Plant Design Report Series
Tehdassuunnittelun raporttisarja No. 96
Espoo 2010

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Mimi Haryani Hassim

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Mimi Haryani Hassim

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Faculty of Chemistry and Materials Sciences for public examination and debate in Auditorium Ke 2 at the Aalto University School of Science and Technology (Espoo, Finland) on the 29th of May, 2010, at 12 noon.

Aalto University
School of Science and Technology
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Department of Biotechnology and Chemical Technology

Aalto Yliopisto
Teknillinen korkeakoulu
Kemian ja materiaalitieteiden tiedekunta
Biotekniikan ja kemian tekniikan laitos

Distribution:
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Helsinki University of Technology
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ISBN 978-952-60-3095-1
ISSN 0358-0776

Multiprint Oy
Espoo 2010

ABSTRACT

Sustainability is now a necessity to process industry. Therefore the safety, health, and environmental (SHE) evaluations are required in process design and operation. Various methods for assessing safety and environmental friendliness have been presented in literature. However, occupational health evaluations have received much less attention even though each year more people die from work-related diseases than are killed in industrial accidents.

Inherent occupational health assessment is an approach to reduce hazards by choosing healthier chemicals and process concepts. I.e. inherent occupational health relies on the healthier and safer properties of chemical substances, process conditions, operations, and work procedures in a process. This thesis presents new systematic approaches for evaluating inherent occupational health of chemical processes in process development and design.

In the R&D stage, the Inherent Occupational Health Index (IOHI) is proposed based on healthier and safer reaction chemistries, properties of compounds present, and process conditions such as pressure, volatility, exposure limits, and temperature etc.

In the preliminary design stage, chronic health risk is calculated due to exposure to fugitive airborne emissions based on flow sheet data and precalculated process modules' emission, estimated process plot areas, and wind velocities. Health Quotient Index (HQI) is used as a health indicator to compare the estimated chemical concentrations to their exposure limits.

In the basic engineering stage, the Occupational Health Index (OHI) utilizes detailed fugitive emission calculations based on piping and instrumentation diagrams. The method evaluates quantitatively chronic inhalation risks to noncarcinogens and carcinogens, acute inhalation risk, and qualitatively dermal/eye risk.

For fugitive exposure estimation new methods were developed. Three approaches for estimating chemical concentration due to fugitive emissions are proposed based on simple PFD, detailed PFD, and PID, which were tested on the actual Borealis Polymers plant in Porvoo. A more realistic approach was developed for estimating health risks of fugitive occupational exposure by using statistical meteorological data.

Finally the integration of the inherent occupational assessment methods with the existing computer aided design tools was studied. Also the correlation between index-based SHE assessment techniques was analyzed to find out, if any interdependency exists between SHE characteristics at the inherent level.

Keywords: inherent occupational health, process development, process design, inhalative exposure, fugitive emission, health risk, index method.

PREFACE

First and foremost, I would like to raise my infinite thanks to God, the Most Gracious, the Most Merciful.

This work was carried out between September 2005 and March 2010 in the Plant Design research unit, Department of Biotechnology and Chemical Technology, Helsinki University of Technology, which is now known as Aalto University, School of Science and Technology. The financial supports from Islamic Development Bank and Universiti Teknologi Malaysia, as well as the research supports from Graduate School in Chemical Engineering (GSCE), Finnish Foundation for Technology Promotion (TES), and The Finnish Work Environment Fund are gratefully acknowledged.

I would like to express my deepest gratitude to my supervisor, Professor Markku Hurme, for his faithful guidance and boundless encouragement throughout my studies. His brilliant ideas, extraordinary creativities, and excellent supervisions were the main reasons for the emergence of this thesis. He has always been very detailed yet practical, and for that I am truly honored to be given a chance to work with and learn from him.

I am also grateful to Professor J. P. Gupta and Dr. Hirokazu Sugiyama for reading the thesis manuscript and I am inspired by their valuable comments. I also owe a debt of gratitude to Dr. David W. Edwards, who was the first to come out with such an interesting research idea and I was lucky to be involved in the project back in the year 2001 to 2002.

I wish to acknowledge all of the other co-authors, Alberto L. Pérez, Miina Grönlund, and Dr. Krisztina Cziner, for their significant contributions to this thesis. I would also like to thank all of my colleagues and the laboratory staffs for a positive and pleasant working environment.

Finally, I would like to express my gratitude to my father Hassim Majid, my mother Normah Derani, parents in-law, sisters, and brothers for their unconditional support and continuous pray. My warmest thanks are dedicated to my beloved husband, Haszlee M. Safuan and my son, Muhammad Adam Abid for their endless love, patience, help, motivation, and understanding. Thank you for believing in me until the end of this challenging yet exciting journey.

Espoo, April 2010

Mimi Haryani Hassim

LIST OF PUBLICATIONS

The thesis is based on the following publications, which are referred by the corresponding numbers:

[1] Hassim, M.H., Edwards, D.W., Development of a methodology for assessing inherent occupational health hazards. *Proc. Safety Environ. Protect.* **84**(B5) (2006) 378-390.

[2] Hassim, M.H., Hurme, M., Inherent occupational health assessment during process research and development stage. *J. Loss Prev. Proc. Ind.* **23**(1) (2010) 127-138.

[3] Hassim, M.H., Hurme, M., Inherent occupational health assessment during preliminary design stage. *J. Loss Prev. Proc. Ind.* **23**(3) (2010) 476-482.

[4] Hassim, M.H., Hurme, M., 2009, Inherent occupational health assessment during basic engineering stage. *J. Loss Prev. Proc. Ind.* **23**(2) (2010) 260-268.

[5] Hassim, M.H., Pérez, A.L., Hurme, M., Estimation of chemical concentration due to fugitive emissions during chemical process design. *Proc. Safety Environ. Protect.* (accepted for publication on 27 January 2010), doi:10.1016/j.psep.2010.01.006.

[6] Hassim, M.H., Hurme, M., Occupational chemical exposure and risk estimation in process development and design. *Proc. Safety Environ. Protect.* (accepted for publication on 29 March 2010), doi:10.1016/j.psep.2010.03.011.

[7] Hassim, M.H., Hurme, M., Computer aided design of occupationally healthier processes. *Comput. Aided Chem. Eng.* Vol. 25, Elsevier, Amsterdam 2008, 1119-1124.

[8] Hassim, M.H., Grönlund, M., Hurme, M., Inherent EHS considerations in process development. *Chem. Eng. Trans.* Vol. 13, 2008, 295-302.

THE AUTHOR’S CONTRIBUTION TO THE PUBLICATIONS

[1] The author developed the method and wrote the paper.

[2] The author introduced the definition of inherent occupational health hazard and developed the method with the co-author and wrote the paper.

[3] The author developed the method with the co-author and wrote the paper.

[4] The author developed the method with the co-author and wrote the paper.

[5] The author developed the methods with co-author Markku Hurme. Co-author Alberto L. Pérez tested the methods on plant data. The author analyzed the results with the co-authors and wrote the paper.

[6] The author developed the method with the co-author and wrote the paper.

[7] The author developed the methods and wrote the paper with the co-author.

[8] The author carried out the study and wrote the paper with co-author Markku Hurme based on the process simulations of co-author Miina Grönlund.

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ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
ACH	Acetone cyanohydrin based route
ALARP	As low as reasonably practicable
C2/MP	Ethylene via methyl propionate based route
C2/PA	Ethylene via propionaldehyde based route
C3	Propylene based route
CAPE	Computer aided process engineering
CDI	Chronic daily intake
CEI	Chemical Exposure Index
CHIP	Chemical Hazard Information and Packaging for Supply Regulations
COSHH	Control of Substances Hazardous to Health Regulations
CPI	Chemical plant industry
CSTR	Continuous stirred tank reactor
CTE	Concentration/Toxicity Equivalency
EC	European Commission
EHI	Environmental Hazard Index
EHS	Environmental, Health & Safety Index
EIA	Environmental Impact Assessment
EPA	Environmental Protection Agency
EU	European Union
EU-OSHA	European Agency for Safety and Health at Work
FE	Fugitive emission rate
HAZOP	Hazard and Operability Study
HDA	Hydrodealkylation
HHS	Health Hazard Score
HIRA	Hazard Identification and Ranking
HIRA-TDI	Toxicity Damage Index

HQI	Health Quotient Index
HTP	Human Toxicity Potential
HTP-arvot	Concentrations known to be harmful (haitallisiksi tunnetut pitoisuudet)
IBI	Inherent Benign-ness Indicator
i-C4	Isobutylene based route
ICSC	International Chemical Safety Cards
IETH	Inherent Environmental Toxicity Hazard
ILO	International Labour Organization
IOHI	Inherent Occupational Health Index
IPPC	Integrated Pollution Prevention and Control
IS	Inherent safety
ISBL	Inside battery limit
ISD	Inherently safer design
ISHE	Inherent safety, health, environment
ISI	Inherent Safety Index
IT	Index of Toxicity
JSOH	Japan Society for Occupational Health
LCA	Life-cycle assessment
LOPA	Layer of protection analysis
MMA	Methyl methacrylate
MSDS	Material Safety Data Sheet
NFPA	National Fire Protection Association
OHHI	Occupational Health Hazard Index
OHI	Occupational Health Index
OSHA	Occupational Safety and Health Administration
PFD	Process flow diagram
PFR	Plug flow reactor
PID	Piping & instrumentation diagram
PIIS	Prototype Index of Inherent Safety
PRHI	Process Route Healthiness Index

R&D	Research and development
REACH	Registration, Evaluation, Authorization & Restriction of Chemicals
SF	Safety factor
SHE	Safety, health, environment
SHI	Substance Hazard Index
SME	Small and medium enterprise
SOCMI	Synthetic organic chemicals manufacturing industry
SPI	Sustainable Process Index
SREST	Substance, Reactivity, Equipment and Safety Technology
SWeHI	Safety Weighted Hazard Index
TBA	Tertiary butyl alcohol based route
TBS	Toxicity-based Scoring
TLV	Threshold limit value
VHI	Vapor Hazard Index
VOCs	Volatile organic compounds
WAR	Waste Reduction Algorithm
WHO	World Health Organization

NOMENCLATURE

A_i	Floor area of process module i
A_f	Total floor areas
A_n	Process cross-section area downwind
C	Chemical concentration
C_{EL}	Occupational exposure limit
Ceq	Chemical’s equilibrium concentration
d	Plot width
h	Height
HQ_a	Health Quotient Index for short-term exposure
HQ_c	Health Quotient Index for long-term exposure to carcinogens
HQ_{nc}	Health Quotient Index for long-term exposure to noncarcinogens
i	Individual chemical substance
I_C	Corrosiveness sub index
I_{EL}	Exposure limits sub index
I_{HH}	Subindices of index for health hazards
I_{MS}	Material state sub index
I_P	Pressure sub index
I_{PM}	Process mode sub index
I_{PPH}	Subindices of index for physical and process hazards
I_R	R-phrases sub index
I_T	Temperature sub index
I_V	Boiling point sub index
m	Fugitive emission rate
max	Maximum
mix	Chemicals mixture
v	Wind speed
v_0	Wind speed at reference height

z	Desired height
z_0	Reference height
α	Scale parameter
β	Shape parameter
γ	Ground surface friction coefficient
$\dot{V}$	Air volumetric flow rate

1. INTRODUCTION

Sustainability is defined as ‘meeting the needs of the present without compromising the ability of future generations to meet their own need’ (Anon, 1987). A generally accepted division of sustainability is to divide it into economic, environmental, and social sustainability. From company point of view corporate responsibility is the term used to cover these aspects. Health and safety are an important part of the corporate responsibility in social sustainability. Therefore workers’ health and safety are among the sustainability indicators used (Al-Sharrah et al., 2010).

Both voluntary and legal requirements related to sustainability have been imposed. Responsible Care, which was introduced in 1988, commits the members of Chemical Manufacturers Association to improve safety, health, and environmental (SHE) performance (Hook, 1996). EU directives have also affected process development and design so that SHE aspects have to be taken into consideration in earlier phase. For example, the IPPC was enacted to achieve a high level of protection of the environment for sustainable development on the basis of what is achievable with the best techniques available in the individual industrial sectors falling within the scope of the directive (O’Malley, 1999). Meanwhile the REACH legislation is necessary to protect lives and workers’ health besides the environment. The European Agency for Safety and Health at Work (EU-OSHA) was set up in 1996 to make Europe’s workplaces safer, healthier, and more productive. The European Risk observatory was then set up in 2005 as an integral part of the EU-OSHA. It describes factors and anticipates changes in the working environment and their likely consequences to health and safety (EU-OSHA, 2010). It aims to identify new and emerging risks and to promote early preventive action. SHE considerations in process development and design have therefore become important because of legal requirements, company image, and economic reasons.

Due to increasing production volumes and higher knowledge about the danger potentials of chemical substances and processes, safety and environmental issues started to get into public, regulatory, and industrial focus during the 1960s. Much effort was put on developing safety technologies for reducing the probability of accidents by installing add-on control systems. End-of-pipe technologies were introduced for converting industrial effluents into less dangerous substances and control systems were adopted to keep processes in a safe state. However, with these add-on technologies, hazards still remained in the processes and accidents were bound to happen because of the hazards persisted. The add-on systems are also costly; estimates show that in the oil and chemical industries, 15 to 30% of capital cost was spent on safety and pollution prevention measures already in the 1980's (Kletz, 1985).

Following the largest peacetime explosion of the Flixborough disaster in Britain in 1974, the concept of inherently safer design was introduced. Inherent SHE is a way of reducing hazards by choosing safer chemicals and process concepts, whereas add-on systems only reduce the risks by keeping the hazards under control. In principle an inherently safe, environmentally friendly, and healthy plant or activity cannot, under any circumstances, cause harm to people or environment (Mansfield, 1996). Protective equipment may fail and human may create errors. Therefore designing a fundamentally safer, environmentally friendlier, and healthier plant is more appealing and should be made as the first choice by designers and engineers. This idea has already been discussed a lot in process safety (Kletz, 1985) and clean technology (Ashford, 1997), but not in health aspect in process design even though Kletz proposed that. This is astonishing since it is a known fact that each year more people die from occupational related diseases than by industrial accidents (Wenham, 2002).

In fact occupational health aspect has not been widely researched in the design of chemical plants, but active work has been done dominantly from medical point of view. CPI involves hazardous chemical substances as main products, byproducts, intermediates, wastes or raw materials. Such potential risks to health must be clearly recognized and considered in the design of the facility. Although more is understood now about some occupational hazards than in the past, every year new chemicals and new technologies are being introduced which present new and often unknown hazards to both workers and the community. Therefore on 1 June 2007, the EC enforced REACH that requires anyone manufacturing or importing a chemical substance to be placed on the market in the EU, in quantities above 1 tonne per year, to register that substances for the uses to which it will be put. Also the hazardous effects of these chemicals need to be reported.

1.1 Aims of the Study

Since the obvious aim is to reduce the hazards and not just to control the risks, this principle has to be introduced also to the consideration of occupational health aspect in process design. Therefore the aim of the study is to develop methodologies for assessing occupational health hazards during the development and process design phases of chemical processes based on the inherent safety principles.

In Chapter 2, the concepts of health and safety are described. Statistics on occupational injuries and diseases are presented and how occupational health differs from process safety is explained to instill understanding on the major subject of the study. Inherent safety concept and its evolvement towards environmental and health aspects are also discussed before inherent occupational health definition is introduced. Chapter 3 discusses health hazards and risks as well as primary chemical route of exposure and exposure assessment in chemical industries. Chapter 4 describes lifecycle stages of a typical chemical process with a focus on development and design phases. Chapter 5 summarizes the existing occupational health-related assessment methods for chemical industries and discusses several important methods in this area. Chapter 6 presents the Process Route Healthiness Index as the first formally published methodology for inherent occupational health assessment and its weaknesses, which motivated this research study. Chapters 7, 8, and 9 discuss in detail the methods developed for the research and development, preliminary design, and basic engineering stages. This is the main contribution of the thesis. Chapter 10 describes the development of methods for estimating fugitive emissions in preliminary design and basic engineering stages based on data from simple process flow diagrams (PFDs), detailed PFDs, or piping and instrumentation diagrams (PIDs). Chapter 11 discusses chemical concentrations calculation due to fugitive emissions as well as air flow rate estimation for the same stages as in Chapter 10. For more realistic health risk assessment, worker exposure estimation approach based on local wind distribution data is also covered in Chapter 12. Chapter 13 describes the feasibility and framework for integrating the methods with the existing computer aided design tools. In Chapter 14, the correlation between SHE characteristics is studied. A universal index that capable of evaluating all the SHE aspects in the case study is proposed. Chapter 15 presents the layout of the overall approach for occupational health evaluation in process development and design. The thesis is finally wrapped up with conclusions in Chapter 16.

2. HEALTH AND SAFETY

2.1 The Concepts of Health and Safety

Before inherent occupational health concept is introduced, it is necessary to understand the related terms of health and safety.

Hazard is a chemical or physical condition that has a potential to cause damage (Crowl and Louvar, 2002).

Risk is a measure concerning both the likelihood and magnitude of loss (Crowl and Louvar, 2002). These terms will be widely used below and therefore their difference is emphasized.

Health in general is defined as a state of physical and mental well-being (as an opposite to illness) (Princeton Encyclopedia, 2010).

Occupational health is the protection of the bodies and minds of people from illness resulting from materials, processes, or procedures used in the workplace (Hughes and Ferrett, 2008) and its aim is the promotion and maintenance of the highest degree of physical, mental, and social well-being of workers in all occupations by preventing departures from health, controlling risks, and the adaptation of work to people and people to their jobs (ILO, 1950).

