could minimise this potential likelihood, by considering an on-site process and by further evaluating the design of the intensified reactor, based on the above factors.

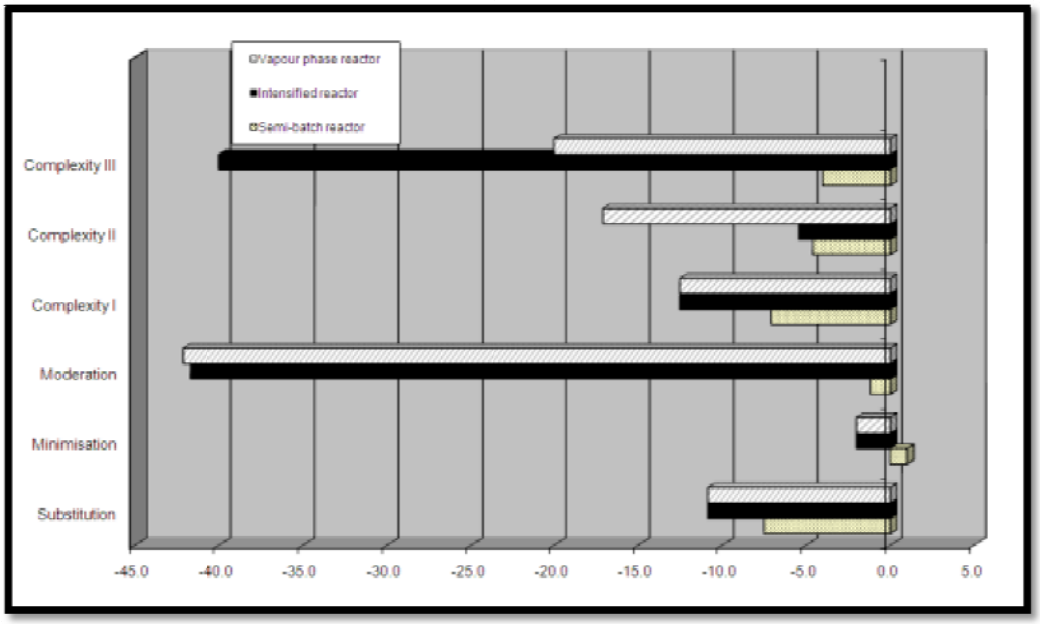


Figure 4.9: Distribution of hazard conflict score, based on LIDIS for all ISD options.

For this case study, the IRDI tool has demonstrated an actual inherent safety performance in eliminating the hazards through design, based on the ISD concept. Although the DIs, which represents potential severity of all options, are lower than the base case value, this value does not totally imply the overall reduction of hazards in the process. Table 4.16 provides the design criticality of all options in this case study, based on the inherent risk approach in supporting the selection of design that AiSAP. The IRDI results prove that the analysis on consequence of process unit alone could not represent the overall inherent safety of the reactor design. It is crucial to consider the potential of conflicts by estimating the likelihood of hazard migrating in the design option, as summarised in Figure 4.10. The results, based on these guidewords, could inform and lead the designer focus on how to strengthen their chosen design option; for example, by attaining better heat transfer in designing the reactor, to avoid auto-ignition of explosive conditions, develop auxiliary control systems that are highly reliable, and considerations for on-site processes during the early stages of the design.

Table 4.16: The criticality of all ISD options

ISD Option	**DI**	**LIHM**	**IRDI**	**Risk Level**	**Design Criticality Descriptions**
Semi-batch reactor	100	1.09	108.97	**High**	Design option is highly critical Redesign is highly required Technical safety measures are highly required
Intensified reactor	48.16	1.43	68.98	**Medium**	Design option is critical Redesign may required Technical safety measures may be required
Vapour phase reactor	72.71	1.40	101.94	**High**	Design option is highly critical Redesign is highly required Technical safety measures are highly required

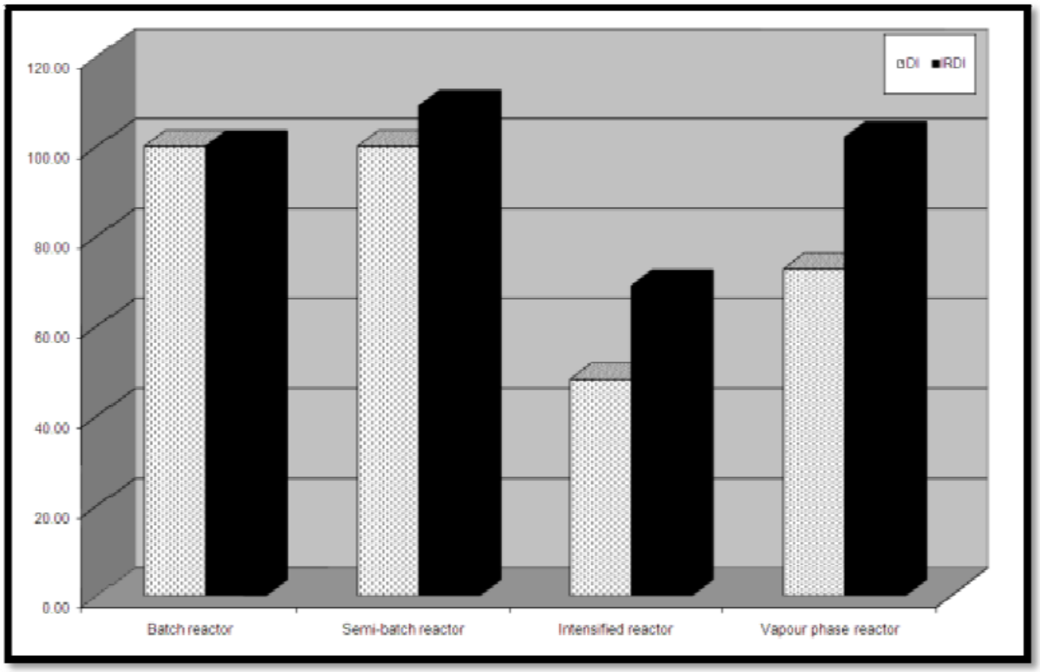


Figure 4.10: The deviation of index values between the Inherent Risk of Design Index (IRDI) and the Damage Index (DI)

It is important to stress that the aim of the IRDI tool is to provide a general guideline in achieving ISD at an early stage of the process design, which depends highly on the accuracy of the information provided on the method. This information depends highly on experience and the expert judgements of the end-user, since most of the parameters to be considered, may not be detailed enough during the early stages of design. However, these constraints or uncertainties will be part of future works in this research. Regardless of this constraint, it could still give better alternatives prior to the performance of costly experimental tests and compilation details of safety data properties, to obtain further accurate information for the design. In addition, these options need to be evaluated further with cost factors, to ensure that the ISD options chosen are not only inherently safer and more robust processes, but are more economical to be implemented. Future research will focus on this issue in order to achieve a design that is AiSAP.

