

NUMERICAL AND GRAPHICAL DESCRIPTIVE TECHNIQUE FOR  
INHERENT SAFETY ASSESSMENT IN PETROCHEMICAL INDUSTRY

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NUMERICAL AND GRAPHICAL DESCRIPTIVE TECHNIQUE FOR INHERENT  
SAFETY ASSESSMENT IN PETROCHEMICAL INDUSTRY

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To my beloved mother and father

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## ABSTRACT

Plants should be built so that they are user-friendly and able to tolerate deviation from ideal performance as a result of operators and equipment failures without serious impacts on safety, productivity or efficiency. Before any effort for hazard reductions can be performed, it is important to first understand the hazards of a process which can be achieved through hazard assessments. Most of the current inherent safety assessment methods are index-based method which suffers from the shortcomings of subjective scaling. The aim of this research is to develop an inherent safety assessment method that eliminates the issue of subjective scaling in index scores assignment. The Numerical and Graphical Descriptive (GRAND) method is developed through the application of logistic functions. In this study, all petrochemical processes data obtained from literature was used in constructing numerical scores through the application of logistic functions. The numerical scores was then translated into graphical form. GRAND Total Score and GRAND Ranking Curve developed in this study can be used for the purpose of comparing alternative process synthesis routes to the desired product by their hazard level for inherent safety assessment during research and development (R&D) stage. Process route with a higher GRAND Total Score indicates greater hazards compared to the route with a lower GRAND Total Score. There are eight parameters involved which are divided into two groups. The first group is chemical safety parameters which consists of flammability, explosiveness, toxicity and reactivity parameters while the second group is process safety parameters which consists of temperature, pressure, heat of reaction and process inventory parameters. A gap elimination test was done on GRAND with the purpose of ensuring the elimination of subjective scaling. The gap elimination test result shows that GRAND has the ability to eliminate the problems of subjective scaling in scores assignment. The method developed was applied on two case studies which are methyl methacrylate manufacturing process and acetic acid manufacturing process. In the case study of methyl methacrylate manufacturing process, tertiary butyl alcohol based route was assessed as the safest route among the six routes evaluated while ethylene via propionaldehyde based route was assessed as the most hazardous one with the score of 311 and 509, respectively. There are ten process routes evaluated in the case study of acetic acid manufacturing process. GRAND assessment shows ethanol oxidation route as the safest route and ethane oxidation route as the most hazardous route with the score of 180 and 402 respectively. Results obtained from the gap elimination test as well as case studies performed proves that the method proposed in this research is successful in eliminating the common problem in index-based method which is subjective scaling for inherent safety assessment in petrochemical industry.

## ABSTRAK

Kilang pemprosesan hendaklah dibina dengan ciri-ciri keselamatan bagi mengelakkan berlakunya kemalangan yang berpunca daripada kecuaiannya pekerja atau kerosakan peralatan. Selain daripada mengurangkan risiko bahaya, pemahaman dalam punca kewujudan risiko melalui penilaian risiko juga adalah penting. Kebanyakan kaedah penilaian keselamatan yang wujud adalah kaedah yang berasaskan indeks dengan kekurangan daripada segi sistem pemarkahannya yang subjektif. Objektif penyelidikan ini adalah untuk membina satu kaedah baru dalam menilai risiko yang dapat mengatasi masalah pemarkahan subjektif. Kaedah *Numerical and Graphical Descriptive (GRAND)* dibina melalui pengaplikasian persamaan logistik. Data-data bagi proses petrokimia yang diperolehi daripada literatur digunakan dalam pembinaan persamaan logistik yang bersesuaian dengan objektif GRAND. Persamaan logistik tersebut kemudiannya ditukarkan ke bentuk grafikal. Perbandingan tahap risiko di antara setiap laluan proses yang dinilai dapat dibuat menggunakan *GRAND Total Score* dan *GRAND Ranking Curve*. Laluan proses dengan *GRAND Total Score* yang tinggi menunjukkan tahap risiko yang tinggi berbanding laluan proses dengan *GRAND Total Score* yang rendah. Ujian bagi membuktikan bahawa GRAND dapat mengatasi masalah pemarkahan subjektif menunjukkan keputusan yang positif. Terdapat dua kumpulan komponen keselamatan yang dinilai dalam GRAND. Kumpulan pertama merupakan komponen keselamatan bahan kimia yang terdiri daripada komponen kemudahbakaran, keletupan, tahap toksik dan tahap reaktiviti bahan manakala kumpulan komponen kedua merupakan komponen keselamatan proses yang terdiri daripada komponen suhu, tekanan, kadar reaksi proses serta inventori proses. Kaedah yang dibina ini telah digunakan ke atas dua kajian kes iaitu proses pembuatan metil metakrilat dan proses pembuatan asid asetik. Kajian kes proses pembuatan metil metakrilat menunjukkan laluan proses berasaskan butil alkohol tertiar adalah yang paling selamat antara enam laluan proses yang dinilai dengan markah 311 manakala laluan proses yang berasaskan etilena melalui propionaldehid adalah yang paling berisiko dengan markah 509. Terdapat sepuluh laluan proses yang dinilai bagi proses pembuatan asid asetik dengan laluan proses pengoksidaan etanol dengan markah 180 dinilai sebagai laluan proses yang paling selamat manakala laluan proses pengoksidaan etana dengan markah 402 sebagai yang paling berisiko. Keputusan yang diperolehi daripada ujian penghapusan pemarkahan subjektif dan juga kajian kes yang telah dilakukan menunjukkan keupayaan GRAND dalam mencapai objektifnya serta dapat diaplikasikan dengan efektif dalam penilaian keselamatan dalam industri petrokimia.

