STUDYING THE RELATIONSHIP BETWEEN INHERENTLY SAFER DESIGN AND EQUIPMENT RELIABILTY

A Thesis

by

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ABSTRACT

During the last decade, inherent safety has emerged as an area of interest in both academic and industrial research. Various regulatory bodies (including US environment protection agency) have enforced the consideration of inherently safer design alternatives. This enforcement, however, may not serve the purpose of reducing the frequency of process incidents due to the drawbacks such as risk migration associated with inherent design philosophy.

This study focuses on analyzing the relationship between inherent safety and reliability as chemical project proceeds from initial to later stages of design. The main objective of this research is to evaluate the possibility of risk escalation caused due to lowering of system reliability during implementation of inherent safety principles applied with an objective to lower the consequence element of risk. This lowering of system reliability can increase the likelihood of a process incident, thus resulting in an increased risk, ultimately defeating the purpose of applying the inherent design philosophy.

The developed methodology involves quantifying inherent safety based on the design stage under consideration using a quantification technique that utilizes process data available during that stage of design. This is followed by determining reliability and availability of the system using reliability databases or static reliability modeling for various design alternatives considered during that design stage. Lastly, the trend observed between quantified inherent safety and reliability/availability is used to determine the required relationship.

The application of the developed methodology to process selection stage, conceptual stage, and detailed engineering stage reveals that the relationship between inherent safety and reliability (and availability) is complicated and varies as per the design stage under consideration. Thus, an important conclusion that can be drawn from this research is that an inherently safer design may not be associated with higher system reliability and lower risk.

Lastly, the developed methodology is validated for the case study of T2 Laboratories explosion and fire. An important observation from these case studies is the ineffectiveness of quantified inherent safety in terms of Dow F&EI to capture the severity of situation revealed by detailed reliability analysis.

DEDICATION

To my parents and elder brother

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NOMENCLATURE

N_F	-	Flammability score
N_E	-	Explosiveness score
N_T	-	Toxicity score
N_R	-	Reactivity score
R_T	-	Temperature score
R_P	-	Pressure score
R_Y	-	Yield score
R_H	-	Heat of reaction score
PRCSI	-	Process reaction and chemical safety index
ICI	-	Individual chemical index
IRI	-	Individual reaction index
HCI	-	Hazardous chemical index
HRI	-	Hazardous reaction index
OCI	-	Overall chemical index
ORI	-	Overall reaction index
OSI	-	Overall safety index
WCI	-	Worst chemical index
WRI	-	Worst reaction index
TCI	-	Total chemical index

I_{EQ}	-	Equipment score
PESI	-	Process equipment safety index
N_j	-	Number of j^{th} equipment
$I_{EQ,j}$	-	Equipment score of j^{th} equipment
OPSI	-	Overall process safety index
MTTF	-	Mean time to failure
MTTR	-	Mean time to repair
A_{inh}	-	Inherent availability
$A_{inh,i}$	-	Inherent availability of i^{th} equipment
$A_{inh,sys}$	-	Inherent availability of system
FCI	-	Fixed capital investment
$OPSI_i$	-	Overall process safety index for i^{th} alternative
AP_i	-	Annualized profit for i^{th} alternative
$N_{OPSI,i}$	-	Normalized overall process safety index for i^{th} alternative
$N_{AP,i}$	-	Normalized annualized profit for i^{th} alternative
W_{OPSI}	-	Weighed overall process safety index for i^{th} alternative
W_{AP}	-	Weighed annualized profit for i^{th} alternative
I_{OPSI}	-	Overall process safety index for ideal solution
I_{AP}	-	Annualized profit for ideal solution
NI_{OPSI}	-	Overall process safety index for non-ideal solution

NI_{AP}	-	Annualized profit for non-ideal solution
A_i	-	Distance of design alternative from ideal solution
B_i	-	Distance of design alternative from non-ideal solution
R_i	-	Relative closeness of design alternative
P	-	Operating pressure of reactor (atm)
k	-	Reaction constant (s^{-1})
MW	-	Molecular weight
M	-	Maximum allowable stress of reactor
X	-	Conversion of reaction
W_{Ao}	-	Initial mass of A
W_A	-	Final mass of A
F_{Ao}	-	Initial flow rate of A
V	-	Volume of reactor
C_{Ao}	-	Initial concentration of A
$\in$	-	coefficient of volume change
D	-	Internal diameter of reactor
L	-	Length of reactor
r	-	Length to diameter ratio of reactor
Γ	-	Residence time of reactor
v_0	-	Initial flow rate of reactor

P_d	-	Design pressure of reactor
t	-	Thickness of reactor
F_1	-	General process hazard factor
F_2	-	Special process hazard factor
F_3	-	Process unit hazard factor
MF	-	Material factor
F&EI	-	Fire and explosion index
S_h	-	Mean hoop stress in the reactor
S_i	-	Mean induced stress in the reactor
σ_h	-	Standard deviation of hoop stress
σ_p	-	Standard deviation of operating pressure
σ_i	-	Standard deviation of induced stress
F	-	Failure probability of reactor due to excess pressure
R	-	Reliability of reactor
m	-	Integral parameter for determining failure probability of reactor

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CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

Due to the current economic downturn of oil and gas industry, more research impetus has been dedicated towards the design of processes that are superior in performance in terms of their profitability. A process that is economically superior tends to be generally safer as well, since a safer process has lesser downtime and thus, more productivity. The concept of inherent safety has increasingly received more importance over the years due to its ability to design processes with reduced hazards. However, a process that is inherently safer with respect to process hazards may not be associated with low risk as well. To understand this drawback of inherent safety, it is essential to understand the difference between hazard and risk. Hazard is defined as the property (physical or chemical) that has the potential to cause harm to people, environment or property whereas risk quantifies the level of human injury, environmental damage, or economic loss in terms of both the incident probability and the extent of the loss or injury (Crowl, 1996). Inherent design philosophy mainly focuses on reducing the consequence element of risk (extent of loss) by reducing or minimizing the associated process hazards, generally ignoring its effect on the likelihood element. Thus, a process that is inherently safer might have increased associated risk due to phenomenon of risk migration caused due to an increase in likelihood element.

This study mainly focuses on a design approach of chemical processes that are inherently safer while preventing risk migration by considering the system reliability. The description of the development of the methodology, application of developed methodology to case studies, obtained results and subsequent analysis followed by conclusions and future work is described in the upcoming chapters.

1.2 INHERENT SAFETY

Inherent safety is the design philosophy primarily based on reduction and elimination of hazards. (Mannan, 2002). The cornerstone of this philosophy was laid after the Flixborough disaster in 1978 and was put forth in the well-appreciated article by Dr. Kletz, "What you don’t have, can't leak" in the 19th Loss prevention symposium of the American institute of chemical engineers (Kletz, 1978). This design philosophy differs from the risk-based design approach for design of safer process in the sense that risk-based design approach is based towards reducing the likelihood of an incident and/or mitigating the consequence element, whereas inherently safer design philosophy is mainly focused on hazards associated with the process.

The principles of inherent safety can be described as follows:

- Intensification or minimization: reducing the amount of hazardous chemicals involved in the process.
- Substitution: substituting a hazardous chemical in the process with a safer one. The hazards associated with a chemical can be related in terms of its flammability, explosiveness, toxicity and chemical reactivity.
- Attenuation or moderation: reducing the severity of the operating conditions (operating temperature and pressure) of the process involving hazardous chemicals.
- Limitation of effects: altering the design (mainly process design and operating conditions) based on the hazards associated with the process to limit the effect of hazardous chemicals.
- Simplicity: designing simpler plants with relatively lesser number of equipment to reduce opportunities for failure in the process.

1.3 REGULATORY SCENARIO OF INHERENTLY SAFER DESIGN

Inherent safety has found its way in various regulations by authoritative bodies. Following the Bhopal disaster in 1984, the state of New Jersey adapted the toxic catastrophe prevention act in 1985. The act was revised in 2003 to include the consideration of inherently safer technologies (ISTs). The Contra Costa County in California has enforced the consideration of ISTs for regulation of hazardous facilities. Concerned about the threat of terrorist attack on facilities processing hazardous chemicals, the U.S Department of Homeland Security considered ISTs as a preventive measure and supplicated the center for chemical process safety to provide a scientific definition of inherent safety. In February 2016, the US Environmental Protection Agency (EPA) put forth a proposal to revise its risk management program to include the consideration of safer technologies and alternatives in the process hazard assessment for regulation of hazardous industrial facilities. This proposal was disapproved by various industrial associations such as US small business administration and American forest and paper association primarily due to the difficulty of implementing ISD in existing facilities as compared to the design stage of grass-root facilities, however, despite this opposition, the amendment was formally accepted by EPA in January 2016. Apart from gaining importance in U.S, inherent safety has received subsequent attention in Europe as well. Inherent safety has been listed as a desired characteristic by U.K health and safety executive. The European Council directive 96/82/EC of 1996 on the control of major-accident hazards involving dangerous substances, in its guidance document states, “Hazards should be possibly avoided or reduced at source through the application of inherently safe practices.”

1.4 EQUIPMENT RELIABILITY AND ITS IMPACT ON PROCESS ECONOMY AND PROCESS SAFETY

Reliability is the probability that a system or a component will perform its desired function at the required time when used under the appropriate operating conditions whereas, availability is the probability that a system or a component will perform its desired function at the required time when maintained or operated in the prescribed manner (Ebeling, 1997). Due to operation of upcoming chemical plants being under severe conditions in large sized equipment to achieve required profitability, the associated reliability analysis of such process systems has become increasingly complex. This has ultimately led to high risk associated with these facilities. An analysis of the occurring process safety incidents revealed that most of these incidents occur during transient operations, such as equipment maintenance, startup, and shutdown (Duguid, 1998). Thus, a process with lower reliability (and thus, higher maintenance downtime) can be associated with a higher risk. Apart from affecting the safety of the chemical plant, reliability controls the downtime (due to preventive and corrective maintenance activities) associated with a chemical plant. A plant associated with lower system reliability tends to have higher maintenance downtime and thus, lower productivity ultimately leading to lower profitability. It is estimated that the loss in revenue resulting from unexpected shutdowns in a chemical plant can be within a range of $500 - $100,000 per hour (Tan and Kramer, 1997). Therefore, significant profits can be derived from design and implementation of technologies with higher system reliability.

Various industries have manipulated this relationship to improve the profitability of their processing systems. Exxon Mobil in 1994 introduced the reliability and maintenance system program which reduced the maintenance cost by $ 30 million (Exxon Mobil, 2001). Shell in its Pulau Bukom refining facility in 1996, made design and operational modifications which resulted in a 4-year long run of a residue catalytic cracking unit with a minimal of 21 hours of downtime (Shell, 2001). British Petroleum saved over $ 1.4 million in pump repairs by escalating the mean time between failure of pumps in their facility in Lima, United States (Griffith.J, 1998).

CHAPTER II

PREVIOUS WORK ON PROCESS DESIGN, INHERENT SAFETY, AND EQUIPMENT RELIABILITY

2.1 PROCESS DESIGN AND INHERENT SAFETY

A considerable depth of study has already been carried out in designing process systems by considering inherent safety design philosophy. To effectively understand and quantify the ease of implementation and associated hazards of the available design alternatives, various assessment methods, and safety indices have been put forth. Prototype index for inherent safety (PIIS) was developed with an objective to quantify the inherent safety of chemical process routes (Edward and Lawrence, 1993). Dow industries put forth the Dow fire and explosion index (Dow F&EI) aimed at quantifying the hazards associated with a process design. The Dow F&EI has received subsequent revision over the years and is widely used in process industry. Inherent safety index (ISI) was formulated with an aim to provide a simpler method for quantification of inherent safety associated with a process design (Heikkila, 1999). Similarly, the i-safe index was developed as a methodology for selection of process routes based on inherent safety (Palaniappan, 2002). A significant contribution towards quantification of inherent safety was the development of fuzzy logic based index for selection of process design alternatives (Gentile, 2003). Apart from focusing only on safety aspects of design alternatives, the substance, reactivity, equipment, and safety technology (SREST) layer assessment method was developed to include health and environment aspects. The integrated inherent safety index (I2SI) was formulated as an improvement to previously developed safety indices (Khan and Amyotte, 2004). An analysis of the implementation of inherent safety throughout process life-cycle phases was carried out effectively using ISI index (Hurme and Rahman, 2005). An important step to include personnel safety and process safety for selection of design alternatives was the formulation of Process Route Healthiness Index (PRHI) which also focused on health hazards of chemicals involved. A significant contribution towards process selection was the evaluation of various methods for assessing the environment, health, and safety hazards in early phases of chemical process design (Adu, 2008). Based on statistical analysis, Inherent Benign-ness Indicator (IBI) was developed for comparing chemical process alternatives (Srinivasan and Nhan, 2008). A significant deviation from the conventional method of using non-dimensional indices for quantification of inherent safety is the qualitative assessment for inherently safer design (QAISP) method for application during preliminary design. The described methods mainly focused on hazards associated with process design alternatives, rather than focusing on the risk associated with these alternatives. This drawback was countered by the formulation of the concept of risk- based inherent safety (Rathnayaka, 2014). A comparative analysis of the well-known safety indices to assess their agreement with each other as well as with expert judgments in various process design stages was subsequently carried out (Kidam, 2008).