4.6 Case V: Application of the IRDI tool in evaluating hydrogen storage systems

Hydrogen (H_2) has been increasingly explored as a potential alternative for future energy, in addition to nuclear, bio-fuels, solar, etc. Among the potential uses of hydrogen, are vehicles, power for buildings, and portable electronics. The application of hydrogen as a fuel cell in vehicles, has reported reductions in air pollution compared to using fossil fuels, such as gasoline (National Hydrogen Association, 2010). However, like most fuels, hydrogen has high energy content and must be handled properly to be safe. In general, hydrogen is neither more nor less inherently hazardous than gasoline, propane, or methane. Thus, it is important to analysis the inherent safety of the hydrogen process system at an early design stage. The focus in this case study is the hydrogen storage system applicable to hydrogen refuelling stations.

A hydrogen safety study by Landucci et al., (2008) for hydrogen storage systems of a medium-scale, is revisited. There are four types of hydrogen storage techniques to be considered: (i) storage of hydrogen gas under pressure, (ii) storage of liquefied hydrogen, (iii) storage as a metal hydride, and (iv) storage as a complex hydride. The first two techniques are considered to be conventional technologies used world-wide by refineries and chemical plants. However, the last two techniques are still under research and development and have been indicated as possible inherently safer alternatives (Browning et al., 1997; Aiello et al., 1999). For the sake of comparison, the same assumptions and conditions used by Landucci et al., (2008) for medium-scale storage, are applied here to demonstrate evaluation by the IRDI tool. Table 4.17 shows the summary of features and process conditions for all types of hydrogen storage systems. Whereas, Figure 4.11 shows the simplified process flow diagram for all hydrogen storage systems and brief descriptions of each process system are given, while the details can be obtained from the above references.

For this case study, the storage unit is set to contain approximately 500kg of hydrogen, stored using alternative technologies. In the case of the gaseous storage technology, the bulk storage was considered at on operating pressure of 25 MPa (Figure 4.11(a)) with 2 commercial tube trailers (D1 and D2). Each trailer was considered to be composed of 7 pressurized cylinders; each containing approximately

Table 4.17: Summary of features and process conditions for H_2 storage systems

Features and process conditions	**Compressed**	**Cryogenic**	**Metal hydride**	**Complex hydride**
Technology	Commercial	Commercial	Research	Research
Pressure (MPa)	25	0.6	1.1	0.1
Temperature (K)	300	20/25	300	300
H_2 mass stored per unit (kg)	35.7	500	105	500
Number of units	2 tube trailers x 7 units	1	5	1

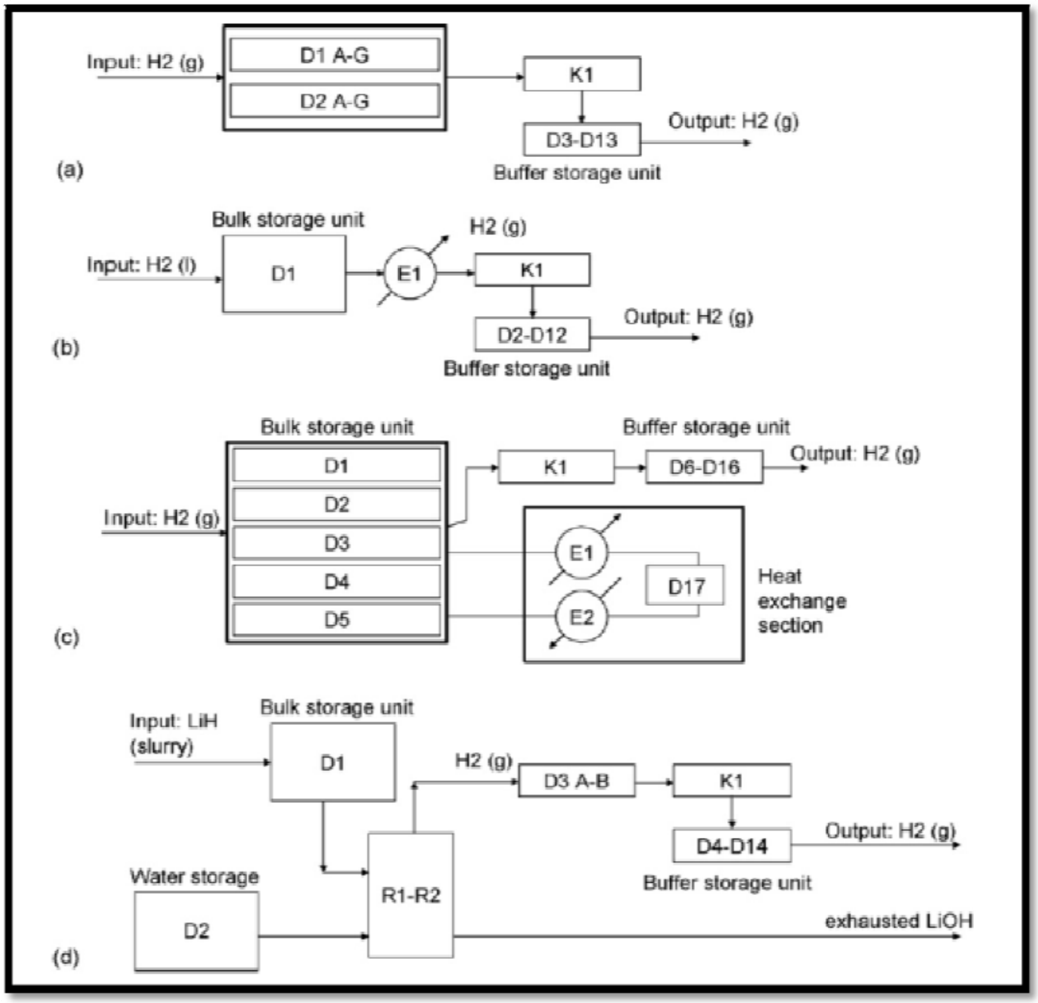


Figure 4.11: Simplified process flow diagram for (a) compressed, (b) cryogenic, (c) metal hydride, and (d) complex hydride

40kg of hydrogen. Since the refuelling of next generation hydrogen vehicles, requires that high pressures will be involved, a compressor (K1), coupled with a buffer storage unit (D3–D13) is needed to provide gaseous hydrogen at 35 MPa.

In the case of the cryogenic storage (Figure 4.11 (b)), hydrogen is stored at 20–25kg at a moderate pressure (0.6 MPa). An external finned tubes heat exchanger (E1) is needed to provide gaseous hydrogen. Also, coupled compression (K1)–high pressure buffer (D2–D12) units are also needed.

The medium-scale reference scheme, for metal hydrides storage technology (Figure 4.11 (c)), was based on the same principle as the small-scale scheme. Each unit was supposed to store up to 100kg of hydrogen by adsorption on metal hydrides. During the discharge phase, hydrogen is released at low pressure (about 1.1 MPa) and compressed as in previous cases.