OSHA (OECD, 2008) defines an *occupational disease* or *illness* as any abnormal condition or disorder, other than one resulting from an occupational injury, caused by exposure to factors associated with employment. Occupational diseases concern with a disease contracted as a result of an exposure over a period of time to risk factors arising from work activity.

Safety is the prevention of accidents (Crowl and Louvar, 2002) through hazards identification and their elimination.

Accident is defined as any unplanned event that results in injury or ill health of people or loss to property, plant, materials, or the environment or a loss of a business opportunity (Hughes and Ferrett, 2005).

Occupational safety is the protection of people from physical injury from accidents at work (Hughes and Ferret, 2008).

An *occupational injury* is any personal injury, disease, or death resulting from an occupational accident (ILO, 1998) e.g. instantaneous exposure in the working environment (National Safety Council, 1999).

Process safety (or loss prevention) can be defined as the prevention of accidents through the use of appropriate technologies to identify and eliminate the hazards of a chemical plant (Crowl and Louvar, 2002).

Consequently *occupational safety and health* is the discipline dealing with the prevention of injuries and diseases of workers resulting from the materials, processes, or procedures used in the workplace (ILO, 1997; Hughes and Ferrett, 2008). The two words are normally used together and the borderline between health and safety is ill defined. Quite often, the classification of health and safety hazards is used to define the difference in duties between the industrial hygienist and the safety professional within a given organization (Talty, 1988). Figures 1 and 2 summarize the concepts of health and safety.

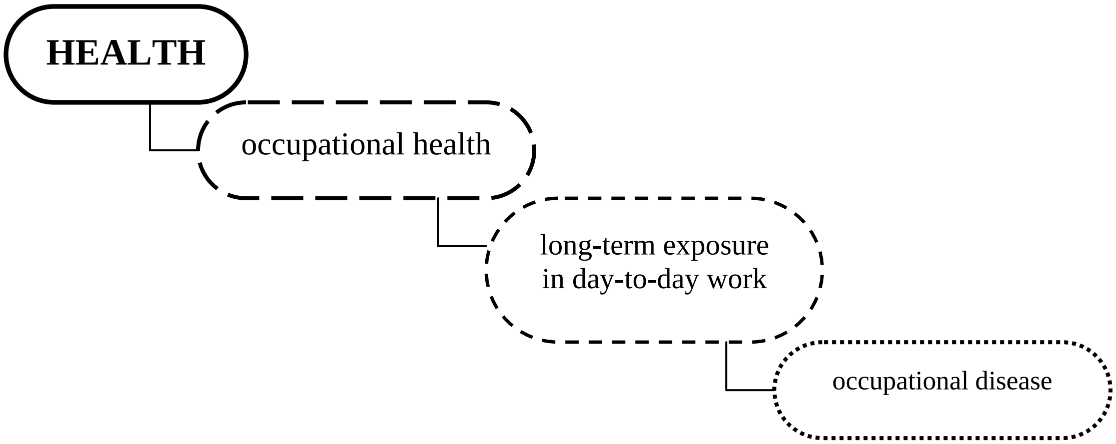

Figure 1. Health concept

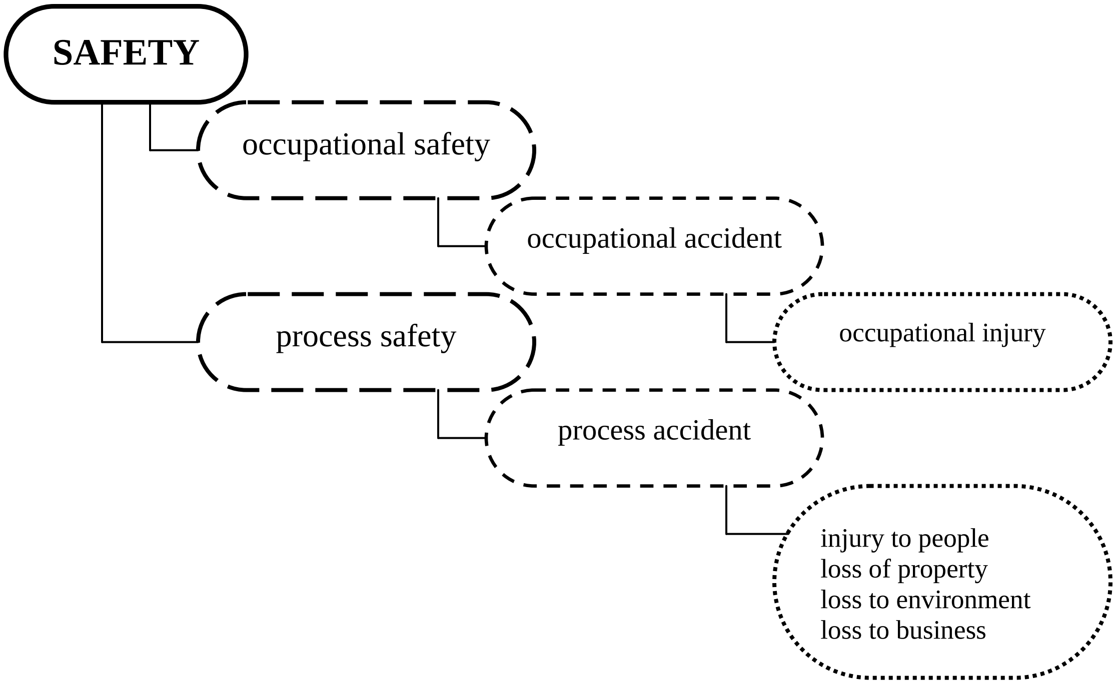

Figure 2. Safety concepts

2.2 Occupational Health vs. Occupational/Process Safety

Occupational health differs from occupational safety and process safety in terms of several criteria; the exposure pattern, duration of event, exposure scenario, and process state. The details about the differences are described in Papers 1 and 2, and are summarized in Table 1.

Table 1. Occupational health vs. occupational/process safety criteria

Criteria	Occupational health	Occupational safety	Process safety
Exposure pattern	Chronic (repeated)	Acute (single)	Acute (single)
Event duration	Long-term	Short-term	Short-term
Exposure scenario	Routine activity	Accident, routine activity	Accident, loss of containment
Process state	Normal	Normal	Abnormal

From Table 1, occupational health is related to normal everyday work activities and long-term exposure to chemicals. Occupational safety also is concerned with normal activity, but short-term accident due to physical hazards. Meanwhile process safety refers to major accidents, loss prevention, and acute short-term exposure in abnormal situations. The occupational health and safety hazards directly affect human's life only compared to process safety hazards, which also have interest on the plant, property, and cost. The nature of risk is also different; since airborne toxic substances are harmful at much lower concentrations than merely corrosive and flammable ones, their effects extend to much greater distances. These imply that although the occurrence of occupational health effect is long-term and less dramatic, the impact could be more serious in the long run than the occurrence of safety-related events. The insidious nature of occupational disease is the reason for it rarely reaches the news and is not well publicized as the industrial accident cases.

Health effects can be divided into acute and chronic effects due to short-term and prolonged exposures, respectively. Occupational health mainly deals with chronic exposure as a result of regular operations and day-to-day (routine) working activities. In large-scale process industry, chronic exposure is mainly contributed by fugitive emissions. Acute exposure may also occur in large-scale process industry primarily due to periodic emissions, which are mainly from occasional but acceptable working practices e.g. manual operations as described in Paper 4. Here occupational health assessment covers both chronic and acute occupational exposures as presented in Figure 3. Acute effects due to major process accidents such as loss of containment, fire, and explosion are the subjects of process safety, hence beyond the scope of the research (see Figure 3).

2.3 Occupational Injuries and Diseases

The concept of occupational health was first introduced by Bernadino Ramazini, an Italian physician, who suggested a rule in the 17th century for evaluating whether a workplace-induced factor could be the cause of a disease in an individual (Harbison and McCluskey, 2001).

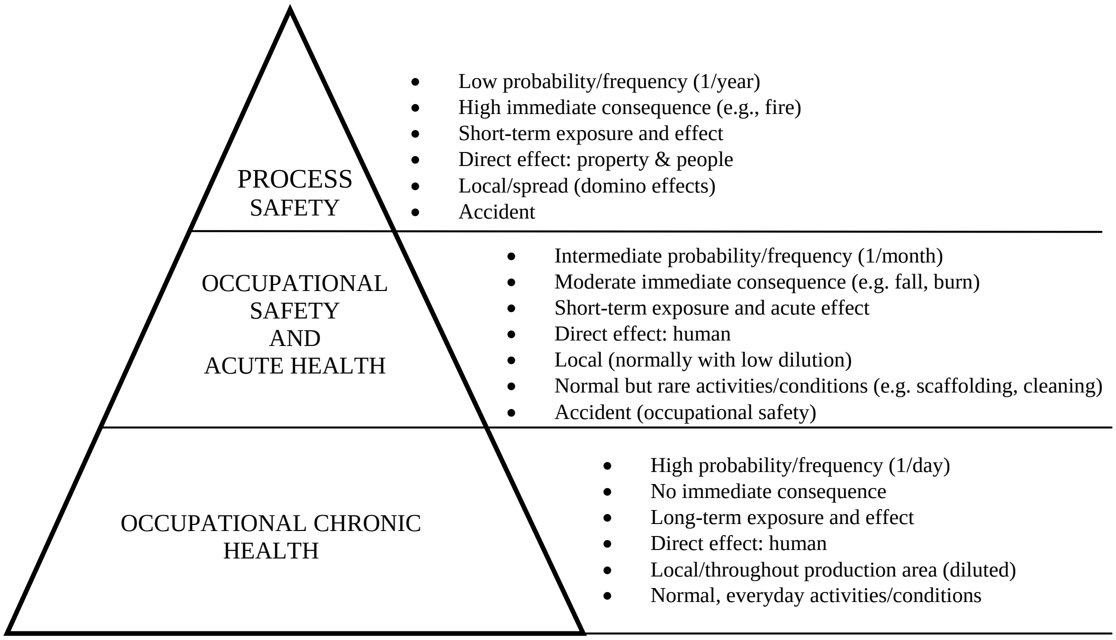

Figure 3. Occupational health vs. occupational/process safety

Still nowadays, hundreds of millions of people throughout the world are working under circumstances that are unsafe and/or foster illnesses. They are exposed to a multitude of workplace hazards such as chemicals, extreme temperature, and noise. More than two million people worldwide die of occupational injuries and work-related diseases each year according to International Labour Office (ILO) (Eijkemans, 2005). Eijkemans (2005) states that the figure might be vastly under-estimated due to poor reporting and varying recording criteria. In the EU27 alone, there are an estimated 167 000 work-related fatalities every year. About 159 000 are attributable to work-related diseases, of which 74 000 may be linked to workplace exposure to hazardous substances (ILO, 2005).

Almost one-quarter of the workers in the EU are exposed to recognized cancer-causing chemicals, whilst 22% of all workers self-report breathing fumes and vapors for at least one-quarter of their working time (Levy, 2004). It is also reported that in the EU, dangerous substances contribute significantly to the 350 million working days lost due to occupational illnesses (Paoli and Merllie, 2001).

In Finland alone, almost 6 800 recognized or suspected cases of occupational diseases (28 cases per 10 000 employed in all occupations) were notified to the Finnish Register of Occupational Diseases in 2005. Meanwhile in chemical, pulp and paper industry 83 cases per 10 000 employees were reported in 2006. The statistic of the occupational disease cases in Finland is presented by the Finnish Institute of Occupational Health (2010).

2.4 Inherent Safety vs. Extrinsic Safety (Add-on)

The losses and occupational injuries and diseases can be reduced by diminishing risks. Risk can be reduced by decreasing the hazards (i.e. hazard potential) or by managing the hazards by add-on or administrative systems (Figure 4). The levels from the highest to the lowest order of effectiveness are inherent safety, engineered or add-on controls, and procedural or administrative controls. This is known as layer of protection analysis (LOPA) (CCPS, 2009). If add-on safety relates to prevention of risk of accidents (prevention of likelihood and magnitude), inherent safety concerns with prevention of hazards (prevention of hazard potential in a system) through the use of more benign chemicals and technologies. The idea of inherent safety is to avoid problems by solving them at their roots rather than to manage the consequences. This is in contrast to the traditional safety that relies on the add-on control systems, which keep the plant hazards under control (extrinsically safer) rather than being intrinsically safer.

Inherent safety is the first layer and most important strategy, because it deals with the elimination or reduction of the inherent hazards at source (i.e. hazard potential). The subsequent layers of protection are frequently used to mitigate the consequences and protect the receptors of the already-accepted hazard, but they do not reduce the hazard potential.

Inherent safety ideology started to develop in 1970’s. Professor Trevor Kletz was the first to propose the concept in 1971 (Khan and Amyotte, 2003); the idea however, remained latent until the explosion at Flixborough four years later. Kletz (1976) delivered the idea on the inventory reduction to avoid Flixborough type of explosions, but the word ‘inherently safer’ was not used. The inherent safety principles were then formalized. In

1977, Kletz gave an annual Jubilee lecture ‘What you don’t have, can’t leak’, which devoted entirely to inherently safer design.

Inherently safer design (ISD) is a different way of thinking in designing chemical products and processes. Applying the concept at the very beginning of a project allows a safe product to be chosen instead of a hazardous one. Then a route that avoids the use of hazardous raw materials or intermediates can be selected (Kletz, 1998). The basic decision on e.g. reaction chemistry affects the hazard potential of a plant more than the initial choice of technology (Anon, 1988), because manipulation of chemistry and physics of the materials is more effective to prevent accidents than dependence on additional elements to stop incipient incidents (CCPS, 1993). Among the earlier methods developed to quantify the inherent safety of a chemical process route is the Prototype Index of Inherent Safety; PIIS (Edwards and Lawrence, 1993), Inherent Safety Index; ISI (Heikkilä et al., 1996), and *i*-Safe (Palaniappan et al., 2002). Other existing inherent safety assessment methods are mentioned in Papers 1 and 4. Once the chemistry has been decided, intensified equipment that does not require large inventories can be chosen during the flow sheet development (Kletz, 1998).

Basically the strategies to the inherently safer design of processes and plants discussed above have been grouped by Kletz (1984, 1991) into four major strategies:

Minimization or *Intensification*
Use smaller quantities of hazardous substances (either material or energy content).

Substitution
Replace a hazardous material or process with a less hazardous one.

Moderation or *Attenuation*
Use materials under less hazardous form, which can be accomplished either by physical (i.e. dilution) or by chemical (i.e. less severe process conditions) strategies (also called Limitation of Effects).

Simplification

Design processes or facilities which eliminate unnecessary complexity, thereby reducing the opportunities for error, and which are forgiving of errors that are made (also called Error Tolerance).

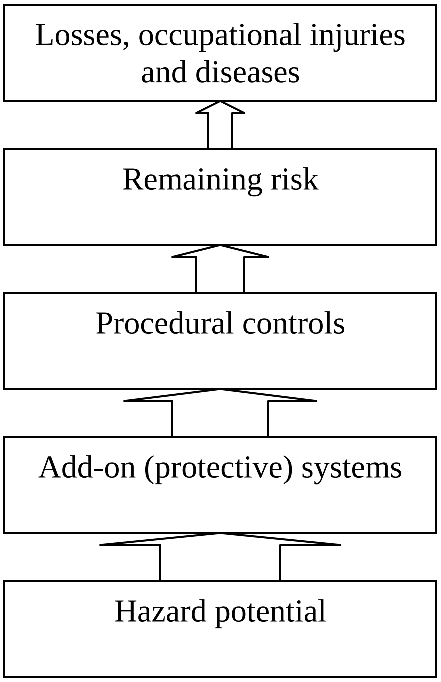

Figure 4. Hazard and risk management strategies

2.4.1 Adoption of inherent safety concept to health

Workers do not create hazards if the working guidelines are proper and they are followed. In many cases the hazards are built into the workplace (Kletz, 1991). It is therefore important to make work safer by designing an inherently safer workplace rather than try to get workers to adapt to unsafe conditions. This rationale of the inherent safety concept makes it interesting for adoption on the environmental and health aspects. Kletz (1984) proposed that the concept also applies to the prevention of pollution (environmental aspect) and the avoidance of small continuous leaks into the atmosphere of the workplace (health aspect), but he did not evolve it further.

The adoption of the inherent concept to health started later than safety and environment. A group from Loughborough University was the first to exclusively work on inherent occupational health subject. Johnson (2001) developed in her Master thesis a method called the Occupational Health Hazard Index (OHHI) for assessing the occupational health hazards in design concepts. The aim was to quantify the health hazards of chemical synthesis routes like the PIIS and ISI for inherent safety. The next development was the Process Route Healthiness Index (PRHI) published in Paper 1 in 2006 and further development was the Inherent Occupational Health Index (IOHI). The first version of the method was published by Hassim et al. (2006). Then the method was further developed in Paper 2.

Paper 2 defines the concept of inherent occupational health for the first time. Inherent occupational health is a prevention of occupational health hazards (i.e. chemical or physical condition) that have the potential to cause health damage to workers by trying to eliminate the use of hazardous chemicals, process conditions, and operating procedures that may cause occupational hazards to the employees. Here inherent occupational health hazards can be defined as a condition, inherent to the operation or use of material in a particular occupation or environment, that can cause death, injury, acute, or chronic illness, disability, or reduced job performance of personnel by an acute or chronic exposure (Paper 2).

There are twofold aims of inherent occupational health (Paper 2): Firstly to reduce the hazards from inherent properties of chemicals (such as toxicity and high vapor pressure) by using friendlier chemicals or the chemicals in safer physical condition (such as lower temperature) to eliminate the exposure. Secondly to reduce such process steps or procedures which involve inherent danger of exposure to the chemicals. Examples of such operations are some manual operations where the worker is in close contact with the material, such as the manual handling and dosing of chemical, emptying, and cleaning of the equipment etc. For reducing the occupational hazards, evaluation methods are of prime importance. In the following chapters, the hazards and the methods for their evaluation are discussed in more detail.