2.2 SELECTION OF ASSESSMENT METHOD FOR QUANTIFICATION OF INHERENT SAFETY

An important theoretical concept was theorized by Dr. Kletz after developing the inherent safety philosophy. The concept stated that implementing inherent safety principles (ISP) becomes more and more difficult, as the design of the chemical process plant progresses from initial stages of design to the later stages (Kletz, 1991). This trend is mainly because major decisions concerning plant and process design are taken during earlier stages of plant design. Therefore, it is essential to assess the possibility of implementing inherent safety principles as early as possible in the design of chemical facilities. However, due to lack of depth of information pertaining to the process during initial stages of design, the required evaluation and decision making become difficult. This paradox is referred to as the design paradox and is well illustrated in the following figure (Hurme and Rahman, 2005):

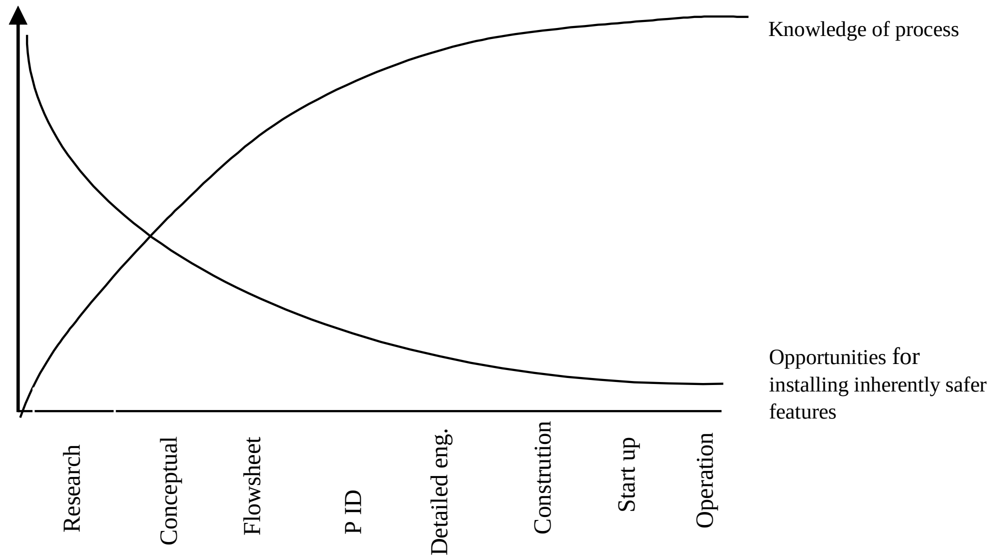

Figure 1: Process design paradox (Hurme and Rahman, 2005)

A possible solution to this design paradox is using different evaluation techniques based on the information available in the design stage under consideration. This can be described by the following table:

Design stage	**Evaluation technique**
Process R&D	Laboratory Screening and Testing
Conceptual stage	ISI, PIIS & i-safe
Project Stage	Suitable Index/Risk assessment method
Basic engineering	Dow F&EI
Detailed Engineering	Dow F&EI
Procurement Fabrication Construction	What-If, Checklist
Start-up	What-If, Checklist

Table 1: Inherent safety evaluation techniques (Heikkila, 1999 and Kidam, 2008)

Although Dow F&EI has been deemed to perform appreciably well in later stages of process design, the formulation of various safety indices for earlier stages of process design such as i-safe index, PIIS, ISI, Dow F&EI presents a conundrum. This issue was resolved by a comparative analysis of these safety indices (Kidam, 2008). This study aimed at evaluating the performance of safety indices to quantify inherent safety by comparing them to each other and with expert judgments during different stages of design. The results obtained from this study included the R^2 value of the correlation of ranking of design alternatives obtained from the different safety indices and expert judgment in the case of production of methyl methacrylate. The results obtained for the process route selection stage are as follows:

Index	PIIS	ISI	i-safe	Expert judgement	Average
DOW	0.8	0.84	0.89	0.74	0.81
PIIS		0.94	0.94	0.87	0.89
ISI			0.96	0.97	0.93
i-safe				0.9	0.92
Expert judgement					0.87

Table 2: Agreement of safety indices (Kidam, 2008)

Thus, an important conclusion from this study was that ISI and i-safe index had the strongest agreement with other indices and expert judgment (due to higher R^2 values) during process route selection stage and thus, are suitable during earlier stages of process design.

2.3 PROCESS DESIGN AND EQUIPMENT RELIABILITY

Significant depth of research has been carried out in reliability, maintainability and availability studies of chemical processing facilities. Reliability analysis of complex systems like chemical piping using simplistic Markov models (Gruhn, 1983) have been put forth. A major contribution towards analyzing the reliability of chemical systems was the development of methodology wherein reliability and availability were obtained through block diagrams (Henley and Gandhi, 1982). A reduction model for analyzing the reliability of chemical facilities involving processing units and storage tank was subsequently developed (Kardos and Lorenz, 1987). Simulation of chemical process systems with a focus on reliability was formulated (Thomas and Zanakis, 1974) which served as a pathway for computer models developed with an objective to determine the reliability of complex integrated process plant systems. The concept of parallel and standby redundancies was put forth, and dynamic programming was applied to determine the optimum configuration of series systems (Rudd, 1962). A significant step in reliability engineering was the development of maintenance strategies based on the reliability of chemical systems (Gall and Kovacs, 1985). The widely-accepted method of fault tree for predicting chemical plant failure served as a breakthrough in the field of reliability analysis (Freeman, 1983).

The developed concepts in reliability theory were effectively applied in process design and optimization (Cos, 1973). A major contribution in this regard was studying and optimizing the relationship between system reliabilities and unit reliabilities by sensitivity analysis (Henley and Gandhi, 1982). Corrective maintenance scheduling optimization based on reliability analysis served as a cornerstone in developing the concept of reliability based maintenance studies (Krishnaswamy and Parker, 1984). A reliability centered maintenance model for initial design phases of chemical facilities using fuzzy reasoning algorithm and expert judgment was put forth (Fonseca, 2000). Reliability optimization was successfully integrated into process design specifically during the conceptual stage of design (Goel, 2003).

CHAPTER III

DEVELOPMENT OF METHODOLOGY

3.1 QUANTIFICATION OF PARAMETERS

To study the required relationship between inherent safety and equipment reliability, it is essential to quantify these parameters. The quantification of inherent safety depends on the design stage under consideration (Table 1). Also, reliability has a direct impact on the maintenance downtime and associated maintenance cost. however, to quantify this effect, it is essential to consider the maintainability of the system since reliability and maintainability share a trade-off which overall contributes towards the availability of the system. Maintenance of process systems can be categorized into corrective maintenance and predictive maintenance. Corrective maintenance is done after equipment failure and its subsequent detection to bring the equipment back to its operating state. Predictive maintenance is the maintenance that includes inspection, detection, and repairing of the equipment prior to their failure to prevent the development of major faults within the equipment. Predictive maintenance is governed by the safety culture and procedures adopted for the chemical facilities which are developed during later stages of design. However, corrective maintenance downtime of the process is governed by the process equipment involved within the chemical process system, specifically the inherent availabilities of the equipment.

Since the number and type of different process equipment involved within the process system are largely dictated within the early stages of design, the corrective maintenance downtime and its associated cost can be estimated during these stages. This estimation can be carried out from the inherent availability of the system that itself depends on the inherent availabilities of the equipment involved within the process system.

3.2 RELIABILITY DATABASE

Various reliability databases have been formulated over the years. Some of the widely-used databases include Process equipment reliability database (PERD), Offshore reliability data (OREDA), PDS handbook for safety instrumented systems, Instrument reliability network (IRN), European industry reliability data bank (EIReDA), Failure rate data in perspective (FARADIP) and Government industry data exchange program (GIDEP).

Due to the requirement of process equipment failure rate data, PERD and OREDA databases are used in this study.

3.3 DESCRIPTION OF METHODOLOGY

The developed methodology for studying the required relationship can be described by the following figure:

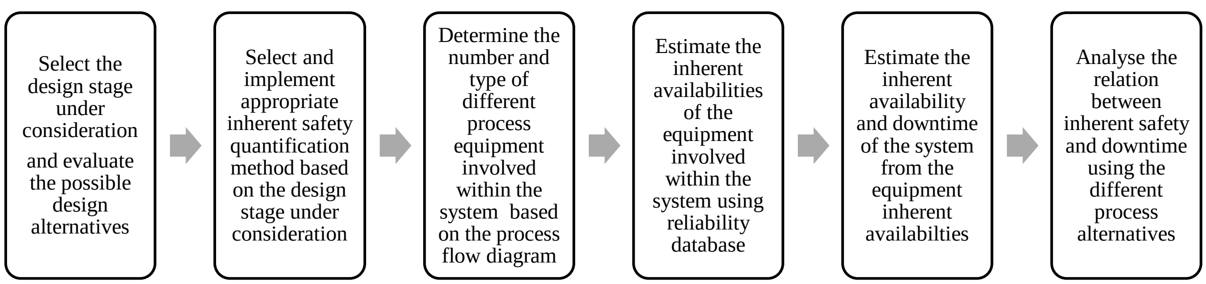

Figure 2: Methodology for assessing the required relationship

The first step towards analyzing the required relationship between inherent safety and equipment reliability is to select the design stage under consideration and all the possible design alternatives. This helps in assimilating the required process data based on the stage of design. This is followed by selecting and implementing an appropriate inherent safety quantification method (as per Table 1). The next step is to determine the number and type of different process equipment involved in the process system from the process flow diagram (PFD) of the system that is generally available during early stages of design. This is followed by determining the inherent availabilities of the involved equipment from appropriate reliability databases. The inherent availabilities of the equipment are then used to estimate the inherent availability and corrective maintenance downtime of the system by using the appropriate series parallel relation between these equipment. Lastly, the required relationship can be obtained by analyzing the trend between quantified inherent safety and corrective maintenance downtime for all the design alternatives under consideration.

CHAPTER IV

PROCESS SELECTION STAGE

4.1 INTRODUCTION TO PROCESS SELECTION STAGE

Process selection stage is one of the preliminary stages in process design that is carried out after the product to be manufactured is determined. In process selection stage, different chemical synthesis routes to manufacture the required product are evaluated, and an optimum process in terms of economics and process safety is selected. The design alternatives in process selection stage vary in terms of the chemicals, reactions, and equipment involved in the process. The principles of inherent safety can be very well understood and implemented during the process selection stage, owing to the ease of implementation of ISPs in early stages of design.

4.2 APPLICATION OF DISCUSSED METHODOLOGY TO PROCESS SELECTION STAGE

The described methodology in chapter II can be applied to process selection stage. The first step in the methodology is to evaluate the design alternatives existing for the design stage under consideration. The design alternatives in process selection stage are the different chemical process synthesis routes existing to manufacture the required product.

4.3 INHERENT SAFETY QUANTIFICATION FOR PROCESS SELECTION STAGE

The next step in the described methodology is to select an appropriate quantification technique for inherent safety. Inherent safety index and i-safe index are deemed to be appropriate for process selection stage (Table 2). However, both indices fail to appropriately reflect the effect of all ISPs mainly simplification. The principle of simplification is important in this study, since, the number of equipment involved in a process directly affect the reliability of the system while simultaneously having an impact on the inherent safety of the process through the principle of simplification. Therefore, a hybrid index that can consider chemical hazards through i-safe methodology and equipment hazards through ISI methodology and effectively reflects the impact of all ISPs has been developed. The safety index is computed by converting chemical, reaction and equipment hazards associated with the design alternatives into non-dimensional indices. The chemical hazards that are considered in the computation of the safety index are reactivity, toxicity, flammability, and explosiveness of chemicals (both reactants and products) involved in the process design alternatives. These hazards are converted into a non-dimensional index as per i-safe methodology (Palaniappan, 2003, originally based on ISI methodology) and are described as follows:

Flammability index:

Flammability	**Nature**	**Score (N_F)**
Flash Point > 55 ^{0}C	Combustible Liquid	1
Flash Point ≤ 55 ^{0}C	Flammable liquid	2
Flash Point < 21 ^{0}C	Easily Flammable	3
Flash Point > 0 ^{0}C	Very Flammable	4
Flash Point not defined	Non-flammable	0

Table 3: Flash point score conversion

Explosiveness index:

Explosiveness (UEL – LEL difference) volume %	**Score (N_E)**
Non - explosive	0
0-20	1
20-45	2
45-70	3
70-100	4

Table 4: Explosiveness score conversion

Toxicity index:

Toxicity (ppm)	**Score (N_T)**
TLV > 10000	1
TLV $\leq$ 10000	2
TLV $\leq$ 1000	3
TLV $\leq$ 100	4
TLV $\leq$ 10	5
TLV $\leq$ 1	6
TLV $\leq$ 0.1	7

Table 5: Toxicity score conversion

Reactivity index:

Reactivity	**Score (N_R)**
Normally Stable	0
Unstable at HTHP conditions	1
Violent Chemical change at HTHP	2
Capable of detonation with an initiating source	3
Capable of detonation at normal temperature and pressure	4

Table 6: Reactivity score conversion

Similarly, hazardous aspects of reactions such as the operating conditions of temperature and pressure and heat of the reaction are converted into non-dimensional indices as per inherent safety index methodology (Heikkila, 1999). The inventory of chemicals required for the process is indirectly considered through the yield of the chemical reactions involved. This yield is again converted into non-dimensional index as per prototype index for inherent safety methodology (Edwards, 1993).