The medium-scale reference scheme for hydrogen storage of complex hydrides (Figure 4.11(d)) consists of three main sections (i) a bulk storage unit for the hydride at atmospheric pressure and ambient temperature, (ii) a reaction section, in which the gaseous hydrogen is produced, and (iii) a compression and buffer storage unit. The hydride is dispersed in a mineral oil, in order to prevent contact with moisture, which may cause unwanted hydrogen release. In the reaction section, the slurry is mixed with water and gaseous hydrogen is released via hydrolysis. Gaseous hydrogen is then compressed (K1) and sent to the high pressure buffer (D4–D14). Two semi-batch reactors are supposed to work alternatively in order to allow a continuous supply of hydrogen to the compression unit.

4.6.1 Results analysis and discussions

The results of DI for all types of storage systems are shown in Table 4.18, which illustrates the reduction in DR and DI when metal hydrides and complex hydrides are considered as the inherently safer alternatives; where the best principles to represent these design changes are through the application of *substitution* and *moderation* principles. The hazardous material, such as hydrogen, is substituted with hydrides material and the hazardous operating conditions in the compressed and cryogenic system are moderated with less hazardous conditions. This implies that metal and complex hydrides technologies are inherently safer for the storage of hydrogen, as stable hydride in solid phase is comparable to compressed and cryogenic storage system.

Table 4.18: DR and DI results for all storage systems

Severity	Compressed	Cryogenic	Metal hydrides	Complex hydrides
Damage Radii (DR)	1587.78	229.68	198.98	91.38
Damage Index (DI)	100	100	99.49	45.69

For the evaluation of the likelihood of hazard migration or conflicts between all storage systems via the LIHM tool, the compressed system is considered as the base case or reference, because this system has achieved the highest DR, due to its hazardous operating conditions and hydrogen's flammable and explosive characteristics. During this evaluation, the process flow diagram of the techniques and the storage technologies applied, are reviewed comprehensively with the support of available literatures related to the process itself, and safety issues (Conte et al., 2004; Zhou, 2005; Sarkar and Banerjee, 2005; Kinzey et al., 2005; Tanaka et al., 2009; Zalosh, 2008). The LIDIS results for all ISD options, with regards to the base case i.e., the compressed system, are reported in Figure 4.12. Table 4.19 shows the estimated PFS for each safety factor in the IS principle, which is done using Equations 3.24 and 3.25. A sample worksheet is available in Appendix II. The selection of safety factors are based on the potential to contribute to the overall risk, with regards to the possibility of accidental human fatality and structural damages, such as by system failure, ruptured storage tank, leakage, etc. The evaluations made for each of the IS principles, are explained here.

The potential conflicts, identified in the *substitution* principle, are the potential hazards of the metal and complex hydrides themselves. The NFPA ranking for these materials are classified as flammable, reactive, and toxic, with levels of hazard at 3, 2, and 2, respectively. In addition, all of these materials were judged to be flammable, pyrophoric, and water reactive, which requires extra safety precautions when handling them (Tanaka et al., 2009). This has resulted in high conflicts to the already highly hazardous characteristics of hydrogen, which are released by the system at 1.1 MPa and supplied to the compression unit. For the cryogenic storage system, since the only hazardous material is hydrogen, thus, the hazardous characteristics in this system are at a par with the compressed system.

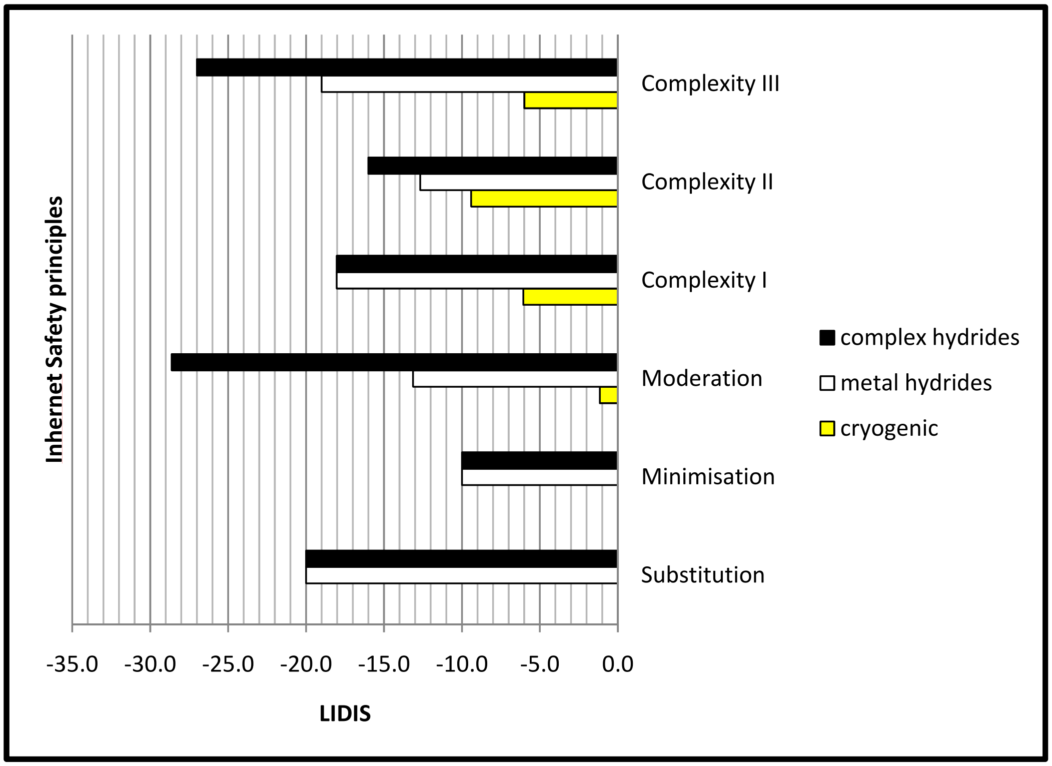
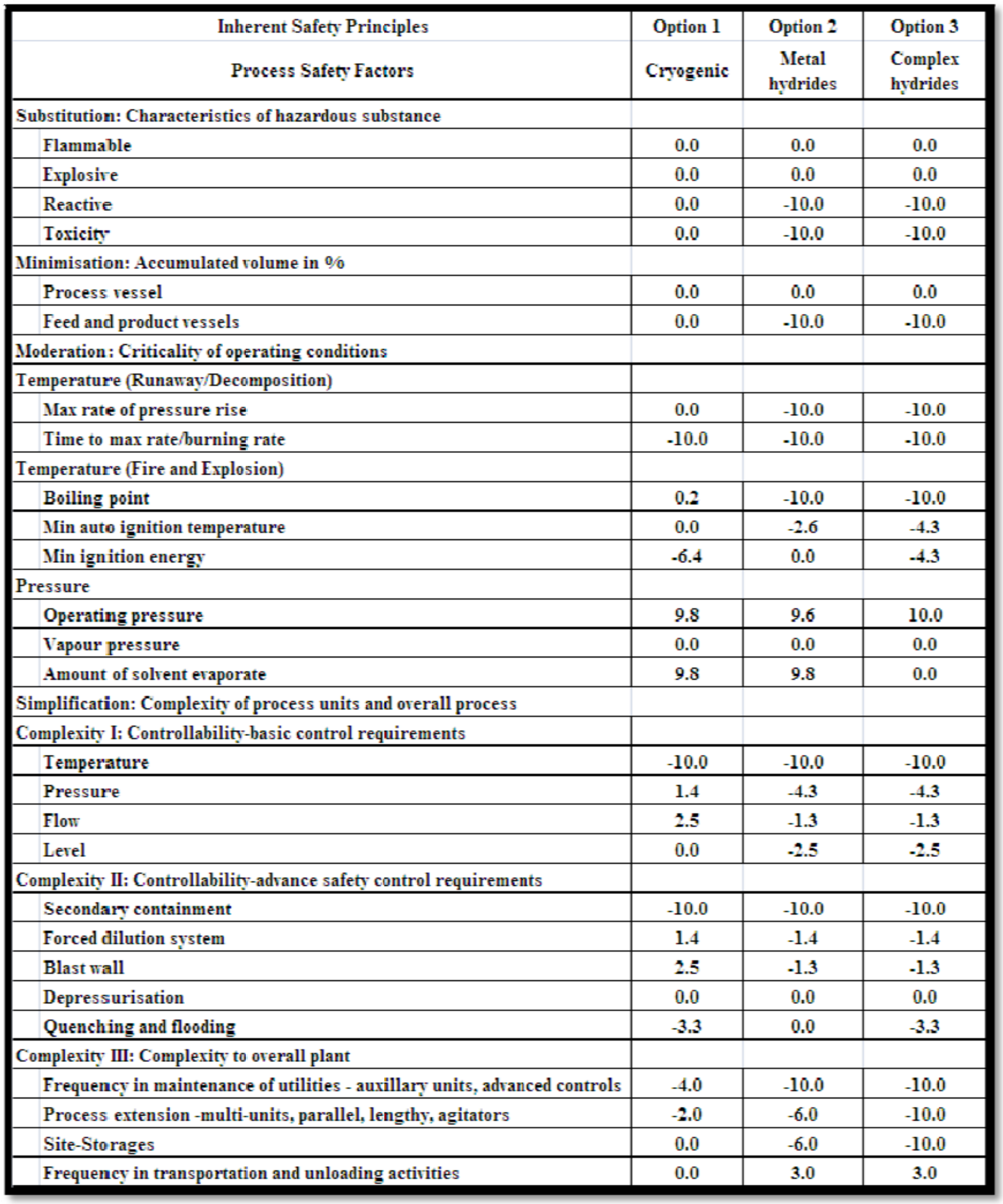