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## LIST OF ABBREVIATIONS

ACGIH	-	American Conference of Governmental Industrial Hygienists
AP	-	Acidification Potential
ATP	-	Aquatic Toxicity Potential
BTX	-	Benzene, Toluene, Xylene
CI	-	Cumulative Index
CSCI	-	Conventional Safety Cost Index
CSTS	-	Chemical Safety Total Score
DI	-	Damage Index
EDP <sub>i,j</sub>	-	Effective Dangerous Property
F&EI	-	Dow Fire and Explosion Index
FET	-	Flammability, Explosiveness and Toxicity
GRAND	-	Numerical and Graphical Descriptive
GWP	-	Global Warming Potential
HI	-	Hazard Index
HTPE	-	Human Toxicity Potential by Inhalation or Dermal Exposure
HTPI	-	Human Toxicity Potential by Ingestion
I2SI	-	Integrated Inherent Safety Index
IBI	-	Inherent Benign-ness Index
ICI	-	Individual Chemical Index
IDEF0	-	Type-zero Method of Integrated DEFinition Language
IOHI	-	Inherent Occupational Health Index
IRA	-	Inherent Risk Assessment
iRET	-	Integrated Risk Estimation Tool
ISCI	-	Inherent Safety Cost Index
ISI	-	Inherent Safety Index
ISPI	-	Inherent Safety Potential Index

LPG	-	Light Petroleum Gas
LSR	-	Light Straight Run
LEL	-	Lower Explosive Limit
MF	-	Material Factor
MMA	-	Methyl Methacrylate
MSDS	-	Material Safety Data Sheet
NFPA	-	National Fire and Protection Agency
OCI	-	Overall Chemical Index
ODP	-	Ozone Depletion Potential
ORI	-	Overall Reaction Index
OSI	-	Overall Safety Index
PCA	-	Principal Component Analysis
PCOP	-	Photochemical Oxidation Potential
PHCI	-	Process and Hazard Control Index
PIIS	-	Prototype Index for Inherent Safety
PoD <sub>ij</sub>	-	Potential of Danger
PRI	-	Process Route Index
PSI	-	Process Stream Index
PSTS	-	Process Safety Total Score
R&D	-	Research and Development
RTHI	-	Reaction Temperature Hazard Index
SAC	-	Safety Assessment Curve
SAW	-	Simple Additive Weighing
SHE	-	Safety, Health and Environmental
SHI	-	Safety/Hazard Indices
SWeHI	-	Safety Weighted Hazard Index
TCI	-	Total Chemical Index
TLV	-	Threshold Limit Value
TLV-STEL	-	Threshold Limit Value Short-term Exposure Limit
TORCAT	-	Toxic Release Consequence Analysis Tool
TTP	-	Terrestrial Toxicity Potential
UEL	-	Upper Explosive Limit
WCI	-	Worst Chemical Index
WRI	-	Worst Reaction Index