Temperature index:

Operating temperature	**Score (R_T)**
< 0 ^{0}C	1
0 - 70 ^{0}C	0
70 - 150 ^{0}C	1
150 - 300 ^{0}C	2
300 - 600 ^{0}C	3
> 600^{0}C	4

Table 7: Temperature score conversion

Pressure index:

Operating pressure	**Score (R_P)**
0.5 – 5 bar	0
0 – 0.5 bar or 5-25 bar	1
25 – 50 bar	2
50 – 200 bar	3
200 – 1000 bar	4

Table 8: Pressure score conversion

Yield index:

Yield (%)	**Score (R_Y)**
100	0
90-99	1
80-89	2
70-79	3
60-69	4
50-59	5
40-49	6
30-39	7
20-29	8
10-19	9
0-10	10

Table 9: Yield score conversion

Note: A lower yield corresponds to a higher score and subsequently a higher safety index as it is assumed that reactants in a chemical process are generally more hazardous as compared to the products.

Heat of reaction index:

Heat of reaction (J/gm)	Nature	Score (R_H)
≤ 200 J/gm	Thermally neutral	0
< 600 J/gm	Mildly exothermic	1
< 1200 J/gm	Moderately exothermic	2
< 3000 J/gm	Strongly exothermic	3
≥ 3000 J/gm	Extremely exothermic	4

Table 10: Heat of reaction conversion

The process reaction and chemical safety index (PRCSI) is a measure of the hazards relating to chemicals and reactions involved in the process and is computed as follows:

- Individual chemical index (ICI) = $N_R + N_T + N_F + N_E$ (ICI is computed for all chemicals involved in the process)
- Individual reaction index (IRI) = $R_T + R_P + R_H + R_Y$ (IRI is computed for all reactions involved in the process)
- Hazardous chemical index (HCI) = max (ICI)
- Hazardous reaction index (HRI) = max (IRI)
- Overall chemical index (OCI) = max (ICI)
- Overall reaction index (ORI) = ∑ IRI
- Overall safety index (OSI) = ∑ (OCI + ORI)
- Worst chemical index (WCI) = max (N_R) + max (N_T) + max (N_F)+ max (N_E)
- Worst reaction index (WRI) = max (R_T) + max (R_P) + max (R_H) + max (R_Y)
- Total chemical index (TCI) = ∑ ICI
- Process reaction and chemical safety index (PRCSI) = ∑ (OSI + WCI + WRI + TCI)/4

Note:

a) OSI, WCI, WRI, and TCI are considered for the calculation of PRCSI to also evaluate the hazards associated with the worst-case scenario possible in a chemical process.

b) Hazardous chemical index (HCI) and overall chemical index (OCI) are numerically identical.

Apart from considering the hazards with respect to chemicals and reactions in a process, it is essential to consider the hazards with respect to the equipment involved in the process. Equipment like furnaces can act as ignition sources leading to fire and explosion, Similarly, failure in reactors handling toxic chemicals can lead to the release of hazardous chemicals to the environment. The scoring of equipment in this study is based on inherent safety index methodology (Heikkila, 1999).

Equipment	**Score (I_{EQ})**
Equipment handling non-flammable, non-toxic materials	0
Heat Exchangers, pumps, towers & drums	1
Air-coolers, reactors & high hazard pumps	2
Compressors & high hazard reactors	3
Furnaces & fired heaters	4

Table 11: Equipment scoring

The Equipment Hazard scores are based on:
Penalties in Dow F&EI, Statistical data listing equipment as the primary cause of incidents and layout spacing recommendations as per general design standards.
The process equipment safety index (PESI) is calculated as,

$PESI = \sum N_j \text{ x } I_{EQ,j}$ for all j

Where j represents the different types of equipment and N_j represents the number of a specific type of equipment involved in the process.

Finally, the overall process safety index (OPSI) is calculated as,

OPSI = PRCSI + PESI

A higher value of OPSI indicates a more hazardous (i.e. less inherently safer) process.

It should be also noted that the quantification of inherent safety through OPSI involves the relative weighing of hazards and thus introduces an inbuilt judgment that may not be consistent with other safety indices and expert judgments.

Since OPSI is used for comparing the inherent safety of design alternatives from hazards with respect to involved reactions, chemicals, and equipment in the process, it is important to understand the effect of different inherent safety principles on OPSI, which is illustrated in the following diagram:

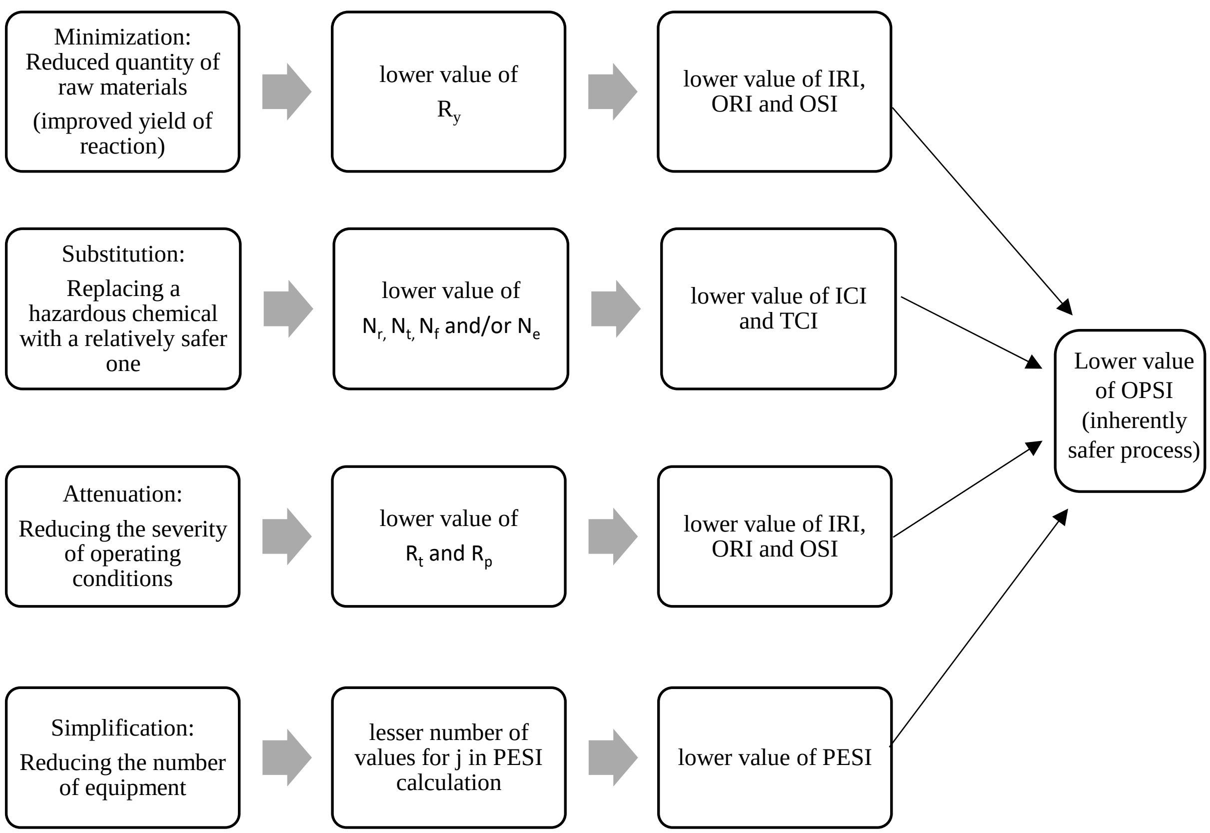

Figure 3: Impact of inherent safety principles on OPSI

4.4 INHERENT AVAILABILITY FOR PROCESS SELECTION STAGE

After quantifying inherent safety in terms of OPSI. The next step is to estimate the inherent availabilities of the equipment involved in the process. Following is the reliability data that has been used in this stage acquired from PERD and OREDA databases:

Equipment	MTTF (hrs.)	MTTR (hrs.)
Pumps	33000	27
Reactors	26300	106
Heat Exchangers	33000	56
Three Phase Separator	91000	37
Flash Drum	91000	27
Distillation Column	17500	47
Compressor	11400	39
Scrubber	12000	100

Table 12: Equipment reliability data

As mentioned in Chapter I, most of the process incidents occur during transient operations such as shutdown and startup. Thus, a process with higher corrective maintenance downtime can be assumed to be a riskier process.

As mentioned before, inherent availabilities are used in this study to quantify the corrective maintenance downtime of process systems. The advantage of analyzing inherent availability is that it is the steady state availability (i.e. it doesn't vary with time) and is an equipment design parameter. The inherent availabilities of the equipment themselves are based on their mean time to failure (MTTF) and mean time to repair (MTTR) of the equipment. The inherent availability of an equipment is given by:

$$A_{inh} = \frac{MTTF}{MTTF+MTTR}$$

The MTTF and MTTR values for general process equipment can be obtained from PERD and OREDA databases.

In the earlier stages of design, redundant equipment are generally not considered. Thus, the equipment in the process system can be assumed to be in series with respect to their reliabilities and availabilities. Therefore, the inherent availability of the system can be expressed as:

$$A_{inh,sys} = \prod_{i}^{n} A_{inh,i}$$

Where,

$A_{inh,i}$ is the inherent availability of i^{th} equipment,

n is the total number of equipment in the process system,

& $A_{inh,\ sys}$ is the inherent availability of the process system.

Thus, from the process flow diagrams (PFDs) of the process designs, different types and number of equipment involved in the process design can be known, and the inherent availability of the system can be estimated from the inherent availabilities of equipment involved in the process. The corrective maintenance downtime for the system is computed using the following expression:

$$\mathbf{A_{inh,sys} = 1 - \frac{corrective\ maintenance\ downtime}{total\ process\ time}}$$

Finally, by computing OPSI and $A_{inh,sys}$ for all process design alternatives, the required relationship between these parameters can be established for the process selection stage.

4.5 CASE STUDY FOR PROCESS SELECTION STAGE – ACETIC ACID MANUFACTURE

The described methodology is applied to the case of Acetic acid manufacturing in the process selection stage. Various processes which utilize different chemicals, reactions and equipment have been developed for Acetic acid manufacture. The processes considered in this study are Ethylene oxidation (U.S. Patent No. 7491843 B2, 2009), Acetaldehyde oxidation (Cheung, 2012), Low-pressure carbonylation (Cheung, 2012), Ethane oxidation (Solimon, 2012) and Butane oxidation (Cheung, 2012).

The results obtained by applying the described methodology on the mentioned case study are as follows:

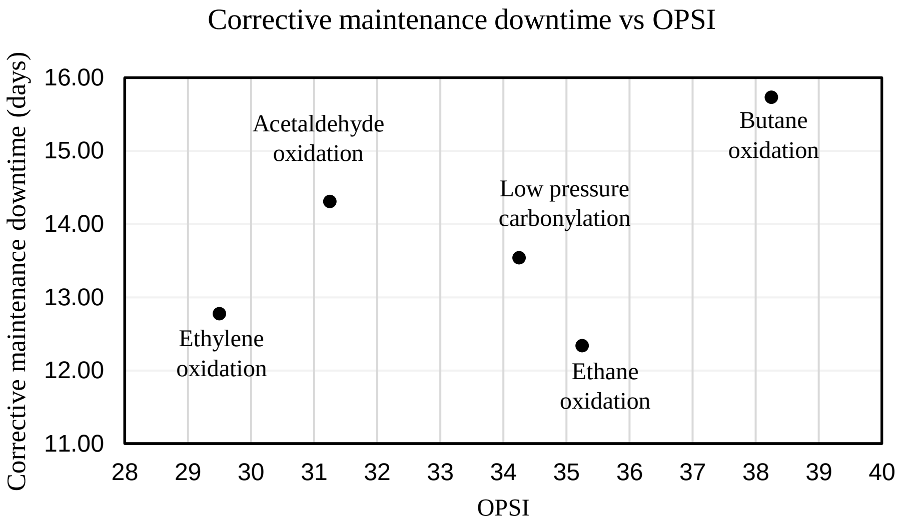

Figure 4: Corrective maintenance downtime vs OPSI, Acetic acid case study

4.6 ECONOMIC ANALYSIS OF DESIGN ALTERNATIVES IN PROCESS SELECTION STAGE

Apart from analyzing the design alternatives from the perspective of inherent safety, it is important to evaluate these alternatives from the aspect of profitability. Since the analysis is carried out in earlier stages of design, the economic analysis is carried out based on widely used engineering thumb rules and estimation techniques since accurately predicting the economics of these processes is difficult due to lack of depth of knowledge of these processes. Following is the procedure used for economic analysis:

- Define the required capacity of plant
- Estimate the current fixed capital investment (FCI) based on a known fixed capital investment at a certain period and chemical engineering plant cost index by:

$$\text{Current FCI} = \text{FCI in period 'T' x } \frac{\text{current chemical engineering plant cost index}}{\text{chemical engineering plant cost index at period T}}$$

$$\text{x } \left(\frac{\text{required capacity}}{\text{capacity for which FCI is known at period T}}\right)^{0.6}$$