Figure 4.12: LIDIS results for all options based on IS principle

For the *minimisation* principle, the inventory of hydrogen in all types of storage system has been maintained at the same amount of 500kg. Although the metal hydrides storage systems involved only 100kg of hydrogen to be discharged per adsorption unit, the multi-units of adsorption (5 units) by metal hydrides are considered to be an equivalent amount of hydrogen to be discharged from the process. In fact, the amount of metal hydrides in the adsorption unit has affected this principle as being the potential negative conflict, since the *minimisation* principle does not only apply to hydrogen, but also to other potentially hazardous materials involved in the system.

Table 4.19: LIDIS analysis for all hydrogen storage systems



Inherent Safety Principles	Option 1	Option 2	Option 3
Process Safety Factors	Cryogenic	Metal hydrides	Complex hydrides
Substitution: Characteristics of hazardous substance			
Flammable	0.0	0.0	0.0
Explosive	0.0	0.0	0.0
Reactive	0.0	-10.0	-10.0
Toxicity	0.0	-10.0	-10.0
Minimisation: Accumulated volume in %			
Process vessel	0.0	0.0	0.0
Feed and product vessels	0.0	-10.0	-10.0
Moderation: Criticality of operating conditions			
Temperature (Runaway/Decomposition)			
Max rate of pressure rise	0.0	-10.0	-10.0
Time to max rate/burning rate	-10.0	-10.0	-10.0
Temperature (Fire and Explosion)			
Boiling point	0.2	-10.0	-10.0
Min auto ignition temperature	0.0	-2.6	-4.3
Min ignition energy	-6.4	0.0	-4.3
Pressure			
Operating pressure	9.8	9.6	10.0
Vapour pressure	0.0	0.0	0.0
Amount of solvent evaporate	9.8	9.8	0.0
Simplification: Complexity of process units and overall process			
Complexity I: Controllability-basic control requirements			
Temperature	-10.0	-10.0	-10.0
Pressure	1.4	-4.3	-4.3
Flow	2.5	-1.3	-1.3
Level	0.0	-2.5	-2.5
Complexity II: Controllability-advance safety control requirements			
Secondary containment	-10.0	-10.0	-10.0
Forced dilution system	1.4	-1.4	-1.4
Blast wall	2.5	-1.3	-1.3
Depressurisation	0.0	0.0	0.0
Quenching and flooding	-3.3	0.0	-3.3
Complexity III: Complexity to overall plant			
Frequency in maintenance of utilities - auxillary units, advanced controls	-4.0	-10.0	-10.0
Process extension -multi-units, parallel, lengthy, agitators	-2.0	-6.0	-10.0
Site-Storages	0.0	-6.0	-10.0
Frequency in transportation and unloading activities	0.0	3.0	3.0

When the same principle applies to complex hydrides, the same conflicts as metal hydrides are identified; which refer to the bulk inventory of the complex hydrides in slurry that needs to be supplied to the semi-batch reactor. As a result, the inventory is increased for a complex hydrides storage system, due to a requirement to have additional bulk storage units, before the discharge of hydrogen via the reactor. Therefore, the risk associated with a catastrophic rupture and leak at the feed pipeline, is high in both of the storage systems, as reported by Landucci et al., (2008).

The potential conflicts in the *moderation* principle, focuses on the severity of the operating conditions. The positive conflict of metal and complex hydrides has been measured as shown in the values of DR and DI in Table 4.18, which are illustrated as moderate operating conditions in the system, where the instability of hydrogen storage can be minimal. However, the evaluation findings by the IRDI tool have revealed that there is a potential for fire and dust explosion in both metal and complex hydrides, due to their pyrophoric properties and other safety parameters, such as burning rate, minimum ignition energy, and maximum rate of pressure rise, as testified by Zalosh (2008) and Tanaka et al., (2009) that could inherently affected the process; when there is a potential of a worst case scenario, such as system failure, human error, etc. in the handling of the storage system. Besides that, the compression unit in both systems also contribute to the negative conflicts under the *moderation* principle, which causes the storage systems to be at a par with compressed and cryogenic systems.

Finally, the result of the potential hazard migration, based on the *simplification* principle, shows the highest total index values for both metal and complex hydrides in comparison with compressed and cryogenics. These negative conflicts come mainly from the complexity of hydride technologies itself, which may have problems of reliability of the auxiliary units, such as the heat exchanger, compressor, and piping connections between the secondary equipment, in order to complete the process. Moreover, the complexity of these storage systems may require additional safety control measures, such as secondary containment, since the system could contain heavy hydrides slurry, as in complex hydrides. Besides that, the bulk storage unit, semi-batch reactor, and compression unit, may require blast walls to protect from the potential of a dust explosion. For transportation activities, as described above, metal and complex hydrides are flammable, pyrophoric, and water-reactive materials, which define the incompatibility of these materials, resulting in them being classified as United Nations Packing Group I; as the most stringent category of container regulations for transporting these materials (Tanaka et al., 2009). This finding is equal to the evaluation which contributes to moderate negative conflicts, but still the transportation of compressed and cryogenic hydrogen is far more hazardous than the other two options.