3. HEALTH HAZARDS AND RISKS FACTORS

It is important to distinguish between hazard and risk terms since they are often confused. Health hazard refers to damaging potential only, which is described by the inherent health properties. The level of health risk in chemical plant is determined by: a) the potential for harm and b) the potential for exposure. The potential for harm is a function of the toxicity characteristics of chemicals present in the workplace. The exposure is determined by materials' physical properties (e.g. volatility), operating and workplace conditions, leaking tendency of equipment, working activities (duration and frequency), and human behavior.

3.1 Health Hazards

Hazard is a chemical or physical condition (substance, activity, or process) that has the potential to cause damage to people, property, or the environment (Crowl and Louvar, 2002; Hughes and Ferrett, 2005). Hazards that might affect workers' health can be divided into five major categories of physical, chemical, biological, ergonomic/mechanical, and psychosocial (Hartley, 1999; Negash, 2002). The focus of this study is the chemical and some physical hazards. The other categories cannot be evaluated due to the limited data available in the early stages of design. At the early design stage e.g. R&D, chemical health hazards are evaluated from toxicity properties of materials whereas physical health hazards are based on process conditions e.g. operating temperature that may cause burn. Later hazards from inhalative exposure to airborne chemicals can be evaluated.

3.2 Health Risks

Risk is the likelihood and the magnitude of damage caused by hazards (Crowl and Louvar, 2002; Hughes and Ferrett, 2005). It can be controlled on several levels (Figure 4). Health risk can be defined as the probability that an individual exposed to a chemical substance may experience an adverse health effect subsequent to the exposure (Kumar et al., 1994). The effect can be either acute or chronic depending on the duration of exposure; short-term or long-term, respectively. In principle chemicals will only be a risk to health once human are exposed to them even though the hazard is basically present all the time because of their presence.

3.2.1 Route of exposure

Route of exposure describes the way chemicals enter an organism after contact. No chemical can harm human until it has actually contacted with or entered the body. The possible routes of exposure are through inhalation, skin or eye contact, ingestion, and accidental injection.

Respiratory system is the most common route for gases, vapors, aerosols, mists, fumes, and small particulates to enter the body. Therefore inhalation is considered as a very important source of exposure occupationally (Lipton & Lynch, 1994). In large scale chemical industries handling volatile or dusty compounds such as most petrochemicals and solvents, inhalation is a primary route for exposure. Physical properties of materials (i.e. boiling point), process conditions (i.e. temperature), equipment types, dilution, as well as work activities influence exposure to chemicals through inhalation. The significant impact of inhalation to cause health hazards in process industries is also recognized by Tyler et al. (1996), when they selected inhalation route in assessing toxicity hazards in the Toxicity Hazard Index. Papers 2, 3, and 6 discuss the evaluation of inhalative exposure.

Skin or eye contact is also typical in chemical plants, especially those that deal with heavy and less volatile substances, though its occurrence is not as frequent as inhalation (Papers 2 and 4). Skin effects - either absorptive, corrosive, or scalding, may be caused by liquids spillage, leakage, or splash. Even though they can be very severe, they are usually confined to a very short distance from the release point, whereas inhalation effects affect a wider area of working environment.

Ingestion is the least common entry route into the body. Despite this, ingesting chemicals by accident may still happen. Typically, chemical exposure via ingestion route may occur through eating or smoking with contaminated hands. Injection is a common type of exposure in laboratories and hospitals, but rare in chemical industries. As for skin contact and ingestion, poor hygiene practices and work procedures appear to be the notable cause. Overall, the ingestion and injection exposures are small and always ranked behind inhalation and skin contact as contributors to the total dose.

3.2.2 Exposure assessment

Exposure is defined as contact of an organism with a contaminant (Watts, 1997). An exposure assessment is used to evaluate the risk from chemical exposure as discussed in Paper 6 and elsewhere by e.g. von Grote (2003). Chemical exposure is determined by the quantity of the substance that is exposed to the organism and the duration of the chemical's presence. For inhalation route, air concentration is used to express the quantity of airborne chemicals, which are the most common exposure agents in chemical industries (Lipton and Lynch, 1994). Often only the quantification of concentration level is done, without the time dimension. For example, the establishment of chemicals' threshold limits is based mostly on this thinking. Paper 6 however uses both concentration and intake-based exposure risk estimations.

It is important to define 'exposure' in more detail - here the term pertains to external exposure. This can be defined as the amount of the substance inhaled, in contact with the skin, or ingested. It does not refer to concentration within the body, which is consistent with some measure of absorbed dose or intake. Chronic exposure by inhalation is the main focus of the study because it represents the routine occupational exposures (8h per day). Here dermal exposure is evaluated as a result of short-term exposure from manual operations, which normally concerns liquids and solids (see Chapter 9.5.2). The exposure assessment approaches are based on the information available in each stage. PFD is the minimum level of process information needed to enable exposure quantification for a proposed plant. However even this requires specialized method, which has been developed in Paper 3. Details about the assessment stages are discussed in Chapter 4.

Papers 5 and 6 give several examples of the existing occupational exposure models such as the EASE (Friar, 1996), POEM (PSD, 1992), and EMKG (ECHA, 2008). The models however, are not suitable for design stage assessment of large petrochemical plants. They are more relevant for indoor work facilities and are task-oriented. Also, they are best applied on existing plants. In this study, the exposure assessment is approached based on reasonable worst-case scenarios. Only exposures from normal operation are considered. Exposures which result from accidents, malfunctions, or misuse are excluded from the assessment.

3.2.3 Assumptions in the exposure assessment

Due to lack of information in process development and design stages and to avoid underestimation of risk, reasonable worst-case scenarios are assumed when assessing the chemical exposure:

a) For chronic inhalative exposure, fugitive emission is the only chemical release source considered.
b) For fugitive emissions, the rate is assumed constant with time; the method does not consider level of maintenance but employs ‘average’ leak rates.
c) No personal protective equipment is considered.
d) All chemical concentrations inhaled by the exposed workers are absorbed by the body.
e) Perfect mixing to air takes place; local concentration differences are not considered. This requires at least moderate wind speed or ventilation.
f) For acute inhalative exposure, only emissions from routine works are considered e.g. manual operations.

3.3 Different Levels of Inherent Health Study

The study of inherent health can be made in three levels (see Figure 5):

i) Inherent health hazard potential

Inherent health hazard potential includes hazards of materials in a process that are potentially harmful to health. However, leak or exposure aspect is not yet considered. Therefore the focus of the very early assessment is typically on material’s toxicity.

ii) Inherent leak hazard potential

In petrochemical plants, process materials may escape from the system through flanges, valves etc. through fugitive emissions. In this case the materials (hazard) are no longer contained but they are released into air. The inherent release rate depends on the complexity of process, the types of equipment involved, and physical properties of fluids. No specific protection layers are considered; therefore the evaluation of material release sources (leak potential) is still a hazard and not a risk-level study.

iii) Inherent exposure potential and risk

Chemical exposure assessment requires information on chemical concentration (a function of leak rate and dilution), exposure (a function of frequency and duration of exposure), protective equipment, and type of work procedure (e.g. manual operation close to the emission source). Here protective equipment is not considered because inherent point of view is used, giving worst-case scenario. Only at this level, some protective layers and human aspect start to get involved, thus allowing health risk to be quantified.

Basically the development of the indices was based on this inherent level division. The index evolves from a hazard-based to a risk-based assessment as progressing from the R&D to basic engineering stage. The presented levels also agree with the LOPA concept (see Chapter 2.4). In the case of reducing health hazard and risk of process plants, the first strategy is to avoid hazardous substances and process conditions (inherent health hazard potential). Next is to have a simple plant with less leak sources (inherent leak hazard potential). If inherent leak potential is too large, it is possible to install a better protective layer using leakless or less-leaking fittings. Finally the effect of dilution by ventilation or wind and the exposure time through work procedures are considered (inherent exposure risk).

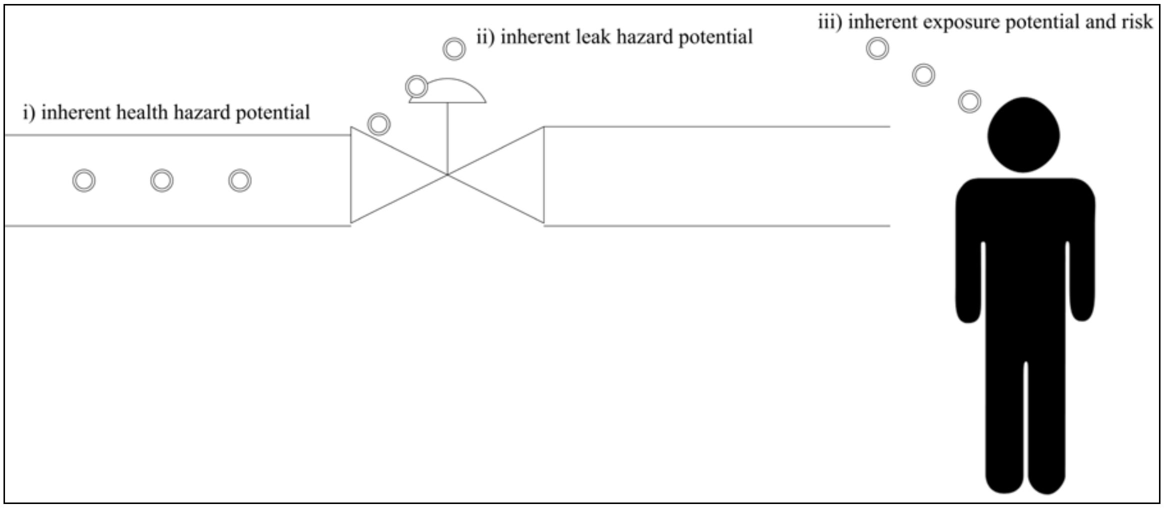

Figure 5. Levels of inherent health study

4. PROJECT PHASES IN DEVELOPMENT AND DESIGN

A process goes through various stages of evolution. Progression through these stages can simply be termed as the process lifecycle. A typical chemical process goes through lifecycle stages of research and development, design, construction, operation, retrofitting, and finally decommissioning The design stages can further be divided into process preliminary design, basic engineering, and detailed engineering (Hurme and Rahman, 2005). As the project is started, the chemical synthesis route is selected in *research and development* phase. In *preliminary design*, process structure is created, material and heat balances are calculated, and flow sheet diagrams are generated. The process piping and instrumentation diagrams etc. are then created in *basic engineering* phase. In *detailed engineering* phase, detailed documents and drawings for procurement and construction are made. The stages are distinguished mainly by the information available on the process as summarized in Table 2.

The search for inherently safer process options should begin early. As plant lifecycle progresses, the major viewpoint changes from a chemical to an engineering one (Koller, 2000). Although the inherent safety principles can be incorporated at any stage of process lifecycle, the best results will only be achieved if it is implemented during the earliest stages of process development, since many of the decisions are conceptual and fundamental (Figure 6, Paper 1). The advantages are discussed in Papers 1 and 2.

At the design stage, process engineers and designers have maximum degrees of freedom in the plant and process specification (Figure 6; CCPS, 1993). However the lack of information especially in early design complicates hazards evaluations and decision-making in general. This is called the design paradox (Hurme and Rahman, 2005). Assessments should become step-by-step more quantitative and precise as the design becomes more detailed. An assessment method claiming to be applicable during the whole rather than at a specific point of the design process therefore neither has a fixed region nor a fixed viewpoint (Koller, 2000). Therefore, the aim of the study is to develop a series of methods for the earlier stages of R&D, preliminary design, and basic engineering. The idea is to provide a package of assessment tools that can be used flexibly. The methods can be used also in series. Basic engineering is the last step where there is still large freedom of making conceptual changes and to adopt ISHE principles (Hurme and Rahman, 2005).

Early SHE assessment will not only benefit from the SHE performance, but it also will reduce the overall plant costs (Edwards and Lawrence, 1993; Kletz, 1998; Shah et al., 2003). Also the cost of fixing a problem (changes) is lower at earlier lifecycle phases – the cost folds ten times as progressing through each phase (Kletz, 1988) (Paper 2).

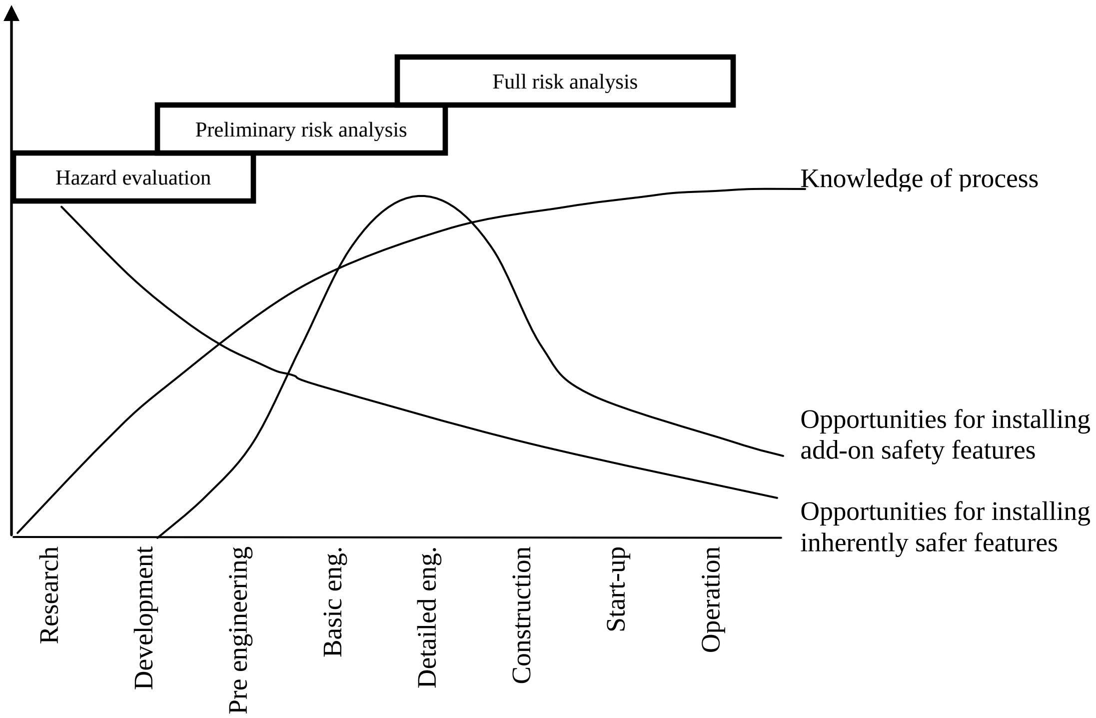

Figure 6. The design paradox and inherently safer design (Hurme and Rahman, 2005)

Table 2. Information availability at different design stages (Paper 2)

R&D design	Process predesign	Basic engineering	Detailed engineering
- First process concept - Process block diagram - Reaction steps - Types of chemicals - Physical/chemical/ toxicity properties - Reaction conditions - Stoichiometric equations - Product yield	- All in R&D stage - Flow sheet (simple or detailed) - Mass/energy balances - Operating conditions - Major unit operations	- All in R&D and predesign stages - PI diagram - Process data on equipment, piping and instrumentation - Plant layout - Preliminary working procedures	- All in R&D, predesign, and basic engineering stages - Detailed equipment, piping and instrumentation - Equipment sizing - Mechanical design/ engineering - Structural, civil, and electrical engineering - Design of ancillary services

5. CONSIDERING HEALTH IN DESIGN IN GENERAL

Most of the existing inherent safety methods discussed earlier include human health effects in the assessment. Mostly only chemical’s toxicity hazard is considered. The basis for toxicity assessment varies significantly within the different methods. The methods use either threshold values for acute toxicity or chronic toxicity or EU hazard symbols or NFPA ratings. Koller et al. (2001) found no correlation between these methods in evaluating health impacts. Therefore they are not suitable for occupational health hazard assessment because of their limitation and inconsistency.

There are several methods available for health hazard assessment in chemical process as shown by Table 3 and discussed in Papers 1 and 2. The methods however, are more diversified due to the complicated underlying principle of the aspect itself. Even though they have been developed for the purpose of health assessment; the scope, approach, and considered aspects vary. The review of 51 chemical ranking and scoring systems demonstrates that there was no consensus regarding an appropriate framework for evaluating adverse impacts to human health from exposure to chemicals (Davis et al., 1994). The methods specifically assessing inherent occupational health during chemical process design do exist but are very few.

The two basic types of health studies are the substance and process-type indices as presented in Table 3. Majority of the methods developed earlier are chemical substance-based and they are widely known as hazard indices. Hazard indices aim to rank substances in a process by their hazard potential. They take into account the volatility and the toxicity of a substance. Several examples of such indices are given in Table 3 under ‘chemical substance-based’ category. As for process-based assessment, the methods are more disparate. Basically, the methods can be classified into those which:

Category 1 – health aspect is addressed only as part of the safety and/or environmental assessments.

Category 2 – health is not being evaluated from the occupational context. For example, some of them focus only on the acute hazards due to accidental chemical release, some concern with the effects on public community, and some address the environmental health impacts.

Category 3 – occupational health assessment is not suitable for process screening during the early design stage, but is intended for process operation.

Category 4 – health impacts are adapted in an existing Life-Cycle Assessment (LCA) method.

Category 5 – inherent occupational health assessment is feasible during the design stage of chemical processes.

EHS (Koller et al., 1999; 2000) is one of the earliest methods that consider health aspect from occupational point of view besides evaluating safety and environmental hazards. They acknowledged the fact that health assessment is usually based on an exposure-effect relationship for the workplace. However the method only assesses the effects and not the exposure – they claimed that information required for exposure assessment is not available at early design phases.