- Annualize the calculated FCI by assuming appropriate number of expected service years of plant
- Estimate the annual operating time of plant from the calculated inherent availability (A_{inh}) of the system by:

Annual operating time of plant = Total annual time x inherent availability of system

- Estimate the corrective maintenance labor cost by:

Corrective maintenance labor cost = Annual operating time x corrective maintenance labor rate x $(\frac{1}{A_{inh}} - 1)$ (Goel, 2003)

- Assuming the corrective maintenance material cost is roughly the same as corrective maintenance labor cost (Branan, 2005) the overall corrective maintenance cost can be estimated as:

Overall maintenance cost = 2 x corrective maintenance labor cost

- Estimate the cost of raw materials required for the desired capacity by appropriate mass balance
- Estimate the overall production cost (excluding overall maintenance cost) from the cost of raw materials by:

Overall production cost = 3.3 x cost of raw materials (Peters and Timmerhaus, 1980)

- Compute the annualized profit obtained for the given alternative by assuming an appropriate selling price of product and using the overall production cost

4.7 RESULTS FOR PROCESS SELECTION STAGE

Following are the results obtained by applying the described methodology and economic analysis for process selection stage for the case study of acetic acid manufacture:

Design Alternatives (1 KTPA capacity)	Overall process safety index (OPSI)	Corrective maintenance downtime (days)	Annualized profit (AP) (MM $)
Ethylene oxidation	29.5	12.78	0.35
Acetaldehyde oxidation	31.25	14.31	0.73
Low pressure carbonylation	34.25	13.54	0.82
Ethane oxidation	35.25	12.34	0.72
Butane oxidation	38.25	15.73	0.29

Table 13: Results for process selection stage – Acetic acid case study

4.8 TOPSIS OPTIMIZATION

Since, the final goal of this study is to select a process that is sufficiently inherently safer while simultaneously being inherently available and profitable, a multi-criteria decision analysis method, TOPSIS has been implemented. TOPSIS refers to Technique for Order of Preference by Similarity to Ideal Solution. This method assigns weight to different criteria, normalizes the decision variables and finally selects the optimum alternative. In this study, the decision variables for selecting the optimum process are inherent safety (in terms of OPSI) and profitability (in terms of annualized profit, AP). The corrective maintenance downtime is indirectly reflected in terms of annualized profit and therefore is not considered a decision variable. Following is the procedure used for TOPSIS optimization:

1) Define the decision variables i.e. $OPSI_i$ and AP_i for design alternative i for all design alternatives
2) Calculate the normalization term for the decision variables by:

   $N_{OPSI} = \sqrt{\prod OPSI^2}$ and $N_{AP} = \sqrt{\prod AP^2}$

3) Normalize all decision variables by:

   $N_{OPSI,i} = \frac{OPSI_i}{N_{OPSI}}$ and $N_{AP,i} = \frac{AP_i}{N_{AP}}$

4) Assign weights to decision criteria, say 0.3 for inherent safety and 0.7 to annualized profit i.e.

   $W_{OPSI} = 0.3$ and $W_{AP} = 0.7$

5) Compute weighted decision variables by:

   $W_{OPSI,i} = W_{OPSI}\ x\ N_{OPSI,i}$ and $W_{AP,i} = W_{AP}\ x\ N_{AP,i}$

6) Determine the most ideal and most negative ideal solutions for the decision variables. The ideal solution should be most inherently safer (i.e. minimum OPSI) and most profitable (i.e. maximum annualized profit) while the negative ideal solution should be least inherently safer (i.e. maximum OPSI) and least profitable (i.e. minimum annualized profit).

   Ideal solutions: I_{OPSI}= min ($W_{OPSI,i}$) and I_{AP} = max ($W_{AP,i}$)

   Negative ideal solutions: NI_{OPSI}= max ($W_{OPSI,i}$) and NI_{AP} = min ($W_{AP,i}$)

7) Determine the distance of the decision variables for a design alternative from ideal and negative ideal solutions:

   $A_i = \sqrt{(W_{OPSI,i} - I_{OPSI})^2 + (W_{AP,i} - I_{AP})^2}$ and $B_i = \sqrt{(W_{OPSI,i} - N_{OPSI})^2 + (W_{AP,i} - N_{AP})^2}$

8) Compute the relative closeness of all the design alternatives by:

   $R_i = \frac{B_i}{A_i + B_i}$

9) Finally, rank the design alternatives based on their relative closeness. The optimum design alternative will have the highest relative closeness.

The TOPSIS optimization is carried out for two different sets of weights for inherent safety and profitability. Following are the results obtained from the described procedure:

	Case I	Case II
Rank	Inherent safety weight = 0.3 Profitability weight = 0.7	Inherent safety weight = 0.6 Profitability weight = 0.4
1	Low-pressure carbonylation	Acetaldehyde oxidation
2	Acetaldehyde oxidation	Low-pressure carbonylation
3	Ethane oxidation	Ethane oxidation
4	Ethylene oxidation	Ethylene oxidation
5	Butane oxidation	Butane oxidation

Table 14: Ranking of process routes for Acetic acid case study

4.9 ANALYSIS OF RESULTS FOR THE CASE STUDY

Analyzing the graph obtained between OPSI and corrective maintenance downtime for process selection stage (Figure 4), it can be observed that a process that is inherently safer in terms of involved reaction, chemicals, and equipment may not necessarily have the least corrective maintenance downtime. This is primarily because, in process selection stage OPSI is governed by the inherent safety principles of minimization, substitution, attenuation and simplification (Figure 3), whereas corrective maintenance downtime depends only on the number and types of equipment present in the process system and thus, only depends on the principle of simplification. Therefore, implementing a process that’s inherently safer in terms of involved reaction, chemicals and equipment might lead to an increase in the associated risk of the system by increasing its corrective maintenance downtime.

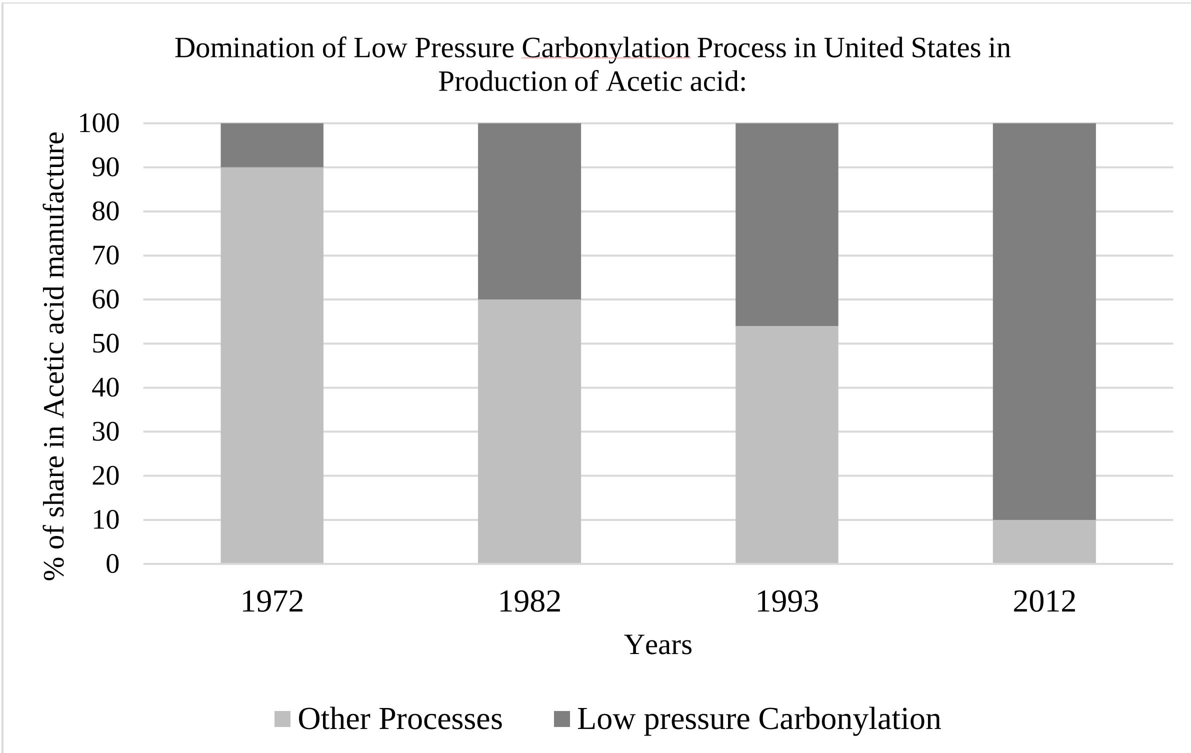

Figure 5: Domination of low pressure carbonylation process in US production of Acetic acid (Cheung, 2012)

In 1972, around 10% of the Acetic acid manufacture was carried out by low-pressure carbonylation. However, due to the economic superiority of this process, its dominance has increased over the years and currently more than 90% of Acetic acid manufacture is achieved using low-pressure carbonylation (Cheung, 2012). Prior to the dominance of low-pressure carbonylation process, a major proportion of the Acetic acid was produced by Acetaldehyde oxidation (Hintermann & Labonne, 2007). Thus, if regulations to enforce the consideration of inherently safer designs are imposed (i.e. transitioning from case I of TOPSIS optimization to case II), upcoming facilities might need to reconsider the potential of Acetaldehyde oxidation (or other synthesis routes with comparable profitability) for Acetic acid manufacture over low pressure carbonylation due to its higher associated inherent safety. This can lead to the implementation of a process that has a higher corrective maintenance downtime and thus, ultimately higher associated risk

CHAPTER V

CONCEPTUAL STAGE

5.1 INTRODUCTION TO CONCEPTUAL STAGE

The conceptual stage is the design stage that follows process selection stage. In conceptual stage, the chemistry used to manufacture the required product is already determined (in the process selection stage). However, the configuration of the flow-sheet (process flow diagram) is to be figured out. Thus, the available design alternatives in this stage are similar in terms of reactions and chemicals. However, they vary in terms of the number and types of different process equipment employed. Different configuration of process flow diagrams can have different advantages, and usually, the most profitable configuration is selected.

5.2 APPLICATION OF DISCUSSED METHODOLOGY TO CONCEPTUAL STAGE

The described methodology in Chapter II can be applied to the conceptual stage as well. The first step in the methodology is to evaluate the design alternatives existing for the design stage under consideration. The design alternatives in the conceptual stage are the different configuration of process flow diagrams for a selected chemistry existing to manufacture the required product.

5.3 INHERENT SAFETY QUANTIFICATION FOR CONCEPTUAL STAGE

Since i-safe and ISI index are proved to be suitable in early stages of design, the developed hybrid index (mentioned in chapter IV) based on these indices is used for the quantification for inherent safety. It is important to note that since the design alternatives for this stage are similar in terms of reactions and chemicals used, the values of PRCSI is same for all design alternatives. However, the value of PESI varies due to variation in number and types of different process equipment employed depending on the process configuration.

5.4 INHERENT AVAILABILITY FOR CONCEPTUAL STAGE

The computation of inherent availability and corrective maintenance downtime of the system in conceptual stage is similar to that in process selection stage. The end results obtained by applying the described methodology to the conceptual stage is the relation between OPSI and corrective maintenance downtime of the system for all the design alternatives.