After consideration of LIDIS, the LIHM results showed that complex hydrides storage has the highest potential conflicts, as shown in Figure 4.13. Therefore, the IRDI values for all storage technologies can be compared, as described in Figure 4.14. The IRDI results shown in Figure 4.15 have shown a similar trend of findings with the total potential index and hazard index obtained by Landucci et al., (2008); although Landucci's method may have different ways to indicate these hazards. However, it can be observed that the outcomes obtained for cryogenic storage by Landucci are higher than the IRDI findings. The discrepancy of results could be due to the applicability of the IRDI tool, to take into account the potential of a dust explosion, which is high in metal and complex hydrides storage systems, compared with the potential of a vapour cloud explosion of liquefied hydrogen released from a cryogenic system. As reported by DeLuchi, (1989), hydrogen has highly diffusive properties, which imply a tendency for hydrogen to accumulate at maximum concentration, equivalent to TNT mass, is highly possible to cause a vapour cloud explosion.

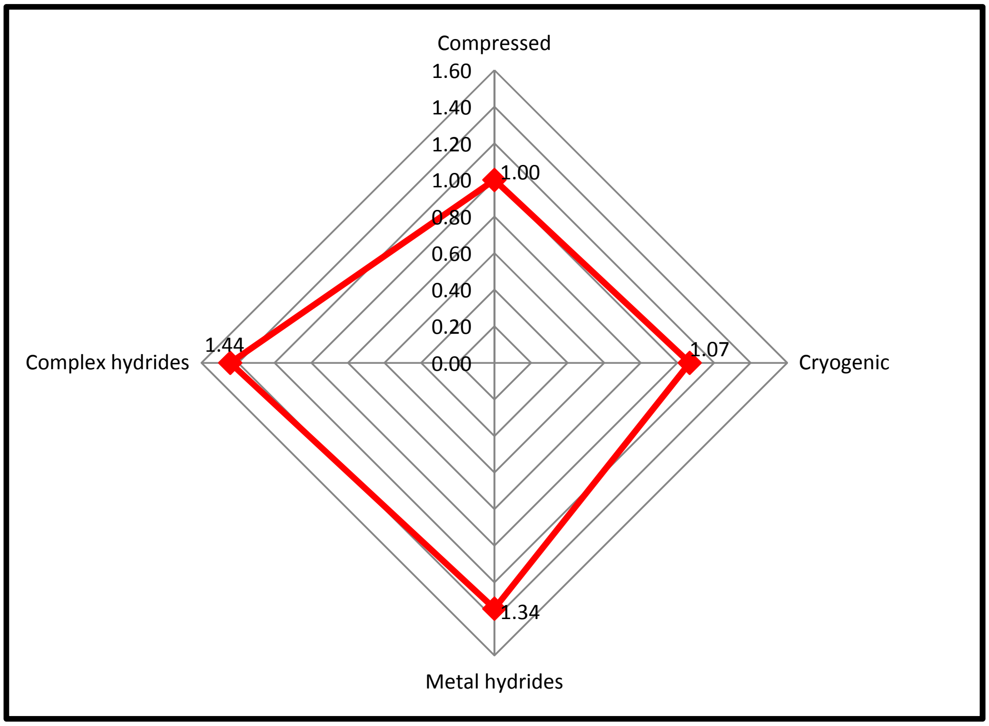


Figure 4.13: LIHM results for all hydrogen storage systems

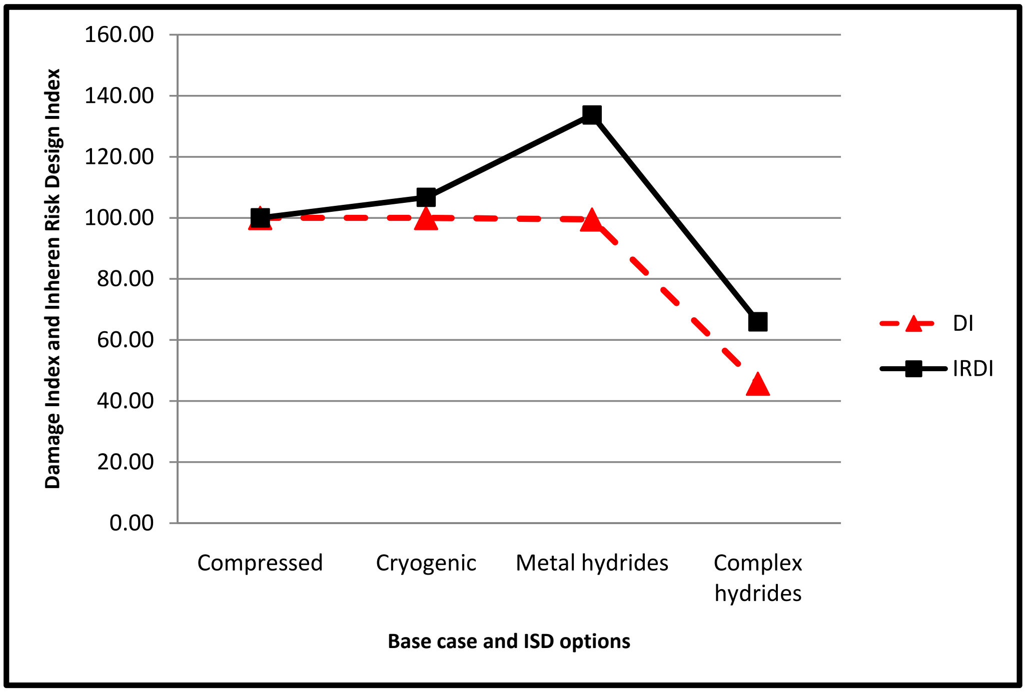


Figure 4.14: Comparison of DI to IRDI for all storage systems

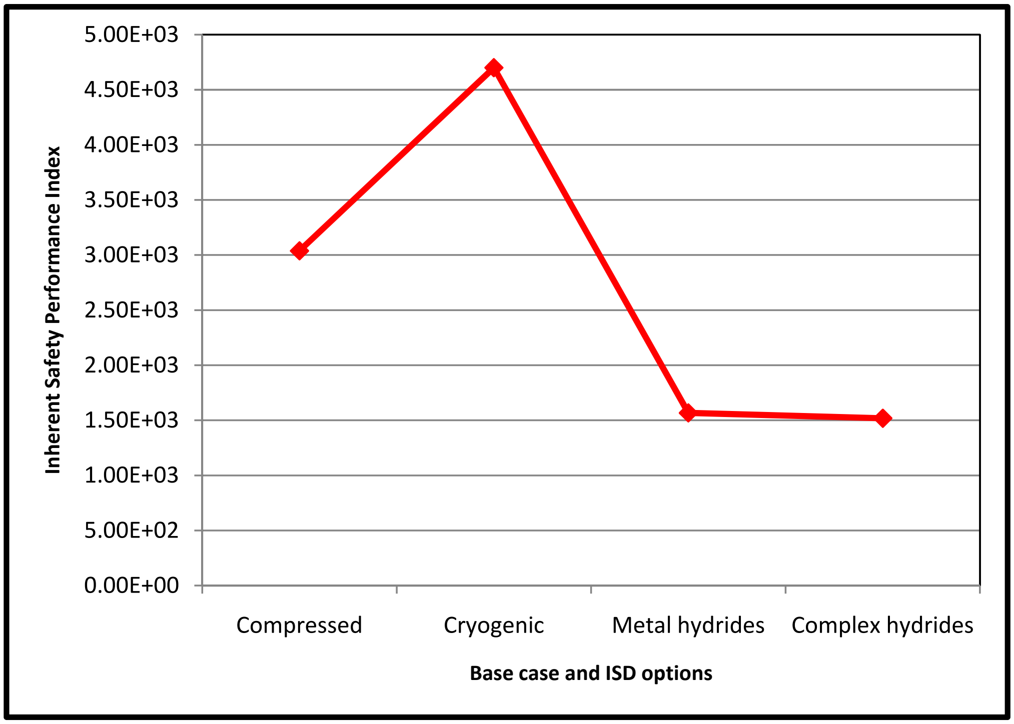


Figure 4.15: Landucci et al., (2008) results after combination of potential and hazard indexes

Unlike the metal and complex hydrides, even with their capability to store more hydrogen in a stable mode, the system still requires an additional process to discharge the hydrogen at a high pressure, as well as a high dust concentration had increased the max rate of pressure rise in the reaction, where the potential to cause a dust explosion is high during any loss of containment, as estimated in Table 4.19.

Based on the IRDI results, the designer may have to carry out further analyse of the metal and complex hydrides, based on the proposed risk ranking and design criticality highlighted by IRDI tool, as shown in Table 4.20, as part of the decision making in selecting the ISD alternative. It can be concluded that the complex hydrides storage system appeared to have low hazards, since the operating conditions of this system are at a moderate level compared to others. However, this storage system contained the highest potential of hazard migration, or conflicts in terms of the potential for dust explosions to occur in the system, the complexity of the design, and the transporting and handling process. Therefore, the IRDI result for this system demonstrates that the design is MEDIUM level, and the designer should look into the identified conflicts, in order to further enhance the overall inherent safety of the storage system.

Table 4.20: The criticality of IRDI for hydrogen storage systems

ISD Option	DI	LIHM	IRDI	Risk Level	Design Criticality Descriptions
Compressed	100	1.0	100	**High**	Design option is highly critical Redesign is highly required Technical safety measures are highly required
Cryogenic	100	1.07	106.71	**High**	Design option is highly critical Redesign is highly required Technical safety measures are highly required
Metal hydrides	99.49	1.34	133.70	**High**	Design option is highly critical Redesign is highly required Technical safety measures are highly required
Complex hydrides	45.69	1.44	65.94	**Medium**	Design option is critical Redesign may be required Technical safety measures may be required

4.7 Concluding remarks

The capabilities of IISDET methodology to identify, generate, and evaluate, design options from the perspective of a design that is AiSAP has been illustrated through the above case studies. This methodology has shown that an inherently safer design can be achieved at the early stage of design through integrated qualitative and quantitative tools, which are developed based on the ISD concept and the explicit use of IS principles. The identification of inherent hazards and the generation of potential ISD options qualitatively, can be obtained at the preliminary hazard stage, which has been demonstrated through Cases II and III. The conflict issues have been shown successfully in Cases III, IV, and V, where their evaluation is also supported by the incorporation of process, design, and safety elements, in one single framework, where the selection of these elements is independent and flexible, according to the end-user's requirement.