The most detailed method for assessing SHE aspects is the INSET Toolkit (INSIDE Project, 2001). The toolkit evaluates the health criteria of chemical process route based on the hazardous material properties relating to health effects, the likely fugitive emission rate of the material as well as the chance that people are exposed to this. For chemical properties, the Health Harm Factor (HHF) is determined from R-phrase and qualitative classification. The Leak Factor (LF) is provided to estimate the fugitive release rate from process equipment and manual activities. The R-phrase classification and the LF score are very brief and incomprehensive. The potential exposure is assessed by estimating the number of equipment leak points and locations where manual-handling operations will be carried out in the process.

The disadvantage of INSET Toolkit is its complexity and requirement of detailed information. It demands a lot of works including process screening, optimization, and further evaluation to reduce process inventories and complexity (Malmén, 1997; Ellis, 1997). The need for analyzing complex issues such as transport hazards, siting, and plant layout, makes the method unattractive for early design stages, but is more suitable for later phases when more process information is available.

Johnson (2001) developed a methodology called the Occupational Health Hazard Index (OHHI) to assess the occupational health of alternative process concepts. The framework of the OHHI is similar to the Process Route Healthiness Index (PRHI), which was later developed by Hassim and Edwards (2006) as an improvement to the OHHI. The OHHI includes unnecessary criteria for occupational health evaluation e.g. material’s flammability and reactivity. It evaluates exposure aspect poorly i.e. fugitive emission in a process is considered from one sample connection only – this makes the accuracy of the method questionable.

Since there are no directly suitable health evaluation methods available for process development and process design steps, new methods have been developed for this purpose as discussed in Chapters 7, 8, and 9.

Table 3. Example of health assessment methods

Type	Method	Reference
Chemical substance-based:	Vapor Hazard Index (VHI)	Pitt (1982)
	Extraordinary Hazardous Substances (EHS)	TCPA (1987)
	National Fire Protection Agency ranking (NFPA)	NFPA (1989)
	Substance Hazard Index (SHI)	API (1990)
	Safety Factor (SF)	Martel (2004)
	Index of Toxicity (IT)	Martel (2004)
Process-based:		
Category 1	Emission Limit	Swiss LRV (1985)
	KEMI	Swedish National Chemicals Inspectorate (1995)
	Waste Reduction Algorithm (WAR)	Mallick et al. (1996)
	CHEMS	Swanson et al. (1997)
	Health Hazard Score (HHS)	Sheng and Hertwich (1998)
	EURAM	Hansen et al. (1999)
	Environmental, Health & Safety Index (EHS)	Koller et al. (1999, 2000)
	Hazard Identification and Ranking (HIRA)	Khan and Abbasi (1998, 2001)
	Substance, Reactivity, Equipment and Safety Technology (SREST)	Shah et al. (2003)
	Inherent Benign-ness Indicator (IBI)	Srinivasan and Nhan (2007)
Category 2	Dow Chemical Exposure Index (Dow CEI)	Dow Chemicals (1988)
	Toxicity-based Scoring (TBS)	Hovarth et al. (1995)
	Sustainable Process Index (SPI)	Narodoslawsky and Krotscheck (1995)
	Toxicity Hazard Index	Tyler et al. (1996)
	Concentration/Toxicity Equivalency (CTE)	Jia et al. (1996)
	Integrated Risk Analysis	Gurjar and Mohan (2003)
Category 3	COSHH Essentials	Maidment (1998)
Category 4	Human Toxicity Potential (HTP)	Hertwich et al. (2001) and McKone and Hertwich (2001)
	EDIP	Hellweg et al. (2005)
Category 5	Occupational Health Hazard Index (OHHI)	Johnson (2001)
	INSET Toolkit	INSIDE Project (2001)
	Process Route Healthiness Index (PRHI)	Hassim and Edwards (2006)

6. PRHI AS THE FIRST INDEX DEVELOPMENT

The first methodology, formally published in the area of inherent occupational health assessment for chemical processes is called the Process Route Healthiness Index (PRHI). The aim of the method is process route selection during the R&D stage based on information from reaction chemistries and block diagram only. However the method aims to be very comprehensive and it becomes therefore complicated and lengthy. The index includes wide range of factors in a single evaluation stage. The PRHI also requires plenty of information and some of the information is not available during the early process design stage. Basically the PRHI comprises of several subindices of the Inherent Chemical and Process Hazard Index (ICPHI), Health Hazard Index (HHI), Material Harm Index (MHI), Worker Exposure Concentration (WEC), and Occupational Exposure Limit (OEL). The HHI, MHI, and OEL are appropriate for the R&D stage because they require for data which are already available such as the chemicals' OSHA Health Effects list, NFPA value for health, and workplace exposure limit, respectively. However the ICPHI and WEC need data beyond the R&D stage such process operations, maintenance works, process leak points, and worker exposure. This information is only available once the process progresses to the later stages such as pre-design and detailed engineering. Due to its complex steps, the PRHI is not suitable for a simple and quick application in the early lifecycle stage. It is also inflexible as a result of the data requirements for the application. Despite of its weaknesses, PRHI served as the starting point for further research.

The lessons learnt from the PRHI are the following:

a) The method should be dedicated to the particular design stage to ensure simplicity.
b) The method should require only the information available in the stage of study to ensure applicability.
c) The method should include aspects that are related to occupational health only. Process safety (loss prevention) related aspects should be excluded.

Based on these findings the improved index methods developed were specific to each process development and design lifecycle stage as discussed in the next chapters.

7. THE EVALUATION AT RESEARCH AND DEVELOPMENT STAGE

7.1 Stage Aim and Tasks

Research and development stage (R&D) is an important stage where the chemical route is selected based on the economic, technical, and SHE criteria. The stage starts when the desired product is fixed and a number of viable process routes are searched or created for analysis. Chemical process route may be defined as the raw material(s) and the sequence of reactions that convert them to the desired product(s) (Edwards and Lawrence, 1993). The choice of route fixes the chemicals present and to great extent the operating conditions in the plant. The other tasks also involve the laboratory and bench scale experiments to acquire required chemical and physical data. The pre-feasibility study of the new route is done in the end. Detailed tasks are given in Table 2.

At the R&D stage, much of the detailed information is still missing because the process is not yet designed (see Figure 6). Reaction chemistries and process block diagram are produced for potential synthesis routes to the desired product. Chemicals involved in the process, their reactions, and basic reaction conditions can be determined. Basic data on the chemicals (physical, chemical, and toxicity properties) needs to be obtained from the literature or measured.

7.2 Inherent Occupational Health Index

Paper 2 presents the Inherent Occupational Health Index (IOHI) developed for the inherent occupational health evaluation in the R&D stage. The health hazards can be estimated on inherent level based on the data available at R&D stage i.e. reaction steps, types of chemicals, physical/chemical/toxicity properties, and reaction conditions.

7.2.1 Principle of the index

The aim of the IOHI is to consider inherent health hazards that are assessed from normal process operations, not for accidents such as loss of containment which are covered by inherent safety methods. The method provides hazard and not risk-based process evaluation since no protective layers and human aspect are considered. The IOHI method is reaction step-oriented. Therefore a whole reaction step is considered as one entity. The main objective of the method is to rank alternative chemical process routes for the production of the desired product by their health level. Both the acute and chronic effects are considered (Paper 2).

The index is based on the data available in the R&D stage. Only chemical and health properties and reaction operating conditions are used (Table 2) because of their availability and their ability to represent the occupational health hazards in inherent level. The factors available are the chemicals present, their chemical properties (boiling point, toxicity, corrosiveness, and phase), the process pressure, temperature, and mode e.g. batch mode of the main process item (typically reactor). The Inherent Occupational Health Index composes of two subindices: Index for Physical and Process Hazards (I_{PPH}) and Index for Health Hazards (I_{HH}), representing potential exposure and harm, respectively.

7.2.2 Physical and process hazards evaluation

The Physical and Process Hazards subindices (I_{PPH}) describe the potential of physical properties of materials, process conditions, and the type of process to cause exposure hazard at the workplace.

The choice of process *operation mode* will contribute to workplace exposure. Batch processes are more hazardous compared to continuous and semi-continuous, because they usually require more frequent manual operations e.g. chemical handling potentially exposing people to chemicals and involve higher number of workers.

Material *phase* subindex is selected, because it affects much on the way a chemical will be handled and exposed to. Solids are often transported in bags or drums and are processed manually e.g. manual loading or bag emptying. This tends to result in higher material releases compared to fluid handling in enclosed piping and equipment, in which liquids and especially gases are commonly handled.

Material *volatility* is another important subindex that influences the propensity of a substance to become airborne and subsequently becomes susceptible for exposure. Volatility of a liquid can be characterized by its vapor pressure or boiling point, whereas dustiness characteristic can be used for solid.

Operating *pressure* subindex is selected because it plays a vital role in releasing materials from the process. A higher pressure poses a higher potential of fugitive emissions through leakages. A higher-pressure process may also present a safety hazard to workers when performing maintenance works such as opening connections.

The significance of *corrosion* in causing chemical releases in chemical plants is well known and therefore is included in the index. At the R&D stage the subindex is evaluated based on the compatible construction materials, in which the chemical will be contained or handled.

Temperature subindex is chosen not only because it affects vaporization of a liquid material upon releases (e.g. due to/after a leak), but it also has possibility of causing burn accidents. Details about the I_{PPH} subindices are discussed in Paper 2 and the subindex values are presented in Table 2 of Paper 2.

7.2.3 Health hazards evaluation

The Health Hazards subindices (I_{HH}) focus on the health hazard of chemicals as a result of exposure. The potential effects depend upon chemicals' toxicity level and the severity of impact. Therefore I_{HH} has both an exposure limit based subindex (I_{EL}), giving information on the chronic hazards of chemicals in the working air and the R-phrase based subindex (I_R) that describes the type of health effect caused by the chemicals. The R-phrases are classified based on the severity of the adverse health effects, which are further divided into chronic and acute. Many earlier scoring systems do not include measures of severity at all. This may yield misleading results since the severity of effect may vary from a temporary to a serious chronic effect. That is why two pertinent parameters were selected for evaluating the inherent toxicity hazard of the chemicals in the process, as described. Details of the I_{HH} are presented in Table 3 of Paper 2.

7.3 Weighting of the Subindices

In an index system, the weighting of different parameters describes their importance and it can be based on e.g. statistical data or expert judgment on their significance (Edwards et al., 1996). Such guideline however, is not available for occupational health. In IOHI the allocation of the penalties is based on the degree of potential hazards or the probability of exposure; the higher the hazard or the probability, the higher the penalty. The level of the consequences caused by the exposure determines the range of penalties assigned. The penalty range set for the I_{HH} parameters is higher than that for the I_{PPH} parameters because it is believed that the toxicity represents the main direct health hazard of the chemicals. More about the weighting is explained in Paper 2.

The penalty score of the I_{PPH} parameters is between 0-3 or 1-3. Corrosiveness however, is assigned with a smaller score because it poses a lower risk for direct hazard exposure.

In the I_{HH} index the chemicals with chronic toxicity effect have a higher range of penalty (maximum value of 5) in comparison to those with acute effect (maximum value of 4). The chronic toxicity was penalized by more severe scale because of its more problematic nature, such as the latency period involved before the long-term health effects appear, which makes the counter measures are often too late.

The penalties are summarized in Tables 2 and 3 of Paper 2. The justification behind the penalty assignation and other relevant information can be found in Paper 2. Instead of the weighting of factors proposed in this work, the user may tailor the method by applying weightings, which describe their own opinion or the company policy.

7.4 Calculation of the Inherent Occupational Health Index

The IOHI method is reaction step-oriented. Therefore a whole reaction step is considered as one entity (Paper 7). The IOHI for each process route is calculated as a sum of the two factors.

$$I_{IOHI} = I_{PPH} + I_{HH} \tag{1}$$

The I_{PPH} and I_{HH} are calculated by summing up the penalty for all subindices.

$$I_{PPH} = I_{PM} + I_P + I_T + \max(I_{MS}) + \max(I_V) + \max(I_C) \tag{2}$$

where I_{PM} is process mode, I_P is pressure, I_T is temperature, I_{MS} is material state, I_V is boiling point, and I_C is corrosiveness subindices.

$$I_{HH} = \max(I_{EL}) + \max(I_R) \tag{3}$$

where I_{EL} is exposure limits and I_R is R-phrases subindices.

The process conditions determine the process mode (I_{PM}), temperature (I_T), and pressure (I_P) subindices. The other factors are penalized based on the dominant (i.e. most hazardous) chemical in the reaction step. The maximum penalty (worst case) received by any chemical in the reaction step will be chosen to represent the subindex for that particular reaction step. The I_{PPH} and I_{HH} scores are finally added up to obtain the net IOHI index value for a process route.

The IOHI can be calculated using three different types of calculations; additive-type, average-type, and worst case-type. The additive-type calculation sums up the subprocess indices to get the route index value. The index value for the route can also be calculated by averaging the subprocess indices. This eliminates the influence of the number of subprocess on the route index value. The worst case-type takes the highest penalty of each subindex to represent the worst potential hazard of the route. This aspect has been discussed relatively little in literature earlier. In almost all the earlier index-based methods, the way of calculating the process route index is the additive approach.

However, this approach has been criticized by Gupta and Edwards (2003) for being much affected by the number of steps in the route. Therefore the alternative ways of calculating the index, which exclude the influence of the number of steps, were proposed in Paper 2. The effect of the method of calculation is discussed in the case study (Chapter 7.6). Details about the index calculation types are discussed in Paper 2.

Several authors have criticized the concept of producing single figure (net score) as a final index value, because it can lead to an information loss problem (e.g. Hendershot, 1997; Gupta and Edwards, 2003). Even so, the approach is still widely used in index-based methods for early design stage, because it enables easy and quick comparison of hazard level in different processes, hence helping in decision-making (Khan and Abbasi, 1998). Subindices values of the processes can also be compared to get more insight on single criteria as proposed by Gupta and Edwards (2003) through their simple graphical method.

7.5 Standard Setting for the Inherent Occupational Health Index

Since the index value is meaningless as an absolute number without a reference, the index cannot be used to determine the level of inherent health hazard as such. Therefore, the applicability of the IOHI is extended by providing the standard setting for the index. The standard was created to have four categories: safe, moderately safe, moderately hazardous, and hazardous. The standard was set up based on the penalty of the subindices. For the ‘safe’ category, the standard was created by summing up all subindices penalty between 0 and 1. Depending on the subindices, penalty between 1 and 2 was totaled up for the ‘moderate’ category, which is further refined into moderately safe and moderately hazardous categories. Penalty between 2 and 5 was added up for the ‘hazardous’ category. The scales for the IOHI standard are provided in Paper 2 (Table 9).

7.6 Case Study

To demonstrate the method, Paper 2 presents a case study on methyl methacrylate (MMA) process route selection. This case study has been widely used earlier to illustrate inherent SHE assessment methods, such as the PIIS and ISI. MMA can be synthesized via various routes (Nagai, 2001). The six routes commonly used as case study are:

a) Acetone cyanohydrin based route (ACH)
b) Ethylene via propionaldehyde based route (C2/PA)
c) Ethylene via methyl propionate based route (C2/MP)
d) Propylene based route (C3)
e) Isobutylene based route (i-C4)
f) Tertiary butyl alcohol based route (TBA)

Additional information about the processes is given by Gupta and Edwards (2003) and Rahman et al. (2005). Sugiyama (2007) collected more current data on these routes and reported different yield for TBA second subprocess.

The IOHI index was calculated for the six processes using additive-type, average-type, and worst case-type calculations. The index value received by each route is:

a) Compared to each other to establish the process ranking, and
b) Compared against the standard to determine the level of the inherent occupational health hazard.

The results show that C2/PA and C3 routes are bad in all types of calculations. ACH route is the worst in averaging type of calculation. The best routes are either C2/MP or TBA in all types of index calculations; which one is the best depends on the type of calculation.

The case study done shows that in additive calculation the routes with more steps get worse index values. The additive calculation mostly reflects the process complexity. Therefore the averaging and worst case calculation approaches give better analysis on the other characteristics of the routes. The comparison of the index values to the standard setting (Table 9 in Paper 2) reveals that all the MMA processes are moderately hazardous. Many of the routes however, have dangerous subprocesses. Detailed discussion about the findings is presented in Paper 2.

8. THE EVALUATION AT PRELIMINARY DESIGN STAGE

8.1 Stage Aim and Tasks

Preliminary design is often done only for one or two most promising process concepts based on a pre-feasibility study done earlier. At this stage, the basic process concept is further developed into process flow sheet diagrams (PFDs). More accurate estimations of cost, profitability, and SHE aspects are made to find out if the project is still promising (Hurme and Rahman, 2005).

8.2 Hazard Quotient Index Method

A more accurate evaluation of inherent health hazards is possible at this stage based on the information available from process flow sheets. Here a method called the Hazard Quotient Index (HQI) was developed, which intends to evaluate the risk of chemical exposure to workers due to exposure to airborne volatile chemicals in the process area. The index is presented in Paper 3 and summarized in Paper 7. The method can be used either with simple PFDs or detailed PFDs. Simple PFDs consist of process drawing and process descriptions only without exact material balance. These concept sketches can be found in patents or encyclopaedias. From detailed PFDs, data on mass and energy balances and actual operating conditions is available. Information like major unit operations is obtainable from both types of PFDs, offering copious insights about health risks in a chemical process. The information availability is presented in Table 2 (Chapter 4).