5.5 CASE STUDY FOR CONCEPTUAL STAGE – HYDRODEALKYLATION OF TOLUENE TO BENZENE

The described methodology is applied to the case of Hydrodealkylation of Toluene to Benzene in the conceptual stage of design. The processes considered are described by Douglas, 1988, Bouton, 2008, Konda, 2006 and Mata, 2003**.**

Douglas process configuration:

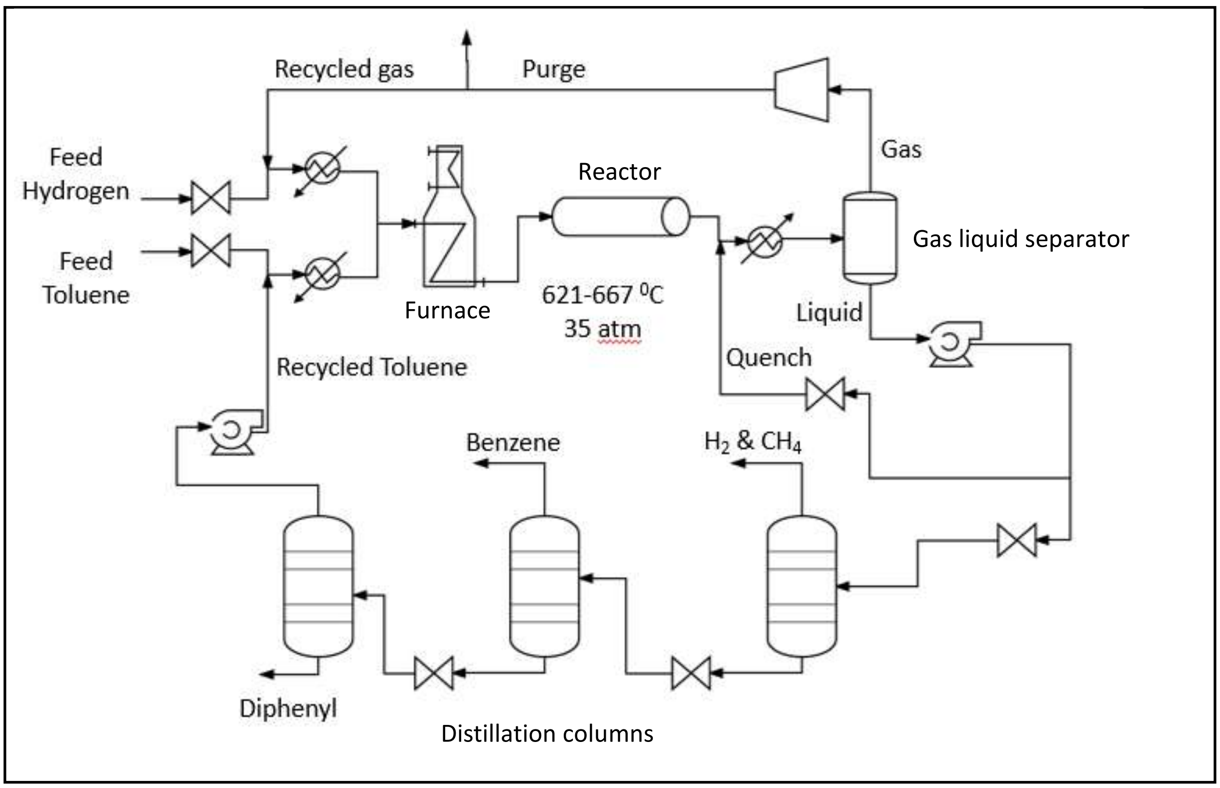

Figure 6: Process configuration (Douglas, 1988)

The Douglas configuration is the conventional process flow configuration for Hydrodealkylation of Toluene to Benzene. Hydrogen and Toluene are heated to the required process temperature and passed through a reactor where the main product Benzene is obtained along with by-products methane, Di-phenyl, and Hydrogen. The hydrogen in the product stream is separated and recycled back to the feed. The remaining by-products are passed through a train of distillation columns where the products and by-products are separated, and the unreacted toluene is sent back to the feed.

Bouton process configuration:

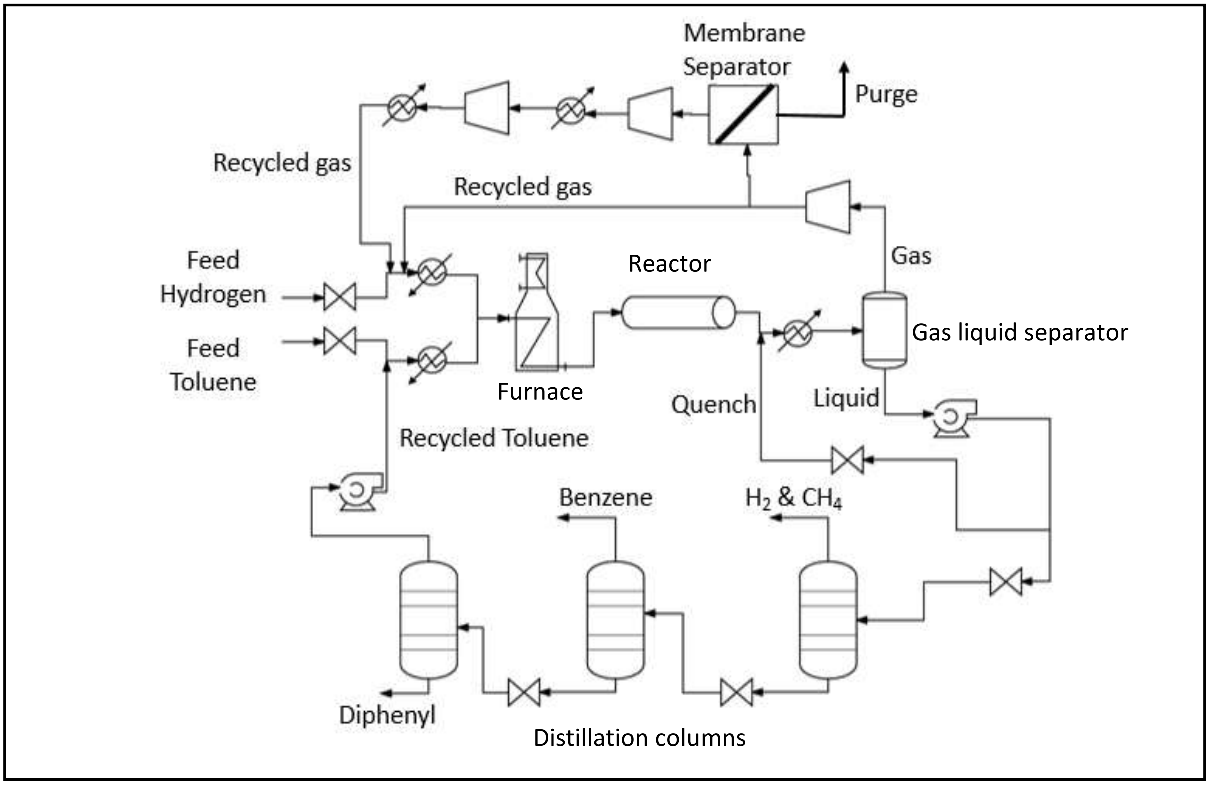

Figure 7: Process configuration (Bouton, 2008)

The Bouton configuration differs from the conventional process configuration in the sense that the gaseous stream from gas-liquid separator split into two components, first stream component is directly sent to the feed, and the other part is sent via a membrane separator where the hydrogen gas is separated from other components and recycled back to the feed. The advantage of this process is the reduction in fresh hydrogen requirements due to hydrogen recovery.

Konda process configuration:

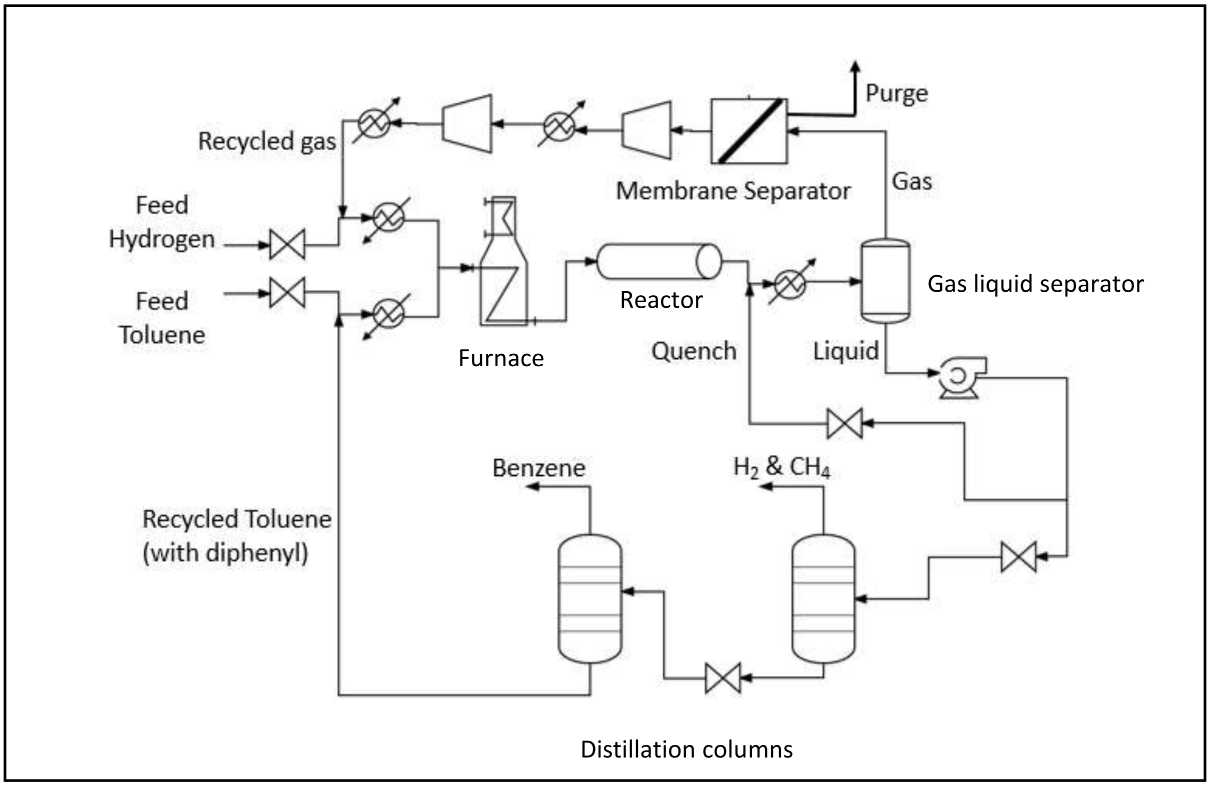

Figure 8: Process configuration (Konda, 2006)

In Konda configuration, the entire gaseous stream from the gas-liquid separator is sent to the membrane separator where hydrogen is separated from other components and is recycled back to the feed. The advantage of this process configuration is that the recycled gas is virtually CH_4 free (which was acting as a heat carrier in previous configurations) thus improving the heat economy of the process.

Mata process configuration:

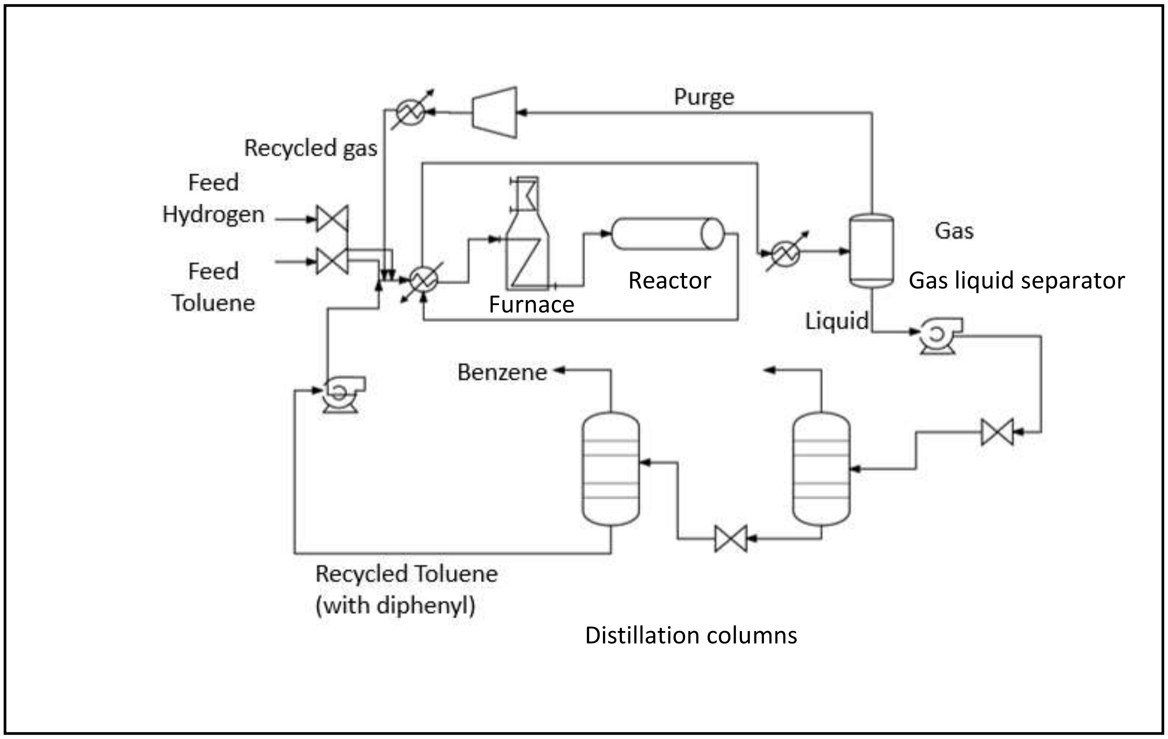

Figure 9: Process configuration (Mata, 2003)

In Mata process configuration, heat integration is achieved by using the product stream from the reactor to preheat the incoming reactants, this improves the heat economy of the process and eliminates the need of quenching the product stream.