## LIST OF SYMBOLS

% Yield	-	Percentage Yield
°C	-	Degree Celsius
A	-	Credits due to Control Measures and Safety Arrangements Made to Counter the Undesirable Situations
ACH	-	Acetone cyanohydrin based route
Atm	-	atmospheric pressure
B	-	Quantitative Measure of the Damage that may be caused by a unit or plant
B1	-	Damage due to Fire and Explosion
B2	-	Damage due to Toxic Release and Dispersion
C2/MP	-	Ethylene via methyl propionate based route
C2/PA	-	Ethylene via propionaldehyde based route
C3	-	Propylene based route
EXP	-	Explosiveness
F1	-	General Process Hazard Factor
F2	-	Special Process Hazard Factor
FL	-	Flammability
H <sub>R</sub>	-	Heat of Reaction
i-C4	-	Isobutylene based route
I <sub>HH</sub>	-	Index for Health Hazards
I <sub>PPH</sub>	-	Index for Physical and Process Hazards
kJ	-	kilo Joule
m <sub>ij</sub>	-	Relevant Mass
P	-	Pressure
PI	-	Process Inventory
P <sub>i</sub>	-	Value for Every Parameter

ppm	-	Parts per Million
REAC	-	Reactivity
S <sub>EXP</sub>	-	Score for Explosiveness Parameter
S <sub>FL</sub>	-	Score for Flammability Parameter
S <sub>HR</sub>	-	Score for Heat of Reaction Parameter
S <sub>P</sub>	-	Score for Pressure Parameter
S <sub>PI</sub>	-	Score for Process Inventory Parameter
S <sub>R</sub>	-	Score for Reactivity Parameter
S <sub>T</sub>	-	Score for Temperature Parameter
S <sub>TOX</sub>	-	Score for Toxicity Parameter
T	-	Temperature
TBA	-	Tertiary butyl alcohol based route
TOX	-	Toxicity

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# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

Advanced technologies as well as economic achievements in modern development brought by petrochemical industries is one of the main factors that helps in upgrading human lifestyle throughout the world. However, it is not surprising that serious safety problems occur from their operations. Equipment malfunction as well as human errors are well-known as major accidents causes in all industries. Many strategies have been introduced in order to reduce or minimizing their impacts. However, it is impossible for operators to continuously maintain an error free performance all day long, throughout their work-lifetime. Thus, plant should be built so that they are user-friendly and able to endure deviation from ideal work routine by operators and equipment failures without serious impacts on safety, output or efficiency (Kletz and Amyotte, 2010).

Since the disastrous explosion in Flixborough in 1974 which causing 28 fatalities, there have been many papers produced on modes of preventing similar incidents from occurring again (Kletz and Amyotte, 2010). Most of the papers suggested the need for additional installation of more and better protective equipment such as gas detectors, fire protection and firefighting equipment, trips and alarms, scrubbers and flare stacks and so on. However, the equipment addition although necessary is also expensive and complex. Thus, plants should be designed so that small amounts of hazardous materials is used so that it does not matter if it all leaks or use safer materials instead of the hazardous ones.

Another approach is to use the hazardous materials at lower operating conditions in order to avoid the hazard problems rather than solving the hazard problems resulting to an inherently safer plants which are more cost efficient and more controllable. Although avoiding hazards plays a major role in designing a user-friendly plant, it is also important to identify and understand hazards posed by the process. According to the hierarchy of controls (Kletz and Amyotte, 2010), avoiding hazards comes after identifying and understanding the hazards which can be achieved through hazards assessment. Many methods had been developed in order to assess inherent safety performance of a process during process design stage for example the Prototype Index for Inherent Safety (PIIS) (Edwards and Lawrence, 1993), Inherent Safety Index (ISI) (Heikkila, 1999), SHE Method (Koller *et al.*, 2000), i-Safe (Palaniappan *et al.*, 2002a, b) and also Inherent Chemical Process Properties Data (Hassim and Ali, 2009).