8.2.1 Principle of the index

The HQI method focuses on fugitive emissions from piping and equipment (Paper 3). Fugitive emissions are the origin of the continuous background exposure of workers especially in chemical plant industries (Lipton and Lynch, 1994). The idea of the method is to estimate the occupational inhalative exposure, which concerns adult workers in good health, with an average 8 hours of exposures per day. The HQI is developed based on the following assumptions:

a) Inhalative exposure from fugitive emissions is the only exposure source considered; this is a valid first assumption for large-scale continuous plants with few manual operations.
b) The emission rate is constant with time; the method does not consider level of maintenance but employs ‘average’ leak rates.
c) All chemical concentrations inhaled by the exposed workers are absorbed by the body (worst-case scenario).
d) Perfect mixing to air takes place. Local concentration differences are not considered. This requires at least moderate wind speed or ventilation.

The HQI method allows for comparison of alternative processes by ranking them based on the risks value. It can also be used to determine the health risk of a single process.

8.3 Development of the Index Method

The HQI method is developed based on the four standard steps in risk assessments (EPA, 1989):

a) *Hazard identification* involves identification of chemicals present and their characteristics, as well as leak sources in the process. Process materials are determined from reaction chemistries for simple PFDs or mass balances for detailed PFDs. Chemical properties, such as physical state can be obtained from safety or mass balances sheets.
b) *Exposure assessment* evaluates potential exposure of the chemicals to receptors and the route of intake. In chemical plants, workers’ exposure to chemicals may be contributed by fugitive emissions, periodic emissions, and other exposures. Here, only fugitive emissions are considered. Fugitive emissions are the main source of background exposure to workers in chemical processes dealing with airborne chemicals (Lipton & Lynch, 1994). Also, only inhalation exposure is assessed due to insufficient information on manual operations as sources of dermal/eye exposure. Both periodic emissions and other routes of exposures are included in the next stage method (Chapter 9).

c) *Toxicity assessment* involves the acquisition and evaluation of toxicity data for each chemical. Threshold exposure limits are used because of their easy availability for a wide range of chemicals. Here, HTP 8h values (HTP Values, 2007) are used since the study concerns continuous exposures to fugitive emissions.
d) *Risk characterization* gives a qualitative or quantitative expression of risk by combining information on exposures and toxicity. Commonly, the risk is quantified by comparing the actual or estimated exposure values to the threshold exposure limits by hazard quotient (Roach, 1994).

The formulation of the HQI is based on the standard hazard quotient approach; that is the ratio of the predicted exposure concentration to the reference exposure limit (Roach, 1994; Mower, 1998). For chemicals mixture, chemicals are assumed to have additive effects. This will be further described in Chapter 8.5.2.

8.4 Estimation of Fugitive Emissions and Concentrations

Leak rate

To calculate the concentration, data on the amount of fugitive emissions potentially emitted from the process is required. A method was developed in Papers 3 and 5 for estimating the fugitive emissions. A method for estimating the average air flow rate in chemical plants during the preliminary design stage is proposed in Paper 3, which is applicable for both simple and detailed PFDs. Since no information on the numbers and types of fugitive emission sources is available, a standard module approach was developed in Paper 5. Processes were divided into standard modules such as distillation, flash etc. systems and the typical number of leak sources was estimated. The methods for simple and detailed PFDs are discussed in detailed in Chapter 10.

Dilution

Chemicals leaked into process area are diluted by ventilation for indoor or wind for outdoor facilities. Ventilation rates or air change rates are widely published for indoor facilities (e.g. Lipton and Lynch, 1994, Jayjock, 1997). However, majority of petrochemical plants are located outdoor and the chemicals are diluted by wind. The chemical leaks dilution in outdoor facility is estimated based on the estimation of average floor area of the standard process modules and their average height, as well as the wind speed. This approach is a simplification since many actual data is still lacking at the conceptual phase. The air flow rate estimation is discussed in Chapter 11 and Paper 5 in more detail.

Concentration

Exposure risk to chemicals can be assessed based on chemical concentration or intake as discussed later in Chapter 12. The latter one is more realistic, but the reference intake limits are not available for many chemicals (Paper 7). Therefore, concentration-based risk estimation is used, which is a common approach as discussed earlier. The average chemical concentration in air (at the downwind edge of the plot area) is estimated from fugitive emission rate, estimated plot area, average height of emission sources, and wind speed in Chapter 11 (Eq. 6).

8.5 Calculation of the Hazard Quotient Index

Various exposure limits data are published for the chemicals by regulatory bodies and organizations (Paper 6). Here the Finnish limit values (HTP) are used (HTP Values, 2007). For occupational setting, reference limit values are provided for both long-term (8h) and short-term (15min) exposures. For the HQI, the 8h values are used to estimate chronic exposure such as the risk of continuous exposures to fugitive emissions. The index can be applied to a single chemical as well as to chemicals mixture.

8.5.1 Single chemical

For a single chemical, the HQI is calculated based on the following equation:

$$\mathrm{HQI_i} = \frac{\mathrm{C_i}}{\mathrm{C_{ELi}}} \tag{4}$$

where C_i is the concentration of chemical i and C_{ELi} is the occupational exposure limit.

8.5.2 Chemicals mixture

The Health Quotient Index for a chemicals mixture (HQI_{mix}) can also be calculated:

$$HQI_{mix} = \sum \frac{C_i}{C_{ELi}} \tag{5}$$

Most often, chemical processes deal with chemicals mixture. Therefore exposure to chemicals mixture is rather a rule than the exception, and health risk assessments should in principle focus on mixtures and not on single chemicals (Feron et al., 2002). The effect of a mixture may be less than the effects of its individual components (an antagonistic effect) or the effect of the components may be additive; i.e. the effect of the mixture may be greater than the sum of the effect of the individual components (synergistic effect) (McCarty and Borgert, 2006).

According to Omae (2006), the effects should be assumed as additive when there is no reliable evidence that the effects of the chemicals are non-additive. This has been practiced by several well-established bodies such as the American Conference of Governmental Industrial Hygienists (ACGIH) and the Japan Society for Occupational Health (JSOH) (Nielsen and ∅vreb∅, 2008). The approach is conservative, but the simplest that can be used for assessing the overall risk due to a mixture of chemicals (Calamari and Vighi, 1993). This assumption is made also in the environmental impact assessment (Cave and Edwards, 1997; Gunasekera and Edwards, 2006).

8.6 Risk Characterization

Paper 6 discusses the benchmarks for interpreting the HQI index value. HQ value < 1 is commonly used to indicate acceptable risk (Table 7). However even below an occupational exposure limit, when exposure is greater than one-tenth the limit, there is still the small risk that some employees may be adversely affected (Roach, 1994). The benchmark (HQ < 0.1) is often applied to carcinogens. Detail discussion on the risk estimation and the benchmarks is given in Paper 6. In principle however, the quantitative value obtained for the index does not provide a value for the probability of harm as the result of exposure. The HQI is basically a measure of the safety margin, which is reflected in the size of the HQI - the smaller the HQI, the larger the margin of safety. The method steps are shown in Figure 7.

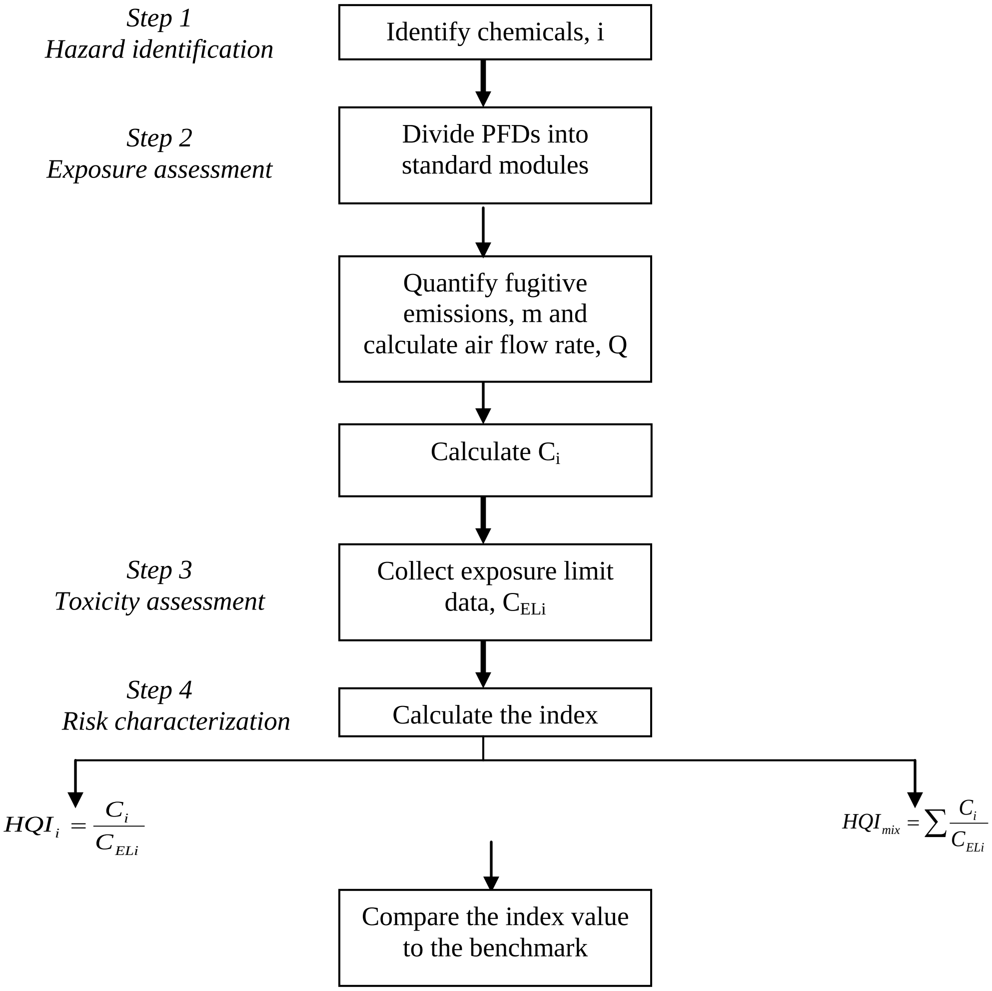

Figure 7. Flow chart of the overall assessment steps (Paper 3)

8.7 Case Study

The Health Quotient Index method was calculated for six process routes for MMA manufacturing in Paper 3 by using the simple PFD approach. First the processes were divided into process modules shown in Table 1 in Paper 3. The number of the modules is summarized in Table 2 (Paper 3).

Results in Table 3 of Paper 3 show that none of the chemicals in the routes have concentrations exceeding their threshold limits ($HQI_i < 1$). This indicates the exposure risk to any of the chemicals is in acceptable level in all the process routes based on this benchmark. The same finding was also obtained for the HQI_{mix} of the combined impact (Table 4 of Paper 3). C2/MP route posses the lowest chemical exposure risk followed by TBA and i-C4 routes. ACH process presents a moderate level of hazard among the alternatives, which is mainly contributed by the significant emission rate of acetone cyanohydrin (Table 3 of Paper 3). Both the C2/PA and C3 routes receive the high index values due to the presence of toxic chemicals formaldehyde and hydrogen fluoride, respectively. Even though the concentrations of both species are below their threshold limits, the HQI_i however, is much closer to the benchmark compared to the other species in the processes.

The resulting ranking order of the processes is compared to those obtained from the PRHI and the IOHI (Table 4). The result shows that HQI_{mix} and IOHI rank the routes in similar way although IOHI cannot separate the two worst routes. PRHI gives different ranking except for the worst route. This indicates that both methods, HQI and IOHI are relatively consistent in this case study. Further discussion is given in Paper 3. The application of the HQI method to characterize the risk of a single process is discussed in Paper 7.

Table 4. Comparison of occupational health indices (normalized) (Paper 3)

Process	HQI_{mix}	Rank order	IOHI	Rank order	PRHI	Rank order
ACH	4.77	**4**	2.63	**4**	9.95	5
C2/MP	0	**1**	0	**1**	2.36	3
C2/PA	6.89	**5**	10	**5-6**	8.55	4
C3	10	**6**	10	**5-6**	10	**6**
i-C4	1.16	**3**	2.11	**3**	1.39	2
TBA	1.03	**2**	1.58	**2**	0	1

Bold represents the ranking order of the process that agrees with the order given by the HQI_{mix}

The HQI index values are then compared to the IOHI and PRHI values calculated for the MMA case study in Papers 1 and 2. The values of the indices are correlated pair wisely by linear regression (see Figure 2 of Paper 3). The comparison shows that the HQI_{mix} and IOHI correlate best. The correlation between the others is worse. This is understandable since these methods are developed for subsequent design stages. The correlation between indices is also discussed in Chapter 14.

9. EVALUATION AT BASIC ENGINEERING STAGE

9.1 Stage Aim and Tasks

A plant construction project starts with basic engineering. The main task is to make the piping and instrumentation diagrams (PIDs) to the accepted for design (AFD) stage and to complete all equipment process datasheets. All process data for equipment is defined (Hurme and Rahman, 2005).

At this stage, more detailed process data becomes available. The main process document generated is the PIDs. Process data on equipment, piping, and instruments is also available. Other useful produced documents for the health hazards evaluation are preliminary layout and preliminary work procedures (see Table 2).

9.2 Occupational Health Index

In Paper 4 a method called the Occupational Health Index (OHI) is proposed. The method focuses on health risk estimation based on the data from the PIDs to give quantitative and qualitative background for analyzing occupational health problems to support risk elimination or reduction.

9.2.1 Principle of the index

The goals of the OHI are to: a) identify occupational risks; b) estimate level of occupational risks to workers; and c) give quantitative and qualitative support for risk reduction (Paper 4).

The characteristics behind the OHI development are: a) the method relies on the data availability in the PIDs; b) the assessment takes into account the realistic aspects of operations under normal conditions (such as local wind conditions etc.); and c) the evaluation addresses both the long-term (chronic) and short-term (acute) exposures in routine work (Paper 4).

9.3 Development of the Index

The OHI method is a combination of qualitative and quantitative assessments. As more process information is now accessible from PI and plot diagrams, additional factors have been included in the index method. In comparison to the HQI, the OHI extends the assessment by incorporating dermal exposures, acute exposures, and manual operations (Figure 8). All the aspects are more comprehensively and realistically assessed. The factors are applicable to both fluids and solids-handling processes except for the acute inhalative exposures, which can only be evaluated for fluids. The assessment will result in four indicators on the occupational health risk of the process. Risk estimation of the three inhalation-based exposures gives numerical (quantitative) results, whereas the dermal-based exposure risk is presented non-numerically (qualitative). Instead of summing up the results to get one net score value, the results of the subindices are presented separately to allow the sources of hazard to be easily identified and distinguished.

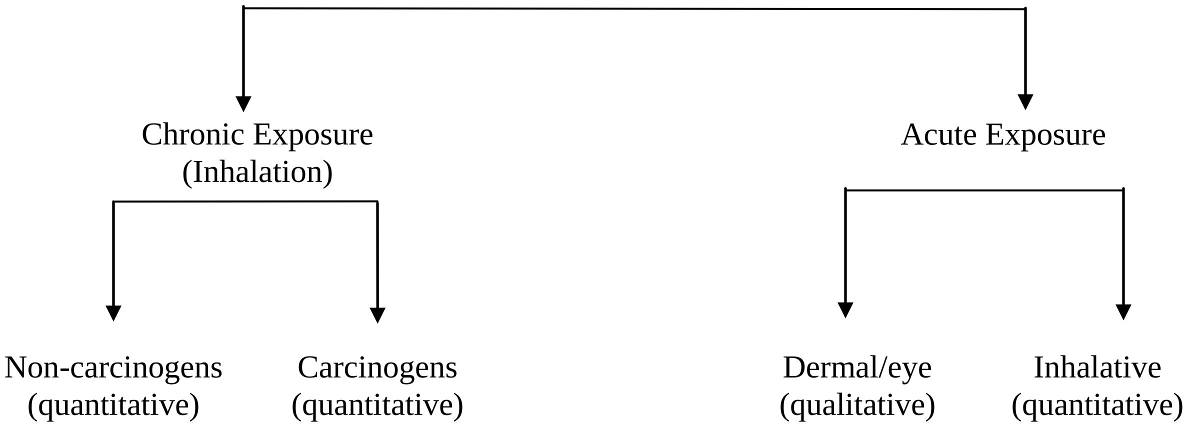

Figure 8. Principle of evaluation in the OHI method

9.4 Chronic Exposure Risk

Chronic exposure refers to continuous exposure. In contrast to the HQI, it is now possible to evaluate the inhalative risk of exposures not only to fluids but also to dusts. To make the results more transparent, the carcinogens are evaluated separately from the non-carcinogens. Also different benchmarks are often used for these compounds.

9.4.1 Calculation of chemical concentration

The overall approach for calculating the chemical concentrations in air is somewhat similar to that for the preliminary design stage. However, the fugitive emissions and air flow rates are now estimated more accurately. Precalculated process modules are not used. Neither is the estimated plot area. This is because the real piping and equipment details are available from the PIDs and they are considered in quantifying the fugitive emissions. The emission rates are therefore determined based on specific types of piping components instead of service type. Details are in Chapter 10. The emission factors for fluids and dusts are summarized in Tables 3 and 4 of Paper 5, respectively.

The air flow rate within the process is calculated based on the real process area, obtainable from plot plan. The local wind speed should be used upon the data availability (Paper 6). The concentration estimation is further discussed in Papers 4 and 5 and Chapter 11.

9.4.2 Non-carcinogens

A non-carcinogenic effect refers to any adverse response to a chemical that is not cancer. The exposure risk to non-carcinogens can be calculated for a single substance (HQI_{nc-i}) and a mixture of chemicals (HQI_{nc-mix}) based on Eqs. (4) and (5). Like in the HQI method, the chemicals in the mixture are assumed to have additive effects. An explanation about this subindex is provided in Paper 4.