The results obtained by applying the described methodology to the described case study are as follows:

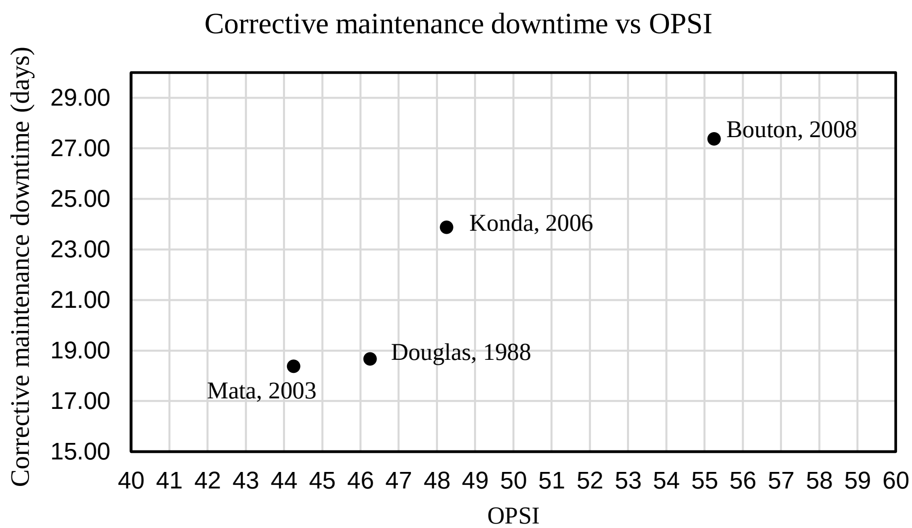

Figure 10: Corrective maintenance downtime vs. OPSI for Toluene case study

5.6 ECONOMIC ANALYSIS OF DESIGN ALTERNATIVES IN CONCEPTUAL STAGE

An economic analysis similar to process selection stage is carried out at the conceptual stage for a capacity of 300 TPA. The data for economic analysis is based on Fischer and Iribarren, 2011. In general, the addition of ceramic membrane separator can lead to substantial increase in capital cost and may counter other benefits such as reduction in hydrogen requirement and improvement in heat economy as compared to the conventional configuration for Bouton and Konda process configuration respectively. However, the improvement in heat economy in Mata configuration is substantial and leads to higher profitability.

5.7 RESULTS FOR CONCEPTUAL STAGE

Following are the results obtained by applying the described methodology and economic analysis for the conceptual stage for the case study of Hydrodealkylation of Toluene to Benzene:

Design Alternatives (300 TPA capacity)	Overall process safety index (OPSI)	Corrective maintenance	Annualized profit (AP)
Douglas	46.25	18.66	0.49
Bouton	55.25	27.38	0.44
Konda	48.25	23.88	0.27
Mata	45.25	18.38	0.70

Table 15: Results for conceptual stage – Toluene case study

5.8 ANALYSIS OF RESULTS FOR THE CASE STUDY – HYDRODEALKYLATION OF TOLUENE TO BENZENE

From the graph obtained for the conceptual stage (Figure 10), it can be observed that the corrective maintenance downtime of process systems increases with increase in OPSI. A detailed analysis reveals that the number of equipment involved in the process systems increases as we move from a process with lower OPSI and lower corrective maintenance downtime to a process with a higher OPSI and a higher corrective maintenance downtime. Due to similarity of process systems in terms of reactions and chemicals in the conceptual stage, inherent safety principles of minimization, substitution and attenuation become redundant, Therefore OPSI is essentially governed by the principle of simplification wherein a process with lesser number of equipment will have a lower value of OPSI and thus will be inherently safer. Similarly, corrective maintenance downtime of process systems increases with the number of equipment involved in the system. This explains the trend observed in the results for the conceptual stage (Figure 10). In terms of economics, a process with least corrective maintenance downtime may not be the most profitable, since the cost of corrective maintenance is generally a very small fraction of the overall production cost.

CHAPTER VI

DETAILED ENGINEERING STAGE

6.1 INTRODUCTION TO DETAILED ENGINEERING STAGE

The next stage under consideration for analysis of the required relationship is detailed engineering stage. One of the key aspects of detailed engineering stage is the design of process equipment involved in the project. Thus, focusing on this stage allows us to obtain the required relationship for a particular equipment as compared to obtaining the relationship for the entire process system (as done in process selection and conceptual stage). This stage also helps in determining the effect of process parameters such as operating temperature and pressure on inherent safety and equipment reliability.

6.2 APPLICATION OF DESCRIBED METHODOLOGY TO DETAILED ENGINEERING STAGE

The described methodology in Chapter II can also be applied to detailed engineering stage with certain modifications. The first step in the methodology is to evaluate the design alternatives existing for the design stage under consideration. The design alternatives in detailed engineering stage for an equipment can be the same equipment design under different operating conditions. The suitable range of operating conditions for an equipment such as a reactor is generally governed by thermodynamics and kinetics of the reaction along with mass and heat transfer occurring within the equipment. Also since, the focus of this stage is the design of an individual equipment and not the entire process system, it becomes essential to analyze reliability alone rather than focusing on availability as the reliability (specifically the static reliability) can be modelled as a function of the operating conditions whereas, the maintainability of the equipment can be considered to be independent of operating conditions.

The modified methodology for detailed engineering stage can be described as:

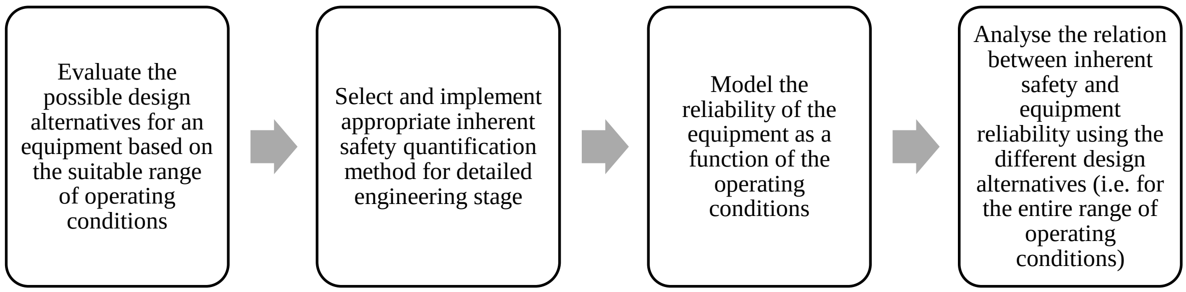

Figure 11: Modified methodology for detailed engineering stage

6.3 INHERENT SAFETY QUANTIFICATION FOR DETAILED ENGINEERING STAGE

Since, detailed engineering stage is one of the later stages of design, Dow F&EI is deemed to be suitable for quantification of inherent safety (as per Table 1). Dow F&EI is widely used in the process and allied industries for quantification of hazards associated with a processing facility and has been revised multiple times since its formulation. The quantification of Dow F&EI is mainly based on general process hazards such as exothermicity of the reaction, ease of material handling and transfer, access to emergency equipment, drainage and spill control measures at the facility, special process hazards such as toxicity of materials involved, whether the process is sub-atmospheric, closeness of operation to flammable range of materials, possibility of leakage, possibility of dust explosion and lastly on material hazards such as reactivity and flammability. The Dow F&EI calculation in this study is based on Dow Fire and Explosion index hazard classification guide, 7th edition.

6.4 RELIABILITY CALCULATION FOR DETAILED ENGINEERING STAGE

The formulated methodology for detailed engineering stage is described using an example of reactor design. The third step of the described methodology requires the quantification of reliability of the equipment (i.e. reactor) with respect to operating conditions, the mode of failure for reactor under consideration is bursting due to excess pressure and thus, the failure probability (mathematical counterpart of reliability) can be modelled as a function of pressure inside the reactor. The relation between this failure probability and operating pressure has been described by Arnold, 1972. In this study, the induced stress in the reactor (due to internal/operating pressure) and the allowable stress of the material of the reactor are assumed to follow a normal distribution, and the overlapping of these distributions governs the failure probability.

6.5 APPLICATION OF DESCRIBED METHODOLOGY FOR DETAILED ENGINEERING STAGE

The problem of reactor design used in this study is partly based on reactor design described by Suardin, 2005. The design problem is described as follows:

- Reaction: A $\rightarrow$ B
- Feasible range of operating pressure (P): 8 to 14 atm
- Required annual capacity: 645 million lbs of B
- Reaction rate constant (k): 0.0025 s^{-1}
- Feasible conversion of reaction: 60 % (defined by mass)
- Molecular weight of A: 100 lb.mol/mol
- Temperature of reaction: 800˚C
- Material of construction of reactor: A312 alloy steel (selected as per operating conditions) with maximum allowable working stress (M) of 17 atm.

6.6 GOVERNING EQUATIONS FOR DESCRIBED METHODOLOGY FOR THE DESIGN OF A REACTOR

The governing equations for described methodology for reactor design can be broadly divided into three sets of equations, equations pertaining to calculating reactor dimensions, equations for reliability calculations and equations for Dow F&EI calculations.

Equations for reactor dimension calculation:

- Conversion of reaction with respect to mass (X) = $\frac{W_{A0} - W_A}{W_{A0}}$

Where W_{A0} and W_A are initial and final mass of A respectively.

- Volume of reactor (V) = $\frac{F_{A0}}{k\,C_{A0}}\left[(1+\in)\ \ln(\frac{1}{1-X}) - \in X\right]$

Where F_{A0} is the initial flow rate of A, C_{A0} is the initial concentration of A and $\in$ is the coefficient of volume expansion.

- Volume of reactor (V) = $\frac{\pi}{4} D^2 L$
- Length to diameter ratio of reactor (r) = L/D

Where D and L are the internal diameter and length of reactor respectively.

- Residence time of reactor (Γ) = $\frac{V}{v_0}$
- Design pressure of reactor (P_d) = $\exp(0.60608 + 0.91615 \ln P + 0.0015655\,(\ln P)^2)$ (Seider, 2004)

Where, v_0 is the initial flow rate of A.

- Thickness of reactor wall (t) = $\frac{P_D\ x\ (\frac{D}{2})}{2M - 0.6\,P_D}$

Equations for Dow F&EI calculation:

The main equations for Dow F&EI calculations are as follows:

- $F_3 = F_1 \ x \ F_2$
- $F\&EI = MF \ x \ F_3$

Where, F_1, F_2, and F_3 are the general process hazard factor, special process hazard factor, and process unit hazard factor.

MF is the material factor.

The Dow F&EI index is calculated for the reactor at different values of operating pressure (from 8 to 14 atm) and a sensitivity analysis is performed as per the procedure described by Suardin, 2005.

The obtained equation relating Dow F&EI to operating pressure is as follows:

- $F\&EI = 1.409 \ x \ P + 112.27$

Equations for reliability calculation:

- Mean hoop stress in the reactor (S_h) = $\frac{P\,(\frac{D}{2})}{t}$ (Arnold, 1972)
- Standard deviation of hoop stress (σ_h) = $\frac{\sigma_p(\frac{D}{2})}{t}$ (Arnold, 1972)
- Where, σ_p is the standard deviation of operating pressure.
- Mean induced stress in reactor (S_i) = $\frac{S_h+P}{2}$ (Arnold, 1972)
- Standard deviation of induced stress (σ_i) = $\frac{1}{2}\sqrt{\sigma_p^2 + \sigma_h^2}$ (Arnold, 1972)
- Failure probability of reactor (F) = $= 0.0014(m^4) - 0.0267(m^3) + 0.178(m^2) - 0.5011(m) + 0.5055$

Where, m is an integral parameter given by,

- $m = \frac{-S_i + S_a}{\sqrt{(\sigma_i^2 + \sigma_m^2)}}$

Where σ_m is the standard deviation of yield point.

- Reliability of reactor (R) = 1 - F

Note: The polynomial equation for F is obtained by carrying out a regression analysis of F and m values as described by Arnold, 1972 and represents the overlapping probability of distribution of induced and allowable stress.

Following assumptions are made for the reactor design:

- The reactor length to diameter ratio (r) is 5.
- Initial flow rate of A (v_0) is 100 ft^3/s
- The reactor follows ideal plug flow and is isothermal in nature.
- The pressure relief valve is set at 15 atm.
- The standard deviation of operating pressure (σ_p) is 10 % of the mean.
- The standard deviation of yield point (σ_m) is 15% of maximum allowable stress.