It can be concluded, that the developed tools are significantly important, in order to support the realisation of ISD at an early stage of design. The exploitation of Inherent Safety principles, to trigger the conflicts or the potential of hazard migrates during design modification, is highly significant in order to highlight potential hidden consequences, which are ultimately not obvious before modification. However, the application of IISDET may require experience and expert judgement when there is a lack of supporting information, especially for the processing of safety database and information, which could cause high uncertainties in the findings. The above constraints are highlighted in Chapter 5, as being one of the potential future works. Regardless of this issue, IISDET is able to support the development of ISD at an early stage of design and it is crucial to be applied as one of the decision making tools, from an inherent safety point of view.

CHAPTER 5

CONCLUSIONS AND FUTURE WORKS

5.1 Conclusions

Application of the ISD concept during the early design stage enables the designer to identify hazards and minimise them through modification of design. However, this new design is not necessarily safe enough, as the creation of new hazard conflicts can occur when the design is changed. This issue is one of the important factors that limit the utilisation of the ISD in the CPI. Therefore, this research seeks to find solutions through the development of a systematic tool that can support the determination of a design that is As inherently Safe As Practicable (AiSAP) during the preliminary design stage.

This research proposes a framework of an Integrated Inherent Safety Design Evaluation Tool (IISDET), which is developed by combining the qualitative and quantitative approaches into a single tool, to ensure that a comprehensive ISD assessment can be conducted. This framework is focused on the potential hazards that are related to fire and explosion, as these types of hazard are the main contributors to damaging structures, people, and the environment.

The qualitative tool, Qualitative Assessment for Inherently Safer Design (QAISD), was developed to identify the inherent hazards, generate the ISD options, screen those options, and evaluate the Inherent Safety conflicts for all ISD options. The identification of inherent hazards is accomplished using a Register, Investigate, and Prioritise (RIP) tool. In addition, the Inherent Design Heuristic (IDH) tool was developed to generate options based on heuristic approaches of the ISD concept. Furthermore, the screening and evaluating of options were performed using the Inherently Feasible Matrix (IFM) and the Inherently Safer Matrix (ISM), respectively.

All of these tools are integrated at the hazard review stage, in order to allow for inherent risk reduction strategies to be implemented as early as possible; especially during the preliminary design of the process.

The quantitative tool, Quantitative Index for Inherently Safer Design (QIISD),was developed to assess the tolerability of the inherent hazards in the design option, in order to generate the ISD options, based on the estimated hazardous energy and penalty factors with the assistance of the IDH tool, and finally, to quantify the potential conflicts of the ISD options. The tolerability of design is assessed by estimating the potential damage caused by fire and explosion from reactivity, and physical and combustion energies, which could be contained in the option, using the Damage Index (DI) tool. The generation of new design options is supported by the Prioritise, IDH, and Assess (PIDHA) tool. Meanwhile, the evaluation of conflicts is estimated using the Inherent Risk Design Index (IRDI) tool, in order to select the best ISD option that will fulfil the concept of AiSAP.