9.4.3 Carcinogens

A carcinogen is a substance that is capable of causing cancer. Cancers are relatively slow to develop and usually require prolonged exposure to carcinogens. In the OHI, the carcinogenic risk is assessed separately from the non-carcinogens to get specific information about the cancer risk. This is required since the main objective of the OHI is not to compare and rank several processes, but to assess the selected process and improve it in a more detailed manner. Unlike the non-carcinogens, the exposure risk is calculated for individual carcinogen (HQI_{c-i}) rather than as a mixture (Paper 4) based on Eq. (4).

For chronic risk assessment, the occupational exposure limit (C_{EL}) in Eqs. (4) and (5) refers to the long-term reference limit value (8h) as explained in Chapter 8.3. The intake-based reference limit, known as a slope factor is available for many common carcinogens as reported by the EPA (IRIS, 1995). Upon the data availability, the carcinogen exposure risk may also be calculated based on the intake expression. This is elaborated in Paper 6 and Chapter 12.3.

9.5 Acute Exposure Risk

In assessing acute risk, potential hazards resulting from short time inhalative and dermal exposures are evaluated. Only exposures due to routine, normal process operations are considered as earlier.

9.5.1 Inhalative exposure

For calculating the inhalative exposure risk subindex, the concept of the hazard quotient is used again. The source of exposures is not fugitive emissions anymore, but periodic emissions with considerably larger release amount. Manual operations and sampling points are among the potential sources of acute exposures in chemical plants. The subindex can be calculated for a single substance ($HQI_{a\text{-}i}$) and chemicals mixture ($HQI_{a\text{-}mix}$) based on Eqs. (4) and (5). However here, instead of fugitive emissions-based concentration, chemical's equilibrium vapor concentration (C_{eq}) is used. Also the reference limit data required is for the short-term exposure.

C_{eq} can be calculated by adiabatically flashing the stream at atmospheric pressure. This corresponds to a situation where a pressurized liquid stream is discharged e.g. for emptying a system or sampling. In case liquid is below atmospheric boiling point, the equilibrium concentration in air can be calculated through the bubble point at process temperature. Alternatively as a simplification, the C_{eq} can be estimated based on the atmospheric vapor pressure of individual chemicals at 20 °C. The estimation of the C_{eq} is discussed in Paper 4.

9.5.2 Dermal/eye exposure

The adverse effects caused by skin exposure can occur locally within the skin or systemically (i.e. related to the whole body) due to absorption through the skin and distribution over body system (Cherrie & Robertson, 1995). Generally dermal/eye effects are local when exposure to hazardous agents is large and within a short period of time. This normally concerns liquids and solids. Systemic effects following continuous exposure (chronic) commonly involve vapours or gases. For airborne chemicals the most important systemic exposure route is the inhalation (van Hemmen & Brouwer, 1995). This has already been considered earlier by the inhalative exposure index.

In larger scale chemical processes, continuous skin contact to liquids and solids is not common because materials in the process are mainly well contained, the number of manual operations is small, and protective clothing is used. Potential rather than actual exposure is used here as the worst-case assumption.

Due to limited dermal/eye exposure data available, a qualitative risk evaluation approach is proposed using matrix system in Paper 4. First the frequency of exposure is determined from Table 5, then the exposure risk is obtained from Table 6.

Table 5. Probability and frequency of dermal/eye exposure (Paper 4)

Prob/freq of exposure	Descriptions	Example(s)
None	- No chance of dermal contact during normal job activities - No chance of accidental dermal contact (no manual handling of chemicals, chemicals are totally contained, no chance of failures/leakages, etc.)	- Online sampling - Sophisticated fully automated sampling system
Improbable/ Low contact	- No dermal exposure during typical job activities, but short periods of exposure on occasion after which all contact surfaces would be washed - Incidental/occasional dermal contact of a minor nature such as splashes - The frequency of dermal contact is low (rare) - Upon contact, the probability for exposure is low	- Closed sampling system but still there is a chance for leaking
Possible/ Daily contact	- Manual handling/contact with chemicals daily (routine activity) - The contact/exposure is expected - Upon contact, the probability for exposure is intermediate	- Samples are collected directly from valve/ line. There is a possibility of spillage, which consequently causing exposure to workers when they handle the sample - Contact with contaminated tool/surface
Probable/ Continuous contact	- Handling/contact with chemicals continuously (routine activity) - The contact/exposure is expected - Upon contact, the probability for exposure is high	- Scooping/weighing samples manually

Table 6. Risk matrix for dermal/eye exposure (Paper 4)

Probability/frequency of exposure	Low toxicity R21, 36, 38	Moderate toxicity R24, 34, 43, 48, 68	High toxicity R27, 35, 39, 41
Impossible/ Zero contact	No risk *No action*	No risk *No action*	No risk *No action*
Improbable/ Low contact	Negligible *No action*	Minor risk *Monitoring needed*	Moderate risk *Measure needed*
Possible/ Daily contact	Minor risk *Monitoring needed*	Moderate risk *Measure needed*	Serious risk *Measure necessary*
Probable/ Continuous contact	Moderate risk *Measure needed*	Serious risk *Measure necessary*	Intolerable risk *Immediate measure*

9.6 Interpretation of the Index Results

Since the results of the assessment are presented separately, different benchmarks are used to characterize the risk of each health aspect as summarized in Table 7. The background of the benchmarks is given in Paper 4 and further discussed in Paper 6. The benchmarks are not definitive, but are guidelines only.

Table 7. Benchmarks for interpreting the OHI assessment results (Paper 4)

Subindex	Exposure duration	Exposure source	Calculation approach	Application	Benchmark of acceptable risk
HQI_{nc} (noncarcinogen)	Long-term	Fugitive emissions	Hazard quotient	Individual chemical, Mixtures	< 1
HQI_{c} (carcinogen)	Long-term	Fugitive emissions	Hazard quotient	Individual chemical	< 0.1 (concentration) $< 10^{-4}$ (intake)
HQI_{a}	Short-term	Manual operations	Hazard quotient	Individual chemical, Mixtures	< 5 000
Dermal/eye risk	Short-term	Manual operations	Qualitative	Individual chemical	Qualitative risk level

9.7 Case Study

In Paper 4 the OHI method was demonstrated on a product distillation system of toluene hydrodealkylation (HDA) process. In the process, toluene is reacted with hydrogen to produce benzene (the desired product) and methane. Sketch of the process is given in Figure 1 of Paper 4.

For chronic exposure risk assessment, fugitive emissions were first estimated by analyzing the number of leak points from the column’s PID (Figure 2 in Paper 4). The total fugitive emissions estimate in each stream was then multiplied with the stream’s weight composition from the PFD to obtain the emission rate of each substance in the process. Plot area and height of the distillation system were determined from the layout plan before the chemical concentrations were finally calculated. The concentration-based risk estimation for a mixture of non-carcinogens as well as the carcinogen (benzene) reveals that based on Table 7, the exposure risk is acceptable (Table 8). The intake-based risk, which was also calculated for benzene, was found to be slightly exceeding the acceptable risk. The result is expected, since the intake risk-based benchmark (slope factors) is stricter than the concentration risk-based benchmark (exposure limits) as discussed in Paper 6.

As an improvement high rating valves and closed sampling points are chosen. By these measures the cancer risk can be reduced well below the benchmark (Table 6 in Paper 4).

The acute inhalative exposures from the manual sampling points also exceed the benchmark (Table 8). The sampling points are the major health problem of this process. Therefore healthier sampling systems e.g. using sample coolers and closed sampling systems are needed. The assessment results are summarized in Table 8. Also a more elaborate analysis of risks through hazard quotient (HQ) is possible as discussed in Paper 6 (Tables 1 and 2).

Table 8. Summary of results from occupational health assessment

Aspect	Subindex	Results	Benchmark	Conclusion	Action
Chronic exposure risk (noncarcinogen)	$HQI_{nc\text{-}mix}$	0.00034	< 1	Acceptable risk	-
Chronic exposure risk (carcinogen)	$HQI_{c\text{-}i}$ Risk	0.07 $5.3x10^{-4}$	< 0.1 $< 10^{-4}$	Acceptable risk Non acceptable risk	- High rating valves needed
Acute exposure risk (inhalation)	$HQI_{a\text{-}mix}$	212 000	< 5 000	Non acceptable risk	Closed sampling needed
Acute exposure risk (dermal)	Risk	Toluene:Low toxicity Benzene:Moderate toxicity	Qualitative risk level	Minor risk Moderate risk	Closed sampling needed

10. FUGITIVE EMISSIONS ESTIMATION METHODS

10.1 Fugitive Emissions

Fugitive emissions are leaks or releases that occur wherever there are discontinuities in the solid barrier that maintains containment. They may occur on process plants from diffuse continuous sources of piping equipment (fittings), from equipment which operates intermittently such as the relief valves, from the 'breathing' of storage tanks, and from the activities such as draining and sampling and the opening up of equipment during operations or for maintenance (Lees, 1996). They may also be generated from wastewater treatment system and procedures like bagging and screening (Lipton and Lynch, 1994). Earlier works in fugitive emissions were driven largely by concern on environmental pollution. However, the information is equally applicable to health evaluations. The scope of this study focuses on the emissions from inside battery limit area (ISBL) (i.e. process area) process equipment, since these are the primary source of fugitive emissions exposure to process workers at a plant. Besides, fugitive emissions from the other sources cannot be easily quantified before the basic engineering stage when the PFDs are the only process information available. The ISBL process area is also the main focus in comparing different alternative processes.

10.2 Estimation of Fugitive Emissions

There are four basic techniques available for quantifying fugitive emissions (Paper 5):

a) *Direct measurement* based on portable gas detectors. It is only applicable to existing processes.

b) *Mass balances* – Despite its straightforwardness, this technique is not accurate since fugitive emissions involve only a very small fraction of material losses. The method is suitable only for existing processes.

c) *Engineering calculation* which is based on detailed models on material losses estimation from equipment or facilities, is complicated and requires detailed inputs and usually involves software tools.

d) *Emission factor* - The U. S. Environmental Protection Agency (EPA) has devised approaches to estimate fugitive emissions from process equipment based on component leak factors (EPA, 1995): 1) Average Emission Factor Approach, 2) Screening Ranges Approach, 3) EPA Correlation Approach, and 4) Unit-Specific Correlation Approach.

For the early design stage, emission factor is the only feasible technique to estimate the fugitive emissions. Among the four approaches in it, the Average Emission Factor is the simplest option, which only requires limited process information; screening values are not needed like in the other three techniques (Hassim and Hurme, 2008a). This approach needs equipment and piping item count as well as average emission factors. Different emission factors are established to estimate the emission rates for each component type (valve, pump, etc.) in different services (gas/vapor, light liquid, or heavy liquid) (Tables 1 and 3 in Paper 5).

In a typical petrochemical plant, valves are the main leaking components, generally responsible for 60% of the total fugitive emissions (McLellan et al., 1997). Emission factors for piping and equipment are established as an ‘average’ value for the component type (e.g. typical pump) or as a value for a specific component type (e.g. pump with double mechanical seal). The former emission factors are used in the preliminary design stage method (since the specific types are not known), whereas the latter ones are used in the basic engineering stage method. The emission estimates based on the average emission factors are expected to be considerably larger than the actual emission estimated with specific emission factors.

10.3 Development of the Estimation Methods for Design Stages

In Paper 5 three methods for quantifying fugitive emissions have been developed for simple PFDs, detailed PFDs, and PIDs.

10.3.1 Simple PFDs

Simple PFDs imply to simplified process diagrams and process descriptions found in patents or literature such as encyclopedias. Quantifying fugitive emissions based only on this limited process data has not earlier been possible. Therefore, the fugitive emission evaluation method was developed based on the idea of precalculated process modules as presented in Papers 3 and 5. Precalculated modules refer to a set of fugitive emission rates data that has been precalculated for standard modules of chemical processes. The standard modules represent regular operations in chemical plants such as distillation, reactor, flash, absorption etc. systems (Appendix 1). The precalculated modules emission data (Table 9) was created by analyzing the number of potential leak sources in these operations. This component data was accomplished by studying typical piping and instrumentation diagrams (PIDs) of the process modules. The emission from each module stream is calculated in Table 9 for all possible types of service; gas/vapor, light liquid, and heavy liquid. The calculation made use of the average emission factors provided by the U. S. EPA for traditional component types (Table 1 of Paper 5). ‘Traditional component types’ refer to those that have conventionally been reported as sources of equipment leak fugitive emissions by the U. S. EPA, e.g. pump, valve, and flange.

The emissions estimation procedure is as follows (Paper 5): First, process flow sheet is divided into standard modules. Next, based on process descriptions, chemicals present in each module stream are identified before the stream’s service type can be determined. A liquid stream is classified under light liquid service if it mainly contains highly volatile chemicals (atmospheric vapor pressure of pure chemical > 0.3 kPa). Otherwise, it is a heavy liquid. The fugitive emissions from the module streams are determined by referring to the precalculated modules data provided in Table 9. The emission rates from all module streams are summed up to obtain the total fugitive emissions from a process.

However, since the research concerns with the risk assessment of health hazards, it is vital to know the emission rate of the individual chemicals in the process. Due to the lacking of detailed mass balance data in this stage, the calculation is done by determining the most toxic chemical (‘worst chemical’) to represent the stream emission rate. The ‘worst chemical’ is the major stream component with the lowest reference limit value (e.g. TLV). For the same ‘worst chemical’, the stream rates are totaled up throughout the process. The flow chart of calculation is presented in Figure 9.

Table 9. Fugitive emission rates for typical chemical process modules (Paper 5)

Process module (fugitive emission rate, kg/h)												
			Normal	Vacuum			Ion			Normal	Vacuum	Total
Stream	Service	Absorber	Stripper		Flash	LEX	Exch	CSTR	PFR	Distillation		Comp
Feed 1	G/V	0.024	0.117	0	0.057		0.052	0.102	0.059	0.044	0	0.454
	LL		0.098	0	0.053	0.048	0.044	0.082	0.127	0.036	0	
	HL		0.060	0	0.046	0.025	0.029	0.044	0.082	0.021	0	
Feed 2	G/V							0.110	0.063			
	LL	0.113				0.235		0.088	0.052			
	HL	0.063				0.125		0.046	0.029			
Outlet	G/V	0.109	0.002	0	0.021		0.123		0.163	0.025	0	
2/3	LL		0.464	0.225		0.055	0.100	0.560	0.271	0.405	0.239	
	HL		0.324	0.127		0.036	0.054	0.378	0.156	0.254	0.137	
	G&LL mix								0.498			
	G&HL mix								0.380			
Outlet	G/V											
3/4	LL	0.236	0.159	0	0.301	0.097				0.217	0.139	
	HL	0.134	0.094	0	0.165	0.059				0.137	0.082	

G:Gas; V:Vapor; LL:Light liquid; HL:Heavy liquid; LEX:Liquid-liquid extractor; Ion Exch:Ion exchanger; Comp:Compressor

10.3.2 Detailed PFDs

Detailed PFDs provide also data on mass and energy balances. The approach for estimating the fugitive emissions is similar to the method used for simple PFDs. However, the way the stream’s service type is determined is different. For a liquid stream under operating conditions, the pure chemical vapor pressure of components at 20 °C in the mixture is determined. The pure vapor pressure information is readily available, e.g. from Material Safety Data Sheets (MSDS). For the chemicals with vapor pressure above 0.3 kPa (at 20 °C), their weight compositions are summed up. If the total composition is ≥ 20 wt%, the stream is in a light liquid service; or else, it is a heavy liquid. The determination of the stream ‘worst chemical’ is now unnecessary. Instead, the stream emission rate is multiplied with the weight composition of the respective components in that particular stream. Weight compositions are used throughout the calculation since the

EPA emission factor data is weight-based. Similarly, the emissions of the same chemical substances throughout the process are totaled up. Step-by-step procedures of calculating the fugitive emissions from simple and detailed PFDs are presented in Figure 9.