6.7 RESULTS OBTAINED FOR DETAILED ENGINEERING STAGE

The described methodology is applied for the pressure range of 8 to 14 atm. The results obtained are as follows:

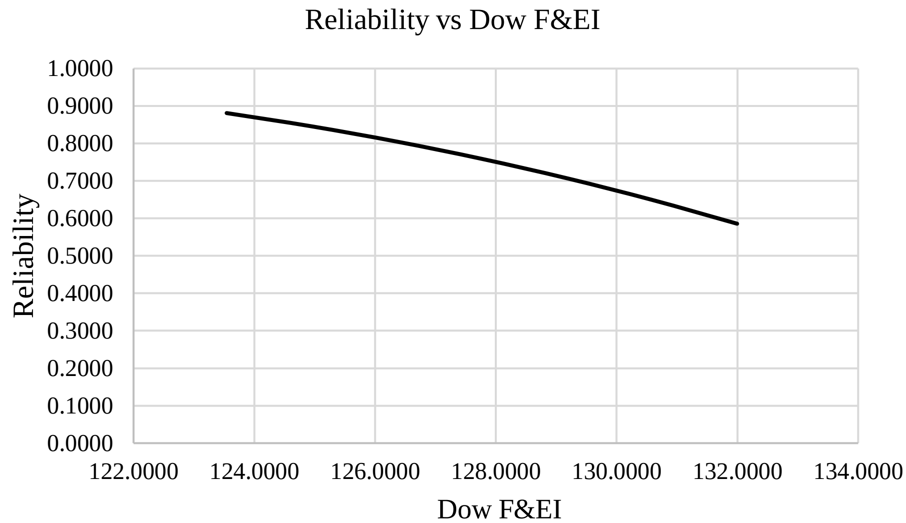

Figure 12: Reliability vs. Dow F&EI for reactor design

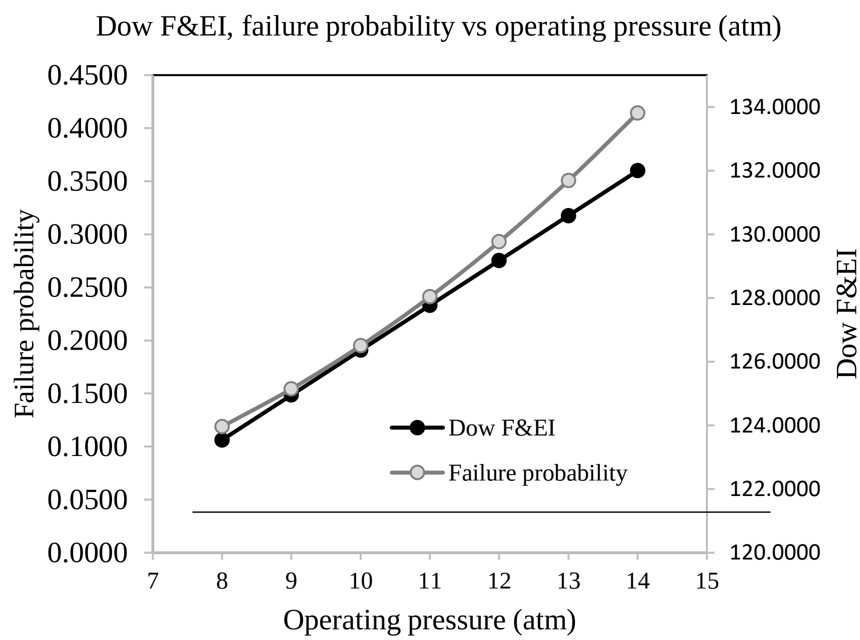

Figure 13: Failure probability, Dow F&EI vs. operating pressure for reactor design

6.8 ANALYSIS OF RESULTS FOR DETAILED ENGINEERING STAGE

As the value of Dow F&EI increases, the reliability of reactor decreases. This trend (Figure 12) exists because as pressure increases, the value of Dow F&EI increases due to an increase in the value of special process hazard factor (F_2). This essentially implies that the process becomes more hazardous at a higher value of pressure. Thus, ultimately, the process becomes less inherently safer owing to the principle of attenuation. Reliability subsequently decreases with increase in pressure as this leads to an increased overlapping of induced and allowable stress distributions. Thus, for detailed engineering design stage, inherent safety and reliability decrease simultaneously with the pressure of the reactor. An important point to note is that at Dow F&EI value of 128 (Figure 13), which is deemed to be intermediately hazardous as per AIChE standards (Dow, 1994), the failure probability of reactor is as high as 0.25. Thus, in the event of failure of all layers of protection designed to prevent bursting of the reactor (such as basic control systems, safety instrumented systems such as pressure relief valve and others), there is a 0.25 probability of the reactor bursting. This severity of the situation is not reflected by the Dow F&EI value. Another important observation from this analysis is that, as the operating pressure of the reactor increases, the value of Dow F&EI and failure probability of reactor simultaneously increase as well (Figure 13). However, the rate of increase in failure probability of reactor is substantially higher than the rate of increase of Dow F&EI.

CHAPTER VII

APPLICATION OF DEVELOPED METHODOLOGY TO INCIDENT CASE STUDIES

7.1 INTRODUCTION TO INCIDENT CASE STUDIES

Apart from serving as a tool for designing of chemical projects, the developed methodology can be used for analysis of past process safety incidents. This study focuses on the incident of T2 Laboratories explosion and fire and Bhopal gas leak incident. The application of described methodology to these incidents not only provides a novel view towards the failure mechanism but also serves as validation for the methodology.

7.2 T2 LABORATORIES EXPLOSION AND FIRE

On December 19, 2007, a fire and explosion occurred at T2 Laboratories in Jacksonville, Florida (CSB, 2009). T2 Laboratories Inc. manufactured specialty chemicals, mainly gasoline additives. This incident resulted in the death of 4 employees and injured 32 (including 4 employees). The 28 public members were working in neighboring areas (CSB, 2009). The explosion occurred in a reactor manufacturing methylcyclopentadienyl manganese tricarbonyl (MCMT). MCMT is used as a supplement for leaded gasoline. The impact of the explosion was so immense that the debris of the exploded reactor was found at a distance of one mile and the shock waves resulting from explosion damaged buildings at a radius of a quarter mile from the facility.

7.3 TIMELINE OF T2 LABORATORIES EXPLOSION AND FIRE

The events leading to T2 Laboratories explosion and fire can be described by the following timeline:

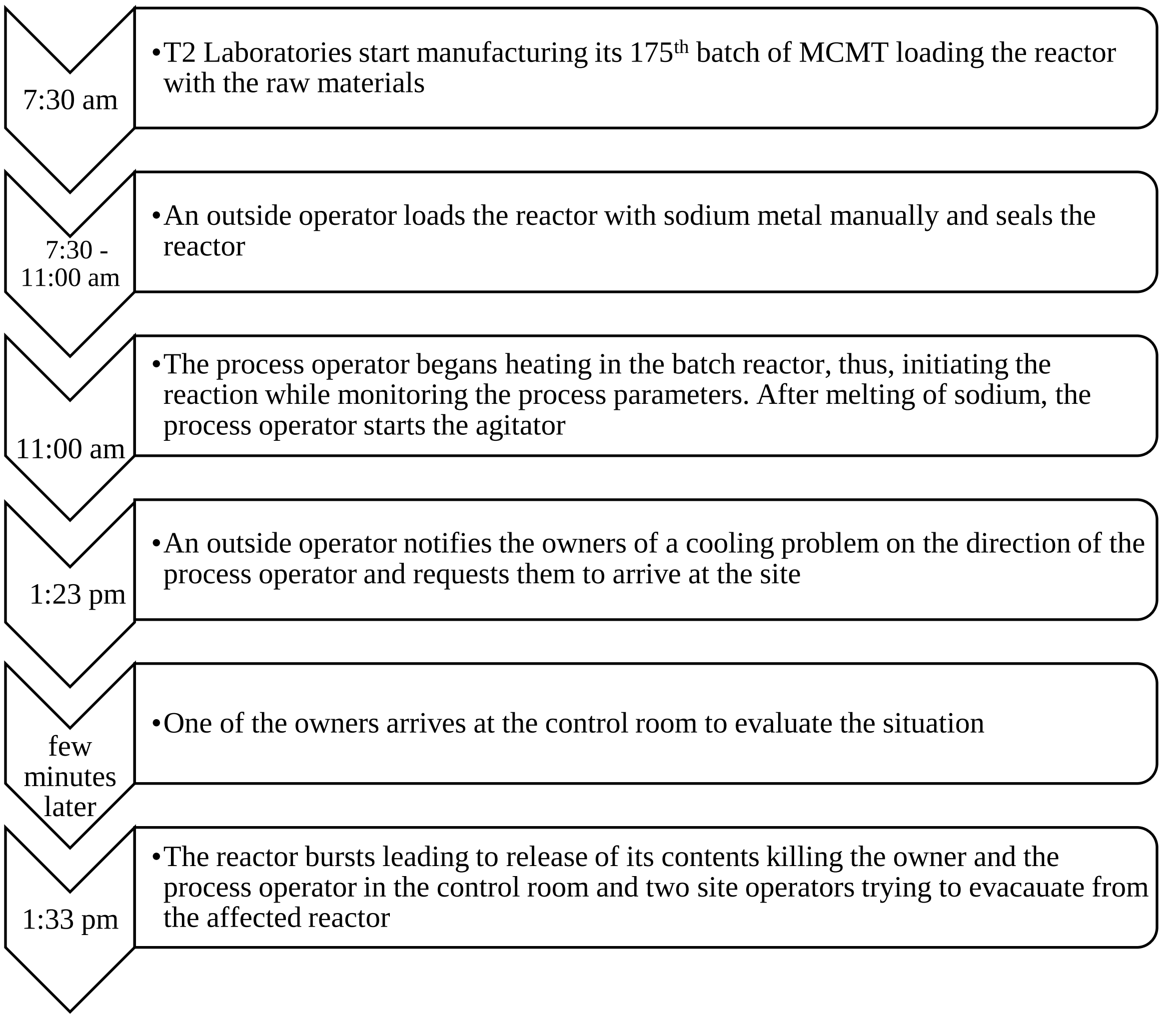

Figure 14: Timeline for T2 laboratories explosion and fire (CSB, 2009)

7.4 ROOT CAUSES FOR T2 LABORATORIES EXPLOSION AND FIRE

Following are the root and contributing causes identified for the incident (CSB, 2009):

- T2 Laboratories were unaware of the hazards associated while manufacturing MCMT
- The cooling system for the reactor manufacturing MCMT was vulnerable to single point failure owing to lack of other protection layers.
- The relief system for the reactor manufacturing MCMT was inaccurately sized and thus, was ineffective in providing the required relief for the runaway reaction.

7.5 INCIDENT INVESTIGATION OF T2 LABORATORIES EXPLOSION AND FIRE

Chemical safety board carried out a detailed investigation of the incident. The energy of explosion was estimated to be 1400 tons TNT equivalent (CSB, 2009). The explosion occurred due to a runaway reaction leading to uncontrolled temperature and pressure elevation. CSB converged on the failure of the cooling system as the primary cause leading to the explosion based on witness interviews and elimination of other likely causes. CSB conducted laboratory testing of the recipe used by T2 Laboratories and observed a runaway reaction occurring at a temperature of 390^0 F apart from the required reaction occurring at 350^0F. The owners of T2 Laboratories were unaware of this runaway reaction leading to the improper design of cooling and relief systems. The reactor involved in the explosion was constructed in 1962 and bought by T2 Laboratories in 2001. After purchasing the reactor, certain modifications were carried out leading to decrease in maximum allowable pressure of the reactor from 1200 psig to 600 psig.

7.6 APPLICATION OF DEVELOPED METHODOLOGY TO T2 LABORATORIES EXPLOSION AND FIRE INCIDENT

The methodology described for detailed engineering stage (Figure 11) was applied to the incident of T2 Laboratories explosion and fire with slight modifications. Since the dimensions of the reactor are known, Dow F&EI and reliability of the reactor can be directly evaluated. An important aspect that can be understood is the variation in Dow F&EI and reliability of the reactor as the pressure of reaction continuously increases due to the occurrence of a runaway reaction.

Following data has been used for application of the developed methodology to T2 laboratories explosion and fire:

Incident data (CSB, 2009):

- Reactor Volume: 2000 gallon
- Reactor thickness: 3 inch
- Operating pressure: 50 psig
- Rate of pressure increase: 32000 psig/min
- Maximum allowable working pressure of reactor: 600 psig
- Raw materials: Molten sodium metal, methylcyclopentadiene (MCPD) dimer and diethylene glycol dimethyl ether

Following assumptions were made based on engineering judgments due to lack of data:

- The reactor length to diameter ratio is 5
- The standard deviation of operating pressure: 35% of mean of operating pressure
- The standard deviation of yield point is 15% of maximum allowable stress

7.7 RESULTS FOR DEVELOPED METHODOLOGY TO T2 LABORATORIES EXPLOSION AND FIRE INCIDENT

Following is the plot obtained by applying the developed methodology to T2 laboratories explosion and fire incident:

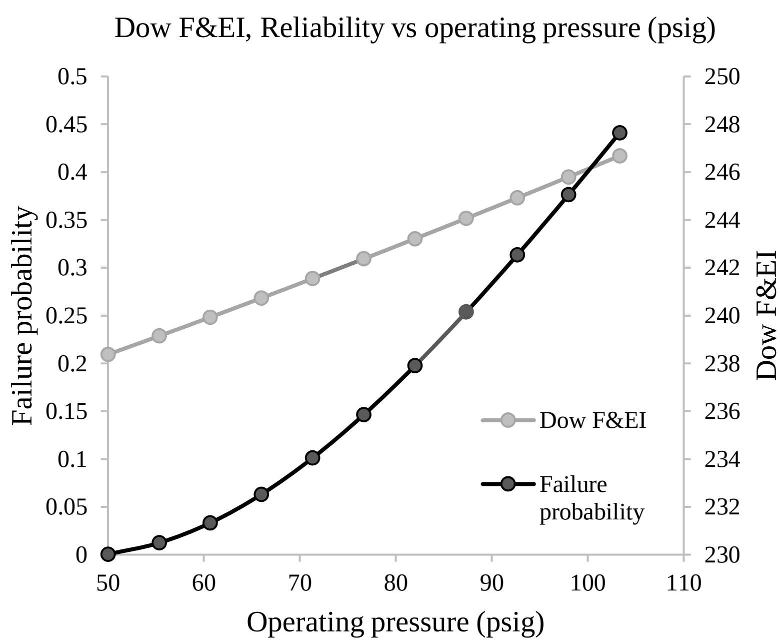

Figure 15: Dow F&EI, Reliability vs operating pressure for T2 laboratories case study

As mentioned previously, one of the contributing causes towards this incident was the decrease in maximum allowable working pressure (MAWP) of the reactor from 1200 psig to 600 psig. Following are the results obtained after 10 centiseconds from the onset of runaway reaction for MAWPs of 1200 psig and 600 psig from the developed methodology.