## 1.2 Problem Statement

As mentioned previously, plants should be built so that they are user-friendly and able to prevent accidents from happens. Process safety evaluation during the very early design stage will assist in selecting the safer process route among several alternatives. The route with less hazardous chemicals and operating conditions is obviously will result in inherently safer and user-friendly plant. Most current safety assessment methods for evaluation of process design stage are mostly index-based method such as the PIIS (Edwards and Lawrence, 1993), ISI (Heikkila, 1999), SHE Method (Koller *et al.*, 2000), i-Safe (Palaniappan *et al.*, 2002a, b) and also Inherent Chemical Process Properties Data (Hassim and Ali, 2009). Index-based methods are attractive for inherent safety assessment due to their ability to be used during early process design stage in which there are limited amount of data available for evaluation. In index-based method, related factors to the process route is reduced to one quantitative factor, thus enables this approach to be used for decision making (Srinivasan and Nhan, 2008). Index-based method is attractive for usage in the industry due to this simplicity (Gupta and Edwards, 2003). Index-based method experienced many shortcomings as highlighted by Srinivasan and Nhan (2008) and

one of them is subjective scaling. Subjective scaling is scaling by dividing physical or chemical properties into subjective ranges and each range is assigned scores according to the authors' judgment for example dividing the value range into ten equal sub-ranges as used in Lawrence (1996). This implies that all chemical or physical values in that particular sub-ranges possessed the same level of hazard when in actual truth that is not the case. Another form of subjective scaling is discontinuity at the sub-range boundary (Gupta and Edwards, 2003). Usually the difference between lower boundary of a sub-range and upper boundary of another sub-range is only one value away. Since the score are assigned to each sub-range instead of each values, process which is one value higher than another process may be interpreted as possessing higher hazard which in reality both process may have similar level of hazard.

Inherent Benign-ness Index (IBI) (Srinivasan and Nhan, 2008) and the Hierarchical Fuzzy Model for the evaluation of inherent safety (Gentile, 2004) are two examples of inherent safety assessment methods that eliminates the shortcomings of index-based method in their methods. In order to eliminate the shortcomings of index-based method, the IBI incorporates a multivariate statistical approach known as Principal Component Analysis (PCA) while the Hierarchical Fuzzy Model incorporates fuzzy logic approach. Although both methods eliminates the shortcoming of index-based method successfully, they have complex development step. Execution of inherent safety assessment can also be done using process design simulator for example HYSYS software as incorporated by Shariff *et al.* (2006) in Integrated Risk Estimation Tool (iRET). Other methods that follows the same execution approach as iRET is Process Route Index (PRI) (Leong and Mohd Shariff, 2009), Toxic Release Consequence Analysis Tool (TORCAT) (Mohd Shariff and Zaini, 2010) and also Process Stream Index (PSI) (Mohd Shariff *et al.*, 2012). Incorporation of process design simulator is helpful in designing inherently safer design process. However, it is not suitable to be used in assessing inherent safety during research and design stage due to limited amount of data available.

Instead of using a complex execution method, this research proposed an inherent safety assessment method which incorporates logistic function in its execution which is simpler and suitable to be used during research and development



stage. Incorporation of logistic function also able to eliminate the subjective scaling problem that exists in the index-based method.

### **1.3 Objectives of Study**

The objective of this research is to develop an inherent safety assessment technique for assessment during research and development (R&D) stage. There are two sub-objectives that need to be fulfilled in order to achieve the main objective.

1. To develop a numerical safety assessment technique which evaluates safety parameters without the shortcomings of subjective scaling.
2. To construct a graphical representation of the assessment results for root-cause analysis of the process.

### **1.4 Scopes of Study**

In order to achieve the main objective of this study, there are four scopes that will be attended.

1. Review the current inherent safety assessment methods on the approaches used as well as the parameters incorporated.
2. Construct numerical safety assessment technique focusing on petrochemical processes chemical and operational data based on logistic function.
3. Incorporates chemical safety and process condition safety parameters available for assessment during research and development stage in the assessment technique developed.

4. Applying the proposed inherent safety assessment on several case studies of petrochemical processes during research and development stage to illustrate the effectiveness of the new technique.

## **1.5 Research Contributions**

The key specific contributions of this work are summarized as follows:

1. Development of a new inherent safety evaluation technique for assessment in petrochemical industry.
2. Application of logistic functions for hazard scoring purposes to overcome subjective scaling issues.
3. Graphical representation of assessment results for root-cause analysis down to the chemical substance level.
4. The proposed technique can be tailored to company's own data.
5. The proposed method is useful for quick yet comprehensive comparison of alternative processes.
6. This method is applicable for inherent safety evaluation during research and development (R&D) stage which requires limited process data.

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