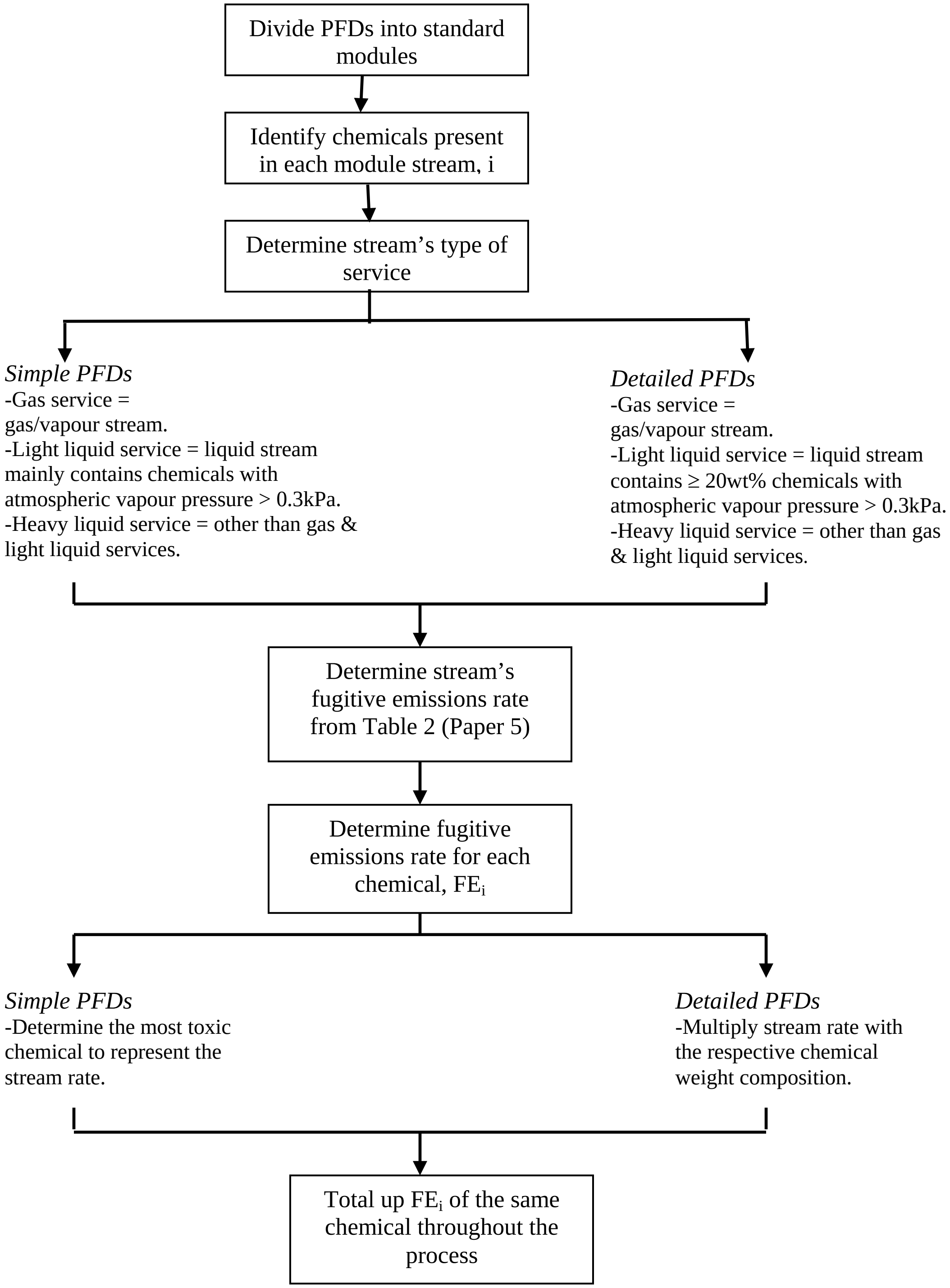

Figure 9. Flow chart of fugitive emissions calculation for simple and detailed PFDs (Paper 5)

10.3.3 PIDs

A more comprehensive assessment can be done when PIDs are available, since these offer piping and equipment details. The fugitive emission rates can be quantified more accurately as the real number and type of components are known from PIDs. Therefore more accurate emission factors can be used (e.g. pump shaft with single mechanical seal or exchanger head), which also contribute to a more accurate estimation. The database (Table 3 of Paper 5) was constructed by compiling data from various references (Schroy, 1979; Carson and Mumford, 1985; EPA, 1995; TCEQ, 2006). Some of the emission factors needed to be recalculated in order to ensure they are compatible with the method. Emission factors for processes handling solids are also provided (Carson and Mumford, 1985) (Table 4 of Paper 5). Likewise in detailed PFDs, the emission rate calculated for each process stream is corrected with the respective chemical weight composition. The flow chart of the method is shown as Figure 10.

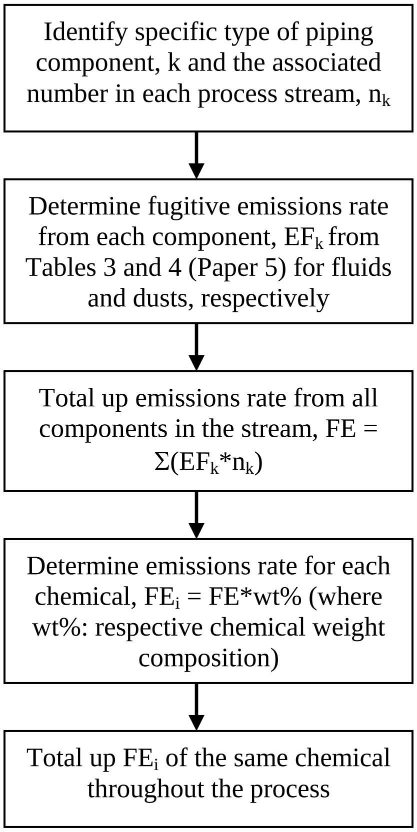

Figure 10. Flow chart of fugitive emissions calculation for PIDs (Paper 5)

11. CHEMICAL CONCENTRATIONS DUE TO FUGITIVE EMISSIONS

Chemical concentration is a necessary data required for calculating the health risk based on the HQI (preliminary design stage) and OHI (basic engineering stage) methods. During the process preliminary design, the concentration can be estimated using the information from simple and detailed PFDs. In the basic engineering stage, PIDs are required as discussed in Paper 5.

Before the principle of concentration calculation is discussed, the estimation of air flow rate needs to be first explained in detail for PFDs and PIDs.

11.1 Air Flow Rate Estimation for PFDs

For simple and detailed PFDs, the air flow rate is estimated based on the typical average floor area of standard process modules and their average height, as well as the average wind speed. The floor areas of standard modules were approximated from a petrochemical plot plans (see Table 5 of Paper 5). The estimation procedure assumes square shape of plot plan. First the floor areas of all modules (A_i) in the process are summed up, $A_f = \Sigma A_i$. Then the width of the square plot is calculated, $d = (A_f)^{1/2}$. Subsequently wind cross-section area (A_n) is determined by assuming the height (h) of majority of piping components in petrochemical plants is below 7 meters (Mecklenburgh, 1985), $A_n = 7d$. Finally air volumetric flow rate is calculated by multiplying the process vertical area with the wind speed, $\dot{V} = vA_n$. The real average wind speed is used for the location. If not available, the typical wind speed for outdoor facility is 4 m/s (Clement Associates, 1982; Baldwin and Maynard, 1998; CCPS, 2000). Figure 11 presents the flow chart of the estimation steps for these design stages.

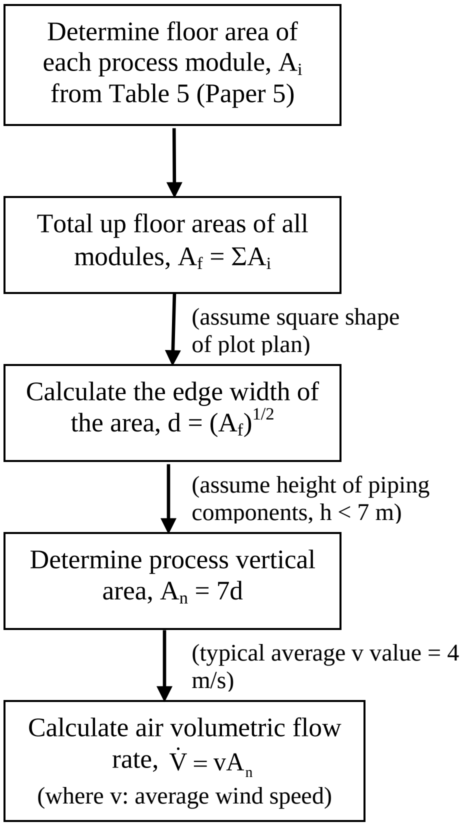

Figure 11. Flow chart of air volumetric flow rate calculation for simple and detailed PFDs (Paper 5)

11.2 Air Flow Rate Estimation for PIDs

A plot plan is readily available at the same time when a PID is produced. This document is showing the location of the equipment in the plant. Based on the actual process area measured from the plot plan, the air flow rate estimate is expected to become more accurate compared to the standard module areas approach. Since the process design phase is now almost reaching to the end, the location of the plant is known to the designers and the average wind distribution data within the location of interest can be obtained. The flow chart of the estimation method is presented as Figure 12.

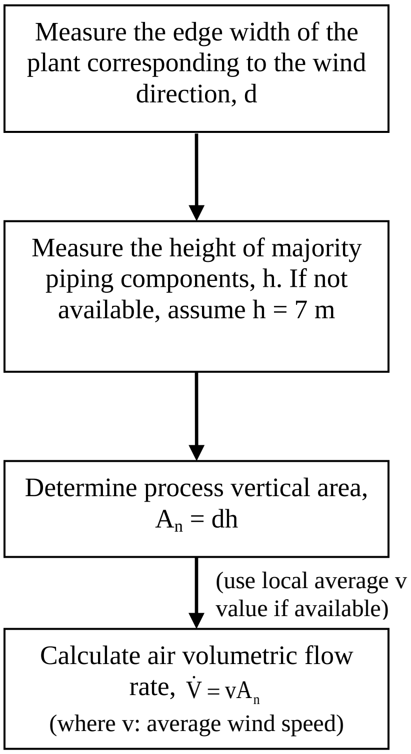

Figure 12. Flow chart of air volumetric flow rate calculation for PIDs (Paper 5)

11.3 Chemical Concentrations Estimation

The concentration of chemical in air (C) can be calculated as follows:

$$C = \frac{m}{vA_n} \tag{6}$$

where m is fugitive emission rate; v is wind speed; A_n is the cross-section area of process downwind.

The estimation basically utilizes data on fugitive emissions rate, m (the numerator in Eq. 6) and air flow rate (the denominator in Eq. 6). The first data is discussed in Chapter 10 and the second data in Chapters 11.1 and 11.2. The calculation assumes full mixing condition and the concentration is estimated at the downwind edge of the plot area.

The concentrations estimation approach discussed above is for outdoor petrochemical plants, which is the scope of the thesis. For enclosed facilities, the concentrations can be calculated using ventilation rate that depends on air change rate and volume of the space. Ventilation rates for indoor facilities are widely published (e.g. Lipton and Lynch, 1994, Jayjock, 1997), thus making the estimation easier.

11.4 Case Study

The concentration estimation approaches developed in this work have been applied on a real benzene manufacturing process (Borealis Polymers Oy in Porvoo, Finland). The benzene production process can be divided into four main stages: pre-distillation of pyrolysis gasoline; second-stage hydrogenation of pyrolysis gasoline; extractive distillation; and benzene purification. A schematic diagram of the Porvoo benzene plant is presented in Figure 8 in Paper 5.

The concentration of benzene in the plant is estimated based on simple PFD, detailed PFD, and PID of the process. Benzene is the substance of interest in the assessment because it is a carcinogen and monitored at the plant. The benzene concentration estimates are compared to the actual concentration value measured at the plant. There are nine measurement points installed throughout the plant (Figure 11 in Paper 5). To compare with measured values, a representative downwind sampling point is selected to represent the emissions from the whole plant.

The fugitive emissions, air volumetric flow rate estimates, and calculated benzene concentrations are presented in Table 10 for the three methods. It is noticed that the estimated plot widths in PFD stages differ from the real plot width (84 m). This is because the real plots are not always square as assumed in the estimation. Also the area is underestimated by the early stage's method. Therefore the concentrations for PFD stages were recalculated based on the real process area as used for the PID (the right most column in Table 10). The trend in the concentration estimation results in Table 10 is that the earlier stage estimates are larger than the PID stage estimate, which is closer to the measured one. When the same plot size is used, the differences in the results are because of the usage of different emission factors in the first stages.

Also local concentrations in the ISBL area were estimated and compared with measured values as shown in Figure 12 in Paper 5. It can be seen that the estimated local values are reasonably close to the actual concentrations except for larger concentrations at the three lower wind velocities ($v < 1$ m/s). This is because the estimation model assumes full mixing of emissions, which is an invalid assumption with low wind velocities. More details on the estimation of the benzene concentration and its comparison with the actual measured values are discussed by Pérez (2008).

In another paper the methods were tested on the C2/PA route first subprocess (Hassim and Hurme, 2008a). The results show a similar pattern with those in Table 10 - the concentration estimates appear to be smaller with later stage methods when more data is available (simple PFD > detailed PFD > PID).

Table 10. Benzene concentration estimation at different design stages

	Fugitive emission rate (kg/h)	Plot width (m)	Air volumetric flow rate (m^3/s)	Concentration (estimated area) (ppm-wt)	Concentration (width = 84 m) (ppm-wt)
Simple PFDs	3.3	33*	930	0.31	0.12
Detailed PFDs	2.3	37*	1026	0.19	0.08
PIDs	1.2	84	2352	0.045	0.045
Measured		84		0.040	0.040

*) Estimated

12. OCCUPATIONAL CHEMICAL EXPOSURE AND RISK ESTIMATION

In reality, worker exposures to chemicals in outdoor facilities are not constant throughout the time. The exposures are expected to be higher when the winds are milder, due to poorer dilution. By using wind velocity statistics at the plant location, health risks of occupational exposure can be estimated more realistically as probability distributions (Paper 6). In addition to the usual process route health characteristics, such as fugitive emissions rate, concentration, and risk of exposure, the method also produces data on the critical wind speed. This new concept defined in Paper 6 refers to the minimum velocity of air necessary to maintain the level of chemicals in exposure limits in local wind conditions. The critical wind speed may already provide an idea about the relative exposure levels of the process concepts studied. The higher the calculated critical value, the higher the wind speed required to keep the chemicals below reference exposure limits, thus implying the greater relative exposure risk. Details of the approach are found in Paper 6.

12.1 Wind Distribution Prediction

The wind is never constant. It is influenced by diverse factors, such as the weather system, local terrain, and height from surface. Weibull distribution is the best density function that can be used to describe the wind speed frequency curve (Patel, 1999). Generally, the Weibull cumulative distribution function can be described as:

$$F = 1 - e^{-\left(\frac{v}{\alpha}\right)^{\beta}} \tag{7}$$

where α is the scale parameter (unit of speed); β is the shape parameter (dimensionless); v is wind speed (Patel, 1999).

The wind speed can be corrected to the height of interest since wind speed near to the ground changes with height. From the context of occupational exposure, the wind speeds of concern are those at the workers' breathing zone level. At heights closer to the ground, the wind speeds are lower, resulting in higher chemical concentrations. The most common expression to correct wind speed with height is the power law as presented in Eq. (10) (Patel, 1999):

$$v = v_0 \left(\frac{z}{z_0} \right)^{\gamma} \qquad (8)$$

where v is wind speed estimated at desired height, z; v_0 is wind speed measured at the reference height, z_0; γ is the ground surface friction coefficient (Patel, 1999).

12.2 Concentration-Based Exposure Risk Assessment

Paper 6 discusses the approaches of estimating the exposure risk to chemicals, which are either based on the concentration or the intake. Basically, the concentration-based risk assessment is easier and it is more applicable to various chemicals since the reference limit values are widely available for a long list of chemicals (e.g. HTP Values, 2007). The benchmark of acceptable risk value for this approach is as already discussed in Table 7 in Chapter 9.6. More elaborate HQ benchmark systems are presented in Paper 6; e.g. a method employing R clauses for determining the HQ benchmark (Table 2 of Paper 6).

12.3 Intake-Based Exposure Risk Assessment

The intake-based assessment is more limited than the HQ-based as it requires slope factors, which are available mainly for carcinogens. However the risk estimation is more realistic. It also provides a more indicative result of the risk value as opposed to the result obtained from the concentration-based approach. The quantitative risk can be calculated as follows (Paper 6):

$$\text{Risk} = \text{CDI x slope factor} \qquad (9)$$

where CDI is chronic daily intake (mg/kg-day).

The common value of acceptable risk level or the benchmark for occupational environment is one cancer case per a ten thousand people per 45-year worktime (Chan et al., 2006). Wherever possible the intake-based approach should be used, especially for the carcinogens.

12.4 Case Study

In Paper 6 the six MMA manufacturing processes were used as a case study to demonstrate the method. For more realistic exposure estimation, wind distribution data in a seaside location in Finland for year 2007 was used (Figure 13). Chemical exposure risks were calculated using both the concentration and intake-based approaches.

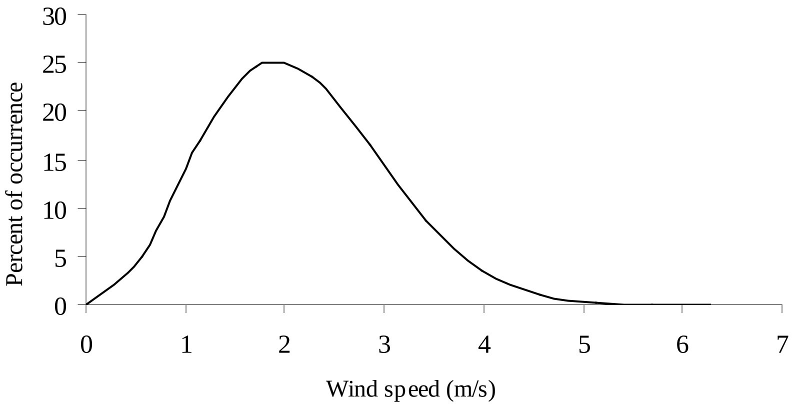

Figure 13. Annual wind probability distribution at 1.5 m height in the case study (Paper 6)

In Paper 6 for the *concentration-based approach*, hazard quotient index for chemicals mixture (HQ_{mix}) was calculated for the MMA routes for different wind velocities. The results are presented in Figure 14(a). The HQ_{mix} value is much larger at lower wind speeds and it decreases gradually as the speed is getting higher due to better dilution. The corresponding figure based on the yearly cumulative wind speed probability (Figure 2 in Paper 6) at a working level is presented as Figure 14(b). The HQ_{mix} curves show that the C3 route is the most harmful process to health, followed by the C2/PA and ACH. The i-C4, TBA, and C2/MP routes are clearly healthier. The same trend is shown by the critical wind speed (HQ ≤ 1) analysis presented in Table 5 of Paper 6. The C3 exhibits significant exposure risk (HQ > 1) for around 623 hours in a year (7.1% of time) whereas the best process C2/MP has only 2 h/a (0.02% of time) chemicals concentration above the threshold limit value at this plant location.

The *intake-based approach* was applied on the C2/PA route. It is the only route containing a carcinogenic substance (formaldehyde). Figure 5(a) of Paper 6 shows the cumulative probability of getting cancer from the exposure to formaldehyde in the same plant location as for the concentration-based assessment. The carcinogenic risk of formaldehyde exposure exceeds the benchmark of one cancer case in ten thousand persons in 45-year worktime for 98.7% of the year. The HQ < 0.1 benchmark is exceeded 87% of time. Therefore the intake-based benchmark is stricter. These two benchmarks are compared in Paper 6 Table 6. The risk benchmark for the 0.1HQ concentration is 1.3-25 times larger than the 10^{-4} benchmark depending on the carcinogen. The ratios vary since the occupational exposure limits are often based on different criteria than the slope factors as discussed in Paper 6.