MAWP (psig)	Dow F&EI	Reactor reliability
1200	246.67	0.9999
600	246.67	0.5588

Table 16: F&EI and Reliability at different MAWPs after 10 centiseconds of runaway reaction

7.8 ANALYSIS OF RESULTS FOR TO T2 LABORATORIES EXPLOSION CASE STUDY

Application of developed methodology to the case study of T2 Laboratories explosion and fire reveals that Dow F&EI although, can capture the increasing hazard associated due to rising pressure from runaway reaction in the reactor, it fails to increase at the same rate as the probability of failure of the reactor due to excess pressure. It is also important to note that, the initial value of Dow F&EI is considerably high since molten sodium (highly reactive in nature and thus, having a high material factor) is involved in the reaction. Also, the methodology can predict the decrease in reliability of reactor (Table 16) due to a decrease in its MAWP which is not reflected by the Dow F&EI value (since F&EI considers the relief set pressure and not MAWP of the reactor). This result is in alignment with the analysis from CSB report.

7.9 BHOPAL GAS LEAK INCIDENT

The Bhopal gas leak incident also referred to as 'Bhopal gas disaster' occurred on the night of 2nd December 1984 in Bhopal, Madhya Pradesh, India. It is estimated that around 8000 fatalities resulted from this incident within 2 weeks, which was followed further by an additional 8000 fatalities resulting due to gas leak related diseases over the years (Eckerman, 2004). This incident has been attributed to 558,125 injuries which include permanently disabling injuries as well (Dubey, 2010). The leak occurred in a tank (referred to as tank E610) storing liquid methyl isocyanate (MIC). It is believed that the incident occurred due to water seeping into the storage tank which resulted in an exothermic runaway reaction leading to a rapid elevation in temperature and pressure. This runaway reaction is believed to be accelerated by contaminants, higher outside temperature, and the presence of iron from corroded steel pipes (Eckerman, 2004).

7.10 TIMELINE OF BHOPAL GAS LEAK INCIDENT

The events leading to Bhopal gas leak incident can be described by the following timeline:

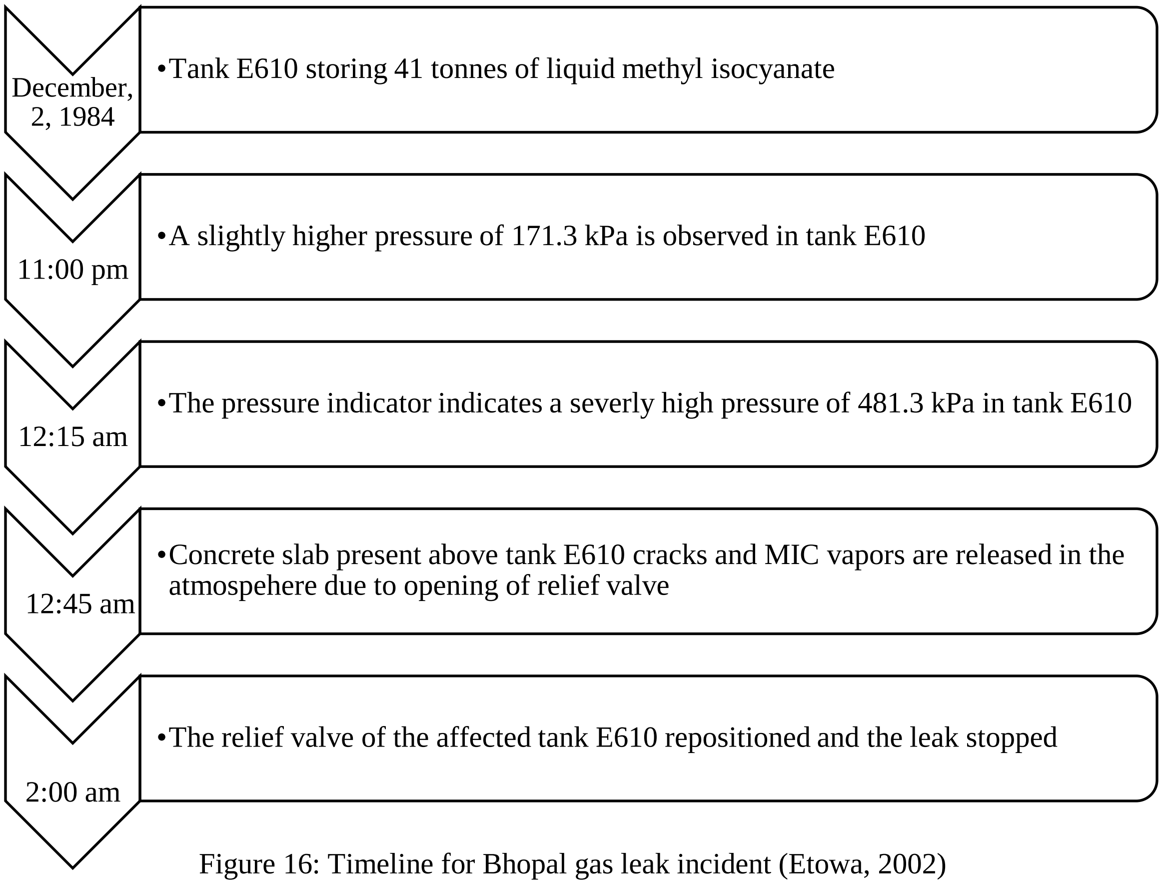

Figure 16: Timeline for Bhopal gas leak incident (Etowa, 2002)

7.11 ROOT CAUSES FOR BHOPAL GAS LEAK INCIDENT

Following are the root and contributing causes identified for the incident (Willey, 2006):

- Management decision to have the scrubber system in standby mode to reduce operating expenses
- Management decision to remove coolant from the refrigeration system responsible for cooling tank E610
- Lack of emergency response and community awareness
- Lack of knowledge and awareness about the hazards associated with MIC
- Inadequate/improper community planning, presence of residential area near hazardous chemical plant

7.12 INCIDENT INVESTIGATION OF BHOPAL GAS LEAK INCIDENT

A report analyzing the Bhopal gas leak was put forth by Retired Vice President, Health, Safety and Environmental Programs, Union Carbide Corporation (Browning, 1993). As per this report, a disgruntled employee intentionally added water to the storage tank to spoil the batch of MIC. A report based on witness interviews, examination of plant logs, scientific experiments and examination of plant equipment concluded that the incident was caused due to direct water connection to tank by an employee and not by water washing off process filter lines (Kalekar, 1988). However, this theory has been subject to argument, has received severe criticism over the years. Although, it is widely accepted that safety systems designed for the tank were unable to handle the conditions developed at the time of the incident (Diamond, 1985).

7.13 APPLICATION OF DEVELOPED METHODOLOGY TO BHOPAL GAS LEAK INCIDENT

The methodology applied to the incident of T2 Laboratories explosion and fire was applied to Bhopal gas leak as well. The variation in Dow F&EI with respect to internal pressure has already been formulated (Etowa, 2002). The application of this methodology to the case study of Bhopal gas leak incident reveals the variation in reliability and Dow F&EI with respect to an elevation in internal pressure caused due to a runaway reaction.

Following data has been used for application of the developed methodology to Bhopal gas leak incident:

Incident data (Etowa, 2002):

- Diameter of tank: 2.44 m
- Operating (internal) pressure: 150 kPa
- Dow F&EI: 0.01 x P + 237 (based on data from Etowa, 2002)
- Maximum allowable working pressure (MAWP): 381 kPa

Following assumptions were made based on engineering judgments due to lack of data:

- The standard deviation of operating pressure: 35% of mean of operating pressure
- The standard deviation of yield point is 15% of maximum allowable stress

7.14 RESULTS FOR DEVELOPED METHODOLOGY TO BHOPAL GAS LEAK INCIDENT

Following is the plot obtained by applying the developed methodology to Bhopal gas leak incident:

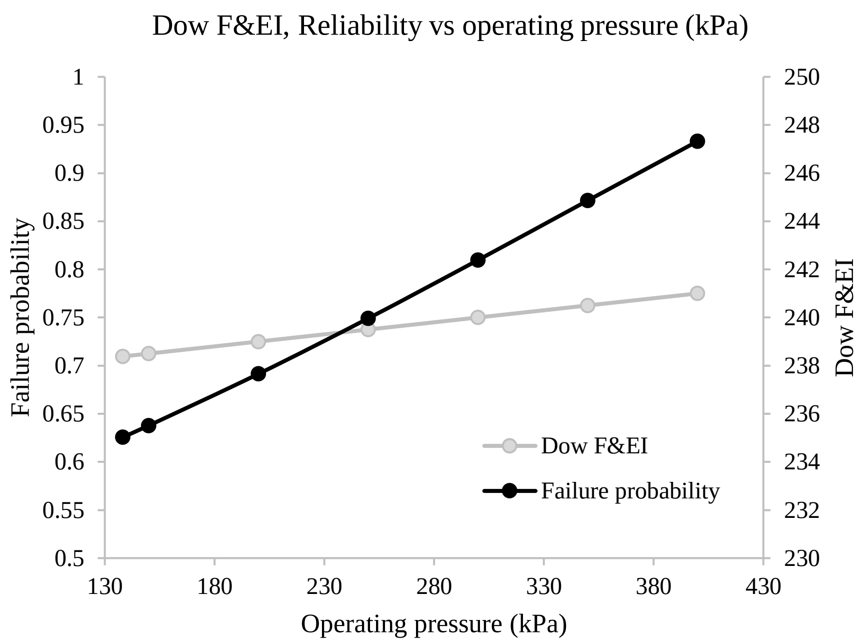

Figure 17: Dow F&EI, Reliability vs. operating pressure for Bhopal gas leak incident

7.15 ANALYSIS OF RESULTS FOR BHOPAL GAS LEAK INCIDENT

Application of developed methodology to the case study of Bhopal gas leak reveals that Dow F&EI can reflect the increasing hazard associated due to an elevation in pressure from runaway reaction in the reactor. However, it fails to increase at the same rate as the probability of failure of the tank due to excess pressure as observed in the case of T2 Laboratories fire and explosion. It is also important to note that, the range of value of Dow F&EI is considerably high since MIC (highly reactive in nature, hazardous to human health and thus, having a high material factor) is involved in the reaction.

CHAPTER VIII

CONCLUSIONS

In this work, the relationship between inherently safer design and equipment reliability has been investigated. The aim of this study was to determine the possibility of risk escalation caused due to lowering of system reliability during the implementation of inherent safety principles applied with an objective to lower the consequence element of risk. This lowering of system reliability can lead to an undesired increase in likelihood element of risk ultimately leading to an increase in the associated risk.

This study included the development of a safety index (OPSI) for earlier design stages that could effectively reflect the impact of inherent safety principles (including simplification) on the associated inherent safety of a design alternative. During the analysis of process selection stage using this index, it was observed that a process alternative that is inherently safer in terms of the reactions, chemicals, and equipment involved, may be associated with a higher corrective maintenance downtime and therefore may in turn be riskier since most of the process incidents occur during maintenance, startup, and shutdown.

When a similar analysis was carried out for the conceptual stage, the number of equipment involved in a process alternative emerged as a critical factor with regards to inherent safety and reliability of the alternative. It was observed that a process with a relatively lesser number of equipment might be inherently safer (owing to the principle of simplicity) and more inherently available.

Finally, when the required relationship was studied for a specific equipment such as the reactor during detailed engineering stage, the severity of operating conditions was determined to play a crucial role in regards to inherent safety and reliability of the reactor. Operating at lesser severity of operating pressure, the reactor was deemed to be relatively inherently safer and more reliable, and these parameters were observed to deteriorate at different rates with an increase in the severity of operating pressure.

An important conclusion that can be drawn from this study is that the relationship between inherent safety and reliability is complicated and varies during different stages of design (Figure 4, 10 & 12). The impact of inherent safety principles on the overall inherent safety of the design alternative is governed by the design stage under consideration, and the cumulative impact of these principles decreases along with the progression of design resulting in this complicated relationship. Application of the developed methodology to the case studies of T2 Laboratories explosion and fire and Bhopal leak incident revealed that the quantification of inherent safety in terms of non-dimensional indices (OPSI or Dow F&EI) is plagued with an inbuilt judgement (relative weighing) of hazards that may not be reflective of the overall risk associated with a design alternative as observed through reliability analysis.

CHAPTER IX

FUTURE WORK

The described study has various scopes for improvement. Apart from relying on non-dimensional safety indices for quantification of inherent safety, carrying out a risk assessment of the design alternatives can be quite beneficial and in turn, eliminates the inbuilt judgment intrinsic in these safety indices calculation. This will help in establishing a relationship between corrective maintenance downtime of design alternatives and their associated risk, thus shedding light on the phenomenon of occurrence of process incidents during maintenance downtime: startup and shutdown and this relationship can serve as a tool for risk estimation in earlier stages of design.

Also, analyzing the effect of improving system reliability by providing redundant equipment (for those equipment prone to frequent failures) on inherent safety and overall risk of a design alternative can prove to be highly beneficial in the field of process design.

Lastly, more focus can be emphasized on risk-based inherently safer design as compared to hazard based inherently safer design, wherein new techniques and methodologies can be developed that can accurately estimate the risk associated with a design alternative in the earlier design stages based on the depth of knowledge about the process available at that stage, by focusing on the risk determining factors (such as toxicity, flammability, system reliability) of that alternative.

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