A total of five case studies were performed to demonstrate the applicability of the above tools. Validation of the energy factors was carried out through Case I, by comparing published data with the present input. The energy factors used in this research showed a close agreement with the published results. Case II was developed to illustrate the RIP and IDH tools, using the nitration of toluene process. The application of the ISM tool was demonstrated in Case III, in order to identify the inherently safer solvent between anhydrous ammonia vapour, aqueous ammonia, anhydrous ammonia liquid, and urea based ammonia, for a Selective Catalytic Reduction (SCR) system, in a refinery. Finally, the integration of qualitative and quantitative methods was demonstrated through Case IV, in order to identify the AiSAP reactor design for nitration of toluene process, by application of the ISM and IRDI tools.

The ultimate objective of the IISDET framework is to provide tools that are able to indicate and assist the designer in his/her decision making, with regard to the inherent safety point of view, especially to identify the best ISD option qualitatively and quantitatively. The application of this framework will have a greater impact on the risk reduction of hazards, a lower potential of new hazards, and produce better performance, in terms of economical production and minimum safety losses, during the design stage. In other words, the changes in process design will not only help to achieve better productivity, but also to produce a design that can operate with a very minimum risk of accidents, since the hazards have been designed-out from the process and are less dependent on active, passive, and safety procedures. In addition, IS conflicts due to ISD modifications, are monitored through the ISM and IRDI tools, by evaluating the potential of hazard conflicts, not only within the process unit itself, but also the overall process plant. Thus, designers will have more options after taking into account the overall safety performance of the process unit and its potential conflicts. Since the safety conflicts are evaluated at an early stage of process design, designers will have more time to conduct further analyses before a detailed design of the process unit is performed.

5.2 Potential future works

There are several constraints in the IISDET framework. Therefore, a number of future works are proposed to extend the capability of the developed framework as follows:

- The extension of IISDET could be developed by considering other types of hazard, such as toxic release, and the analysis of conflicts could be broadened to the conflict of Inherent Safety with the environment, and other performance factors, as described in Chapter 1.
- The qualitative tool, QEISD, could be extended as an expert system by developing the ISD database and properties, including a detailed development of algorithms, such as Fuzzy Logic for example.
- The quantitative tool, QIISD, needs to be further developed by considering cost factors. Cost-benefit analysis for the ISD option should be evaluated using an indexing procedure for the preliminary design stage, which is comprised of the cost of losses, ISD costs, and preliminary process design costs, to assist the designer in selecting the design that is an “As inherently Safer As Practicable” (AiSAP) alternative.

- The uncertainties that are developed in QIISD, due to a reliance on experience and expert judgement, should be studied further by developing an integrated tool to estimate detail process safety databases that can be integrated with this tool. In addition, prioritisation or ranking of IS principles could contribute to the extensive results of IRDI, as in this study, all IS principles are considered to carry equal importance.

- The quantitative tool could also be extended to estimate the criticality of the instability of the process conditions, such as to estimate the propagation of explosive conditions in a reactor.

LIST OF PUBLICATIONS

Conference Proceeding:

Rusli, R. and Shariff, A.M., Inherently Safer Design Options using Qualitative Method presented at 22nd Symposium of Malysian Chemical Engineers (SOMChE), Kuala Lumpur, Malaysia, 2ndand 3rd December 2008.

Rusli, R and Shariff, A.M., Using Risk Approach to Indicate Potential of Hazard Migration in Inherently Safer Design Alternatives accepted for HAZARDS XXII Conference, Institute Chemical Engineers UK, 11th-14th April 2011.

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Rusli, R. and Shariff, A.M., Qualitative Assessment for Inherently Safer Design (QAISD) for Preliminary Design Stage, *Journal of Loss Prevention in the Process Industries*, Volume 23, Issue 1, January 2010, Pages 157-165.

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APPENDIX I

Proposed Classification of Inherent Safety Criteria as a Guideline for RIP tool (Heikkila, 1999) – the classification in increasing order of hazards

Process Safety Factors	**Suggested Reference/Basis**	**Parameters**	
Inventory	Scaled from Mond values using expert recommendations in Lawrence's work. Different for ISBL and OSBL.	ISBL (tons)	OSBL (tons)
		0-1	0-10
		1-10	10-100
		10-50	100-500
		50-200	500-2000
		200-500	2000-5000
		500-1000	5000-10000

Temperature	Based on the danger posed to human, material strength. Beyond 300^{o}C carbon steel strength is decreased considerably compared to room temperature	$<0^{o}$C
		0-70^{o}C
		70-150^{o}C
		150-300^{o}C
		300-600^{o}C
		$>600^{o}$C

Pressure	Based on the Dow F&EI	0.5-5 bar
		0-0.5 or 5-25 bar
		25-50 bar
		50-200 bar

Heat of reaction	From safety point of view, it is important to know how exothermic the reaction is. The classification used by King (1990)	$\geq$3000J/g
		$<$3000J/g
		$<$1200J/g
		$<$600J/g
		$\leq$200J/g

Flammability	Classification based on EU directives	Non flammable
		Combustible (fp$>55^{o}$C)
		Flammable (fp$<55^{o}$C)
		Easily flammable (fp$<21^{o}$C)
		Very flammable (fp$<0^{o}$C and bp$>35^{o}$C)

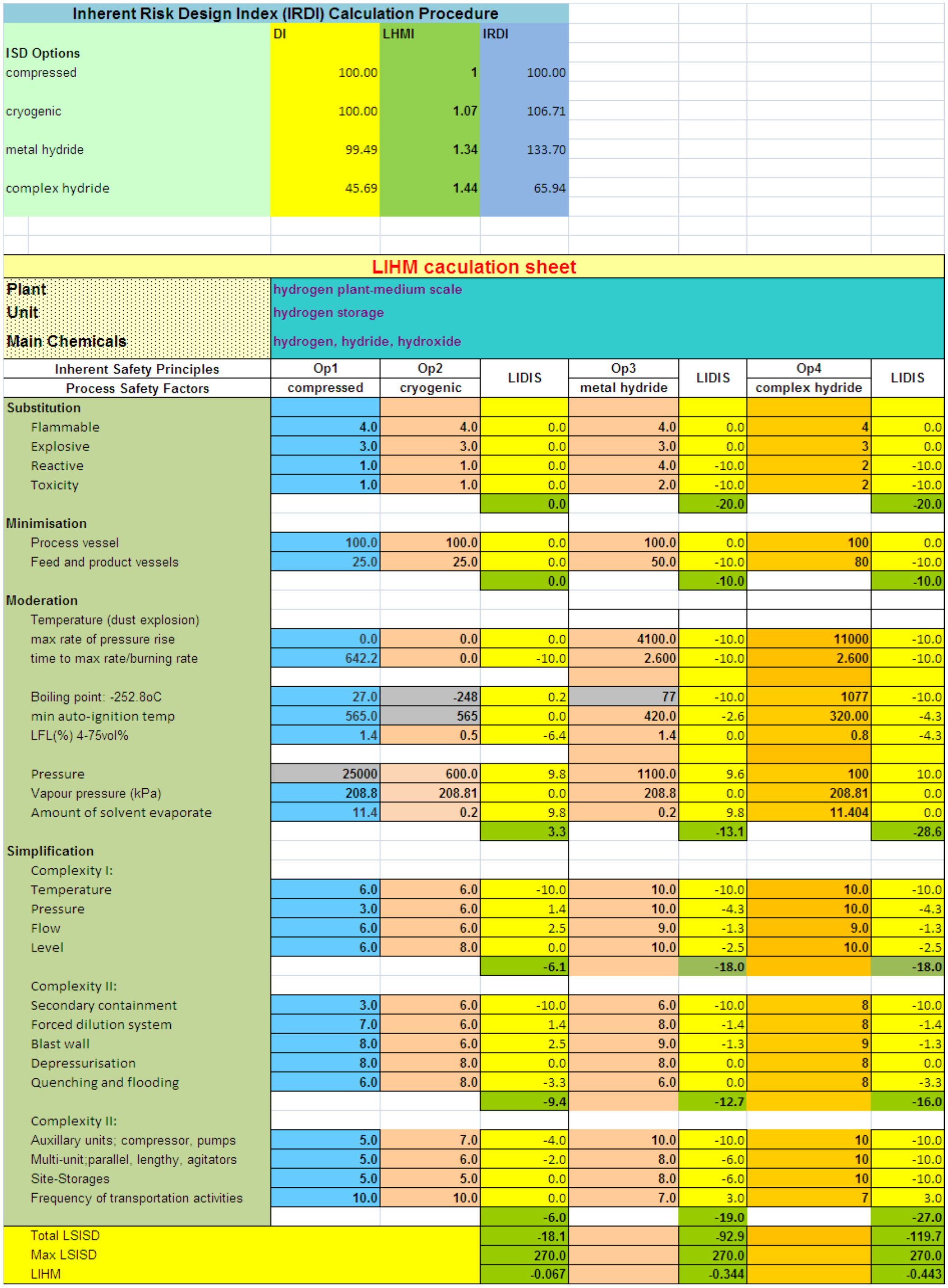
Explosiveness	Sub dividing the difference between UEL and LEL	Non explosive
		0-20
		20-45
		45-70
		70-100

Process Safety Factors	**Suggested Reference/Basis**	**Parameters**
Corrosiveness	Based on construction materials required	Carbon steel
		Stainless steel
		Better materials
Toxicity	Classified based on Mond index	TLV>10000
		TLV≤10000
		TLV≤1000
		TLV≤100
		TLV≤10
		TLV≤1
		TLV≤0.1
Chemical interaction	Based on EPA's matrix (Hatayama et al., 1980). Used to consider unwanted reactions of process substances with materials in the plant area. These reactions are not expected to take place in reactor and therefore not discussed in side reaction index.	Heat formation
		Fire
		Formation of harmless, non-flammable gas
		Formation o flammable gas
		Explosion
		Rapid polymerisation
		Soluble toxic chemicals
		Formation of toxic gas

Type of equipment	Based on various studies and statistics of failures and qualitative arguments the following set of index is derived and used.	ISBL	OSBL
		Equipment handling non-flammable, non-toxic materials	Equipment handling non-flammable, non-toxic materials
		Heat exchangers, pumps, tower, drums	Atmospheric tanks, pumps
		Air coolers, reactors, high hazard pumps	Cooling towers, compressors, blowdown systems, pressurised or refrigerated storage tanks
		Compressors, high hazard reactors	Flares, boilers, furnaces
		Furnaces, fired heaters	

APPENDIX II

Sample worksheet for Case V – Hydrogen storage systems



Inherent Risk Design Index (IRDI) Calculation Procedure

	DI	LHMI	IRDI
ISD Options			
compressed	100.00	1	100.00
cryogenic	100.00	1.07	106.71
metal hydride	99.49	1.34	133.70
complex hydride	45.69	1.44	65.94

LIHM caculation sheet

Plant	hydrogen plant-medium scale
Unit	hydrogen storage
Main Chemicals	hydrogen, hydride, hydroxide

Inherent Safety Principles	Op1	Op2	LIDIS	Op3	LIDIS	Op4	LIDIS
Process Safety Factors	compressed	cryogenic		metal hydride		complex hydride	
Substitution							
Flammable	4.0	4.0	0.0	4.0	0.0	4	0.0
Explosive	3.0	3.0	0.0	3.0	0.0	3	0.0
Reactive	1.0	1.0	0.0	4.0	-10.0	2	-10.0
Toxicity	1.0	1.0	0.0	2.0	-10.0	2	-10.0
			0.0		-20.0		-20.0
Minimisation							
Process vessel	100.0	100.0	0.0	100.0	0.0	100	0.0
Feed and product vessels	25.0	25.0	0.0	50.0	-10.0	80	-10.0
			0.0		-10.0		-10.0
Moderation							
Temperature (dust explosion)							
max rate of pressure rise	0.0	0.0	0.0	4100.0	-10.0	11000	-10.0
time to max rate/burning rate	642.2	0.0	-10.0	2.600	-10.0	2.600	-10.0
Boiling point: -252.8oC	27.0	-248	0.2	77	-10.0	1077	-10.0
min auto-ignition temp	565.0	565	0.0	420.0	-2.6	320.00	-4.3
LFL(%) 4-75vol%	1.4	0.5	-6.4	1.4	0.0	0.8	-4.3
Pressure	25000	600.0	9.8	1100.0	9.6	100	10.0
Vapour pressure (kPa)	208.8	208.81	0.0	208.8	0.0	208.81	0.0
Amount of solvent evaporate	11.4	0.2	9.8	0.2	9.8	11.404	0.0
			3.3		-13.1		-28.6
Simplification							
Complexity I:							
Temperature	6.0	6.0	-10.0	10.0	-10.0	10.0	-10.0
Pressure	3.0	6.0	1.4	10.0	-4.3	10.0	-4.3
Flow	6.0	6.0	2.5	9.0	-1.3	9.0	-1.3
Level	6.0	8.0	0.0	10.0	-2.5	10.0	-2.5
			-6.1		-18.0		-18.0
Complexity II:							
Secondary containment	3.0	6.0	-10.0	6.0	-10.0	8	-10.0
Forced dilution system	7.0	6.0	1.4	8.0	-1.4	8	-1.4
Blast wall	8.0	6.0	2.5	9.0	-1.3	9	-1.3
Depressurisation	8.0	8.0	0.0	8.0	0.0	8	0.0
Quenching and flooding	6.0	8.0	-3.3	6.0	0.0	8	-3.3
			-9.4		-12.7		-16.0
Complexity II:							
Auxillary units; compressor, pumps	5.0	7.0	-4.0	10.0	-10.0	10	-10.0
Multi-unit;parallel, lengthy, agitators	5.0	6.0	-2.0	8.0	-6.0	10	-10.0
Site-Storages	5.0	5.0	0.0	8.0	-6.0	10	-10.0
Frequency of transportation activities	10.0	10.0	0.0	7.0	3.0	7	3.0
			-6.0		-19.0		-27.0
Total LSISD			-18.1		-92.9		-119.7
Max LSISD			270.0		270.0		270.0
LIHM			-0.067		-0.344		-0.443