The presented methods employing wind distributions and risk benchmarks allow foreseeing the potential exposure risk of competing processes already in the process route selection stage for a chosen plant location. This allows early actions on route selection or the choice of dedicated technology to reduce exposure risks.

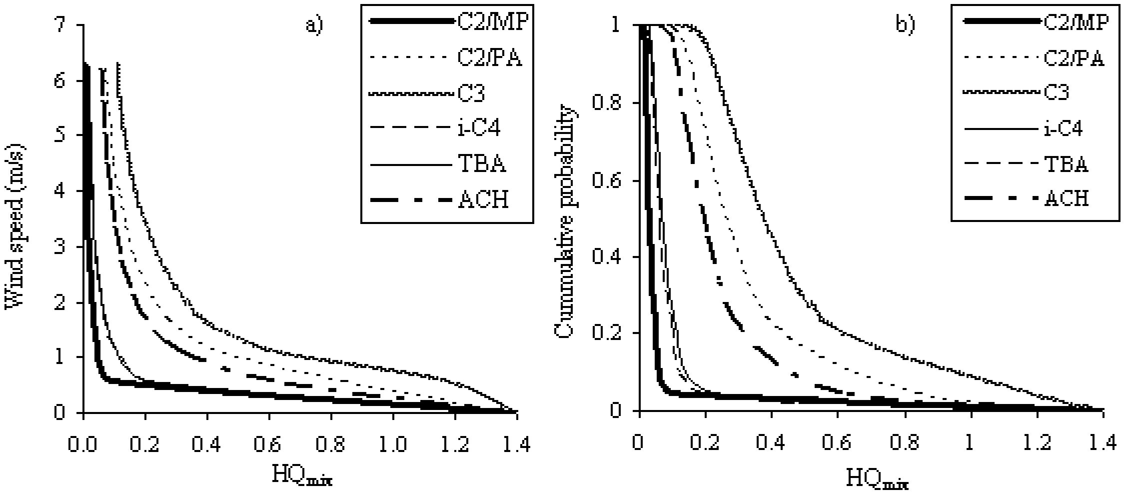

Figure 14. The Health Index of chemical mixtures for MMA processes based on: (a) wind speed (b) wind speed probability over year (Paper 6)

13. ADAPTATION TO COMPUTER SYSTEM

Paper 7 presents the principle of integrating the IOHI, HQI, and OHI methods with the existing computer aided design tools. Such integration is obviously needed as most of design works are currently done by using CAPE tools such as flowsheeting programs, and later 3D design tools.

One principle of the integration is to interface these tools with a spreadsheet tool, in which hazard and risk can be calculated using the HQI or OHI methods. For the IOHI (R&D stage), simulation results are not yet available, hence only other data sources such as safety property database and user input are used. In process flowsheeting stage it is also possible to integrate the safety properties database and the standard emission module database directly to the flowsheeting program. The data integration principle and data flows are presented in Figure 15.

The data requirements and the integration needs of each method are somewhat different, since they are intended for different process design stages. The required data (and sources) can be classified into five major types of:

a) Health and safety data; MSDS health database.
b) Fugitive emission related data; standard module database, emission factors database.
c) Process data; simulation, user input.
d) Physical property data; MSDS database, flow sheets databank.
e) Diagram data; block, flow sheet, PI, layout diagrams.

The sources of the data are summarized in Table 11. The configuration of the computer system for all the three methods is presented in Figure 15.

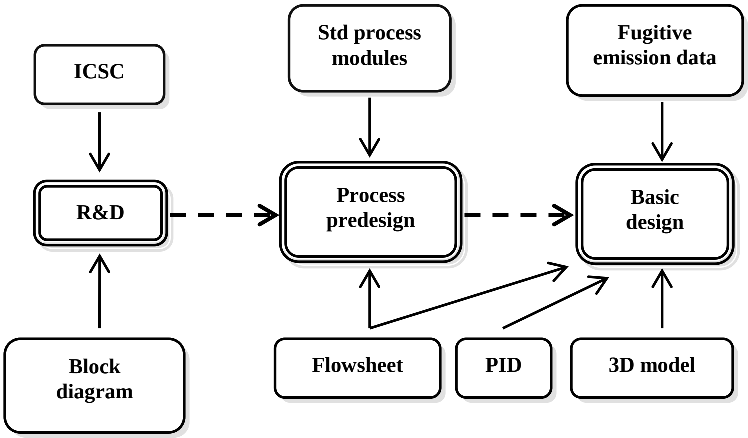

Figure 15. Configuration of the computer system for the three evaluation methods (Paper 7)

Table 11. Data sources for the occupational health assessment

Stage	R&D	Process predesign	Basic engineering
Index	IOHI	HQI	OHI
Process data	Temperature[a] Pressure[a] Phase[a,b]	Phase[d] Composition[d]	Phase[d] Composition[d]
Physical property data	Boiling point (atm) [b,c] Corrosivity[a,b]	Vapor pressure 20°C[b]	Vapor pressure 20°C[b]
Health data	OEL 8-h[b] R-phrase[b]	HTP 8-h[b]	HTP 8-h[b] R phrase[b] HTP 15-min[b]
Fugitive emission data		Standard module emission rates[e]	Emission factors[f]
Diagram data		Modules present[d,g]	Leak source items[g] Plot plan area[g] Manual operations[a]

[a]User input; [b]Safety sheet (database); [c]Flowsheeting program databank; [d]Flow sheet simulator; [e]Standard emission module database; [f]Emission factor database; [g]Diagrams

14. CORRELATION BETWEEN SHE CRITERIA

In literature several index-based methods have been presented for safety, health, and environmental aspects as discussed in Chapters 2 and 5. The methods are much based on the same parameters (Table 1 of Paper 8). It would be interesting to know if any interdependency exists between the methods. Therefore a correlation analysis was done in Paper 8 on the methods. High correlation would mean that the inherent SHE properties are dependent on each other. In this case it might be possible to create a universal index for all the SHE properties.

14.1 Methodology

Twelve inherent assessment approaches were chosen for the study; three or four from each SHE aspect. The selected methods and the ground for their selection are described in Paper 8. The methods are characterized by three major criteria of: a) type of index calculation – additive vs. average, b) operating scenario – catastrophic event vs. normal operation, and c) time scale – short-term vs. long-term. The characteristics of the methods are shown in Table 2 of Paper 8.

14.2 Case Study

The evaluation was done by using the six process routes for MMA in Paper 8. The correlation between the SHE assessment methods was determined by performing pair-wise linear regression between MMA process route index values. Linear regression was considered appropriate, since the index-based methods are mathematically linear. The correlation between the methods compared is indicated by the R^2 value, which is the coefficient of determination. The R^2 describes, which amount of the dependency of the variable is explained by the other variable.

Each method was paired with other method and the resulting R^2 values of pairs were determined (Table 3 in Paper 8).

Correlation of health indices

Table 12 presents the correlation of MMA route health index values in normal font (from Paper 8) and in italic (from Paper 3). FE is the fugitive emissions rate. Interestingly the results differ especially for the HQI and IOHI correlation. The best correlation (R^2 = 0.85) is between HQI and IOHI methods in Paper 3. In Paper 3, the index values for IOHI and HQI were based on the three main ACH subprocesses only, whereas in Paper 8 the values were based on six ACH subprocesses. All the methods in Table 12 are based on additive type calculation except for the HQI, which is based on average toxicity risk approach. Therefore the difference in correlation results reflects the additivity problem discussed earlier in Chapter 7.4 and Paper 2. When the additivity aspect was diminished by considering only the three main process steps in Paper 3 ACH case, the similarity of the indices became more evident. However correlation with PRHI is not affected much since the index calculation approach was different from IOHI. The nature of the PRHI index is less additive than the IOHI.

Table 12. Correlation of MMA route index values of different health methods (R^2 value) (Papers 3, 8)

Index	PRHI	IOHI	HQI	FE
PRHI	-	0.66 *0.51*	0.72 *0.77*	0.15
IOHI			0.24 *0.85*	0.18
HQI				0.36

(normal fonts are from Paper 8; italics are from Paper 3)

Correlation between SHE criteria

The average correlation between SHE indices was calculated in Paper 8 to find out if inherent SHE characteristics are interdependent. The result is that the safety & health and safety & environmental criteria have stronger correlation than health & environment (Table 13).

Table 13. Average correlation between SHE criteria (Paper 8)

Criterion 1	Criterion 2	Average R^2
Safety	Health	0.78
Safety	Environment	0.78
Health	Environment	0.55

The universal index

Finally, the possibility of a universal index, that is a single index capable of evaluating all the SHE aspects, was studied by using either IOHI, ISI, or IETH index to substitute the other two. The outcome of the analysis is that the IOHI or ISI method alone can estimate all the SHE properties at least in the MMA case study for route selection with about 95% correlation (Table 14). One should remember however that the health aspects do not in this case include the fugitive-based inhalative exposures directly.

Table 14. Correlations if only one index is used for all criteria in MMA routes evaluation (Paper 8)

Index 1	Instead of:	Average R^2
IOHI	ISI and IETH	0.95
ISI	IOHI and IETH	0.94
IETH	ISI and IOHI	0.92

15. OVERALL APPROACH FOR HEALTH EVALUATION IN PROCESS DEVELOPMENT AND DESIGN

As a summary, an overall approach for occupational health evaluation in chemical process development and design is presented in Figure 16. The IOHI method acts as the first layer to select the chemical process route with the lowest health hazard potential. The selected route can then be analyzed to identify the harmful steps. Inherent safety keywords are applied to reduce the hazard level as low as reasonably practicable (ALARP). The new IOHI value can be calculated after the modification is made.

The route is then further developed into process flow sheet diagrams (PFDs). The inhalative risk of chronic exposure can be calculated based on fugitive emissions, dilution, and exposure limits data. Likewise in the IOHI method, inherent safety keywords are applied on the risky streams (HQI > 1 or more elaborate criteria in Paper 6) to reduce the risk.

After the PIDs of the process are created, the OHI is used to evaluate more aspects of health risks. Inhalative chronic exposure risk is calculated similarly as in the HQI but in more detail. Manual operations or periodic emissions sources can be analyzed from the PIDs. Acute inhalative and dermal exposure risks can be estimated using the OHI. From the calculation, hazardous stream or operation can be easily identified. Design modifications can be applied based on inherent safety keywords to reduce the risk as low as possible.

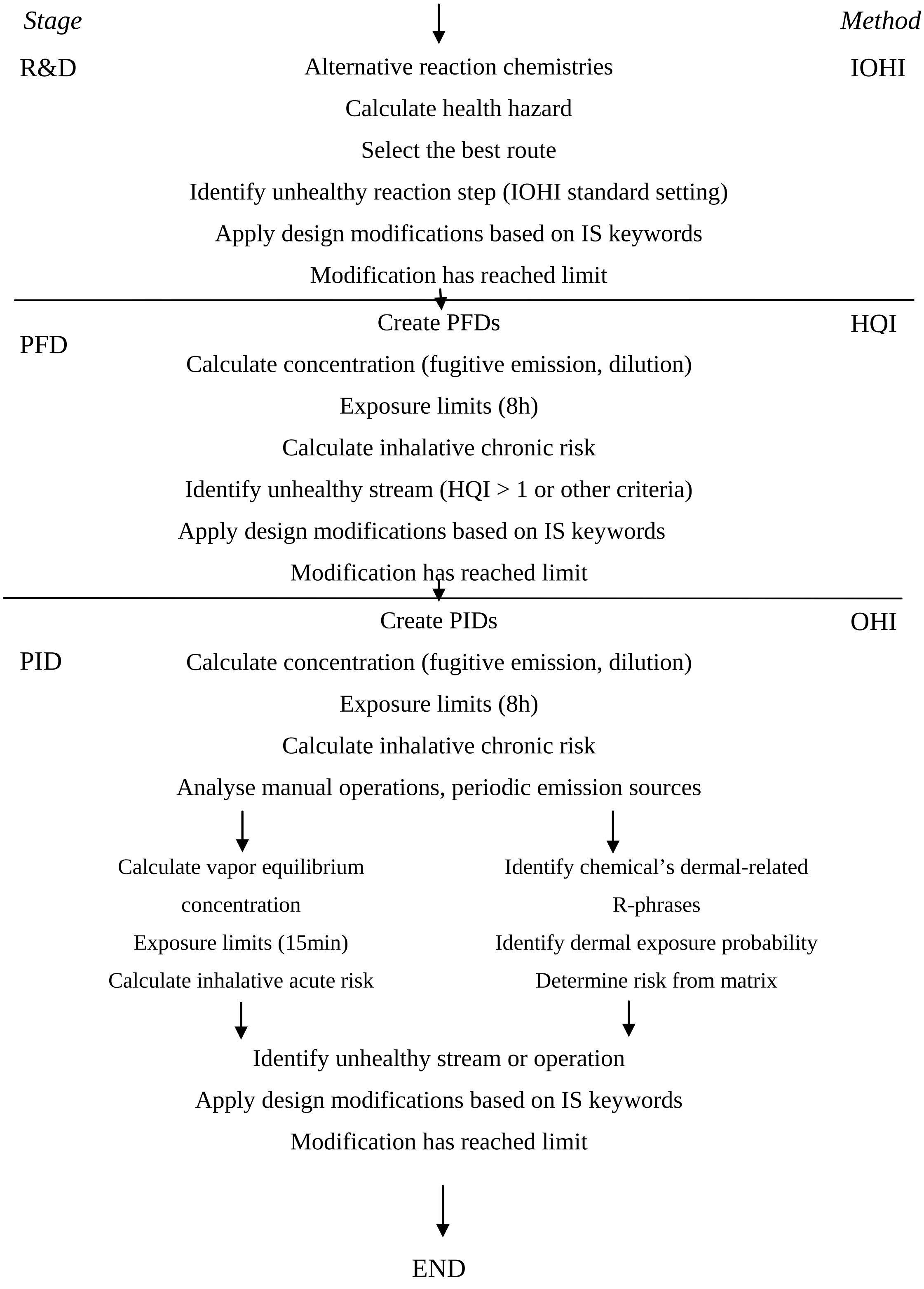

Figure 16. An approach for occupational health evaluation

16. CONCLUSIONS

Occupational health is an important part of sustainability together with process safety and environmental issues. Each year, more people die from work-related diseases than are killed in industrial accidents. Therefore health characteristics of processes should always be evaluated preferably as early as possible, starting from the inherent level. Basic decisions made during the design phase have a major effect on the later performance of the process.

This study introduces a new concept; inherent occupational health. Inherent occupational health is a prevention of occupational health hazards by trying to eliminate the use of hazardous chemicals, process conditions, and operating procedures that may cause occupational hazards to the employees.

Methods capable of assessing occupational health hazards of chemical process concepts are highly required but lacking. Therefore the aim of this research has been to create methods tailored to the first process lifecycle stages. Three occupational health assessment methods have been developed for the research and development, preliminary design, and basic engineering.

For the process R&D stage, the Inherent Occupational Health Index (IOHI) was developed as a qualitative hazard ranking method based on material properties and reaction conditions data only. The Hazard Quotient Index (HQI) is proposed for the preliminary design stage; HQI focuses on chronic inhalative exposure risk from fugitive emissions based on the data from process flow diagrams. For the basic engineering stage the Occupational Health Index (OHI) covers additional health risk factors such as acute inhalative and dermal exposures due to manual operations based on data from the PIDs. Basic engineering is the last step where conceptual changes can still be made at moderate costs. The fundamental idea is to introduce methods that are based on the available data in each design stage. Therefore the R&D stage method is reaction step oriented, the PFD stage method is process module oriented, and the PID method deals with the piping and equipment level. As the project progresses from research and development to basic engineering stages, more comprehensive assessments are therefore feasible, hence leading to more detailed results.

The IOHI method is based on exposure inherent characteristic (such as physical properties of chemicals and operating conditions of process) and harm related aspects (exposure limits and R-phrases). The HQI and OHI methods are mainly based on fugitive emissions estimates of the process. In the PFDs stages, the emissions are estimated by precalculated process modules. When material balance is available in the detailed PFD stage the composition data is utilized to give a more accurate estimate. In the PIDs stage, fugitive emissions are quantified based on the real number and type of piping and equipment components.

Chemical concentrations due to the emissions are calculated based on the typical plant cross-section area and wind velocity. The cross-section area is based on the plot area, which is a floor area of standard process modules or an actual process area from plot plan for the PIDs. Also wind speed data, either real value in the location or average value, is required.

The concentration estimation approach was applied on an existing benzene plant. The estimated benzene concentration became closer to the actual measured value as the methods progressed from simple PFDs to PIDs stage (accuracy: PIDs > detailed PFDs > simple PFDs). The results were very satisfying for the PIDs stage (0.045 estimated vs. 0.04 measured ppm). The estimates from the PFDs were farther from the actual due to the underestimated areas of standard process modules and the use of average emission factors.

Using real wind distribution data allows a realistic comparison of process concepts at the real plant location and an estimation of e.g. the cancer risk quantitatively. Different risk evaluation methods and benchmarks were also studied and compared. It turned out that the exposure level related risk (concentration-based) evaluations are more applicable. For carcinogens, it is also possible to use quantitative evaluations. For them the quantitative risk benchmark (10^{-4}) was found to be stricter than the 0.1HQ benchmark. A new term, critical wind speed, was introduced to characterize the wind speed required to keep the concentration of chemicals in air below the exposure limits. Also local benzene concentrations could be estimated on an existing plant with relatively good accuracy as long as the wind velocity was large enough to allow a proper mixing.

The IOHI, HQI, and OHI methods have also been studied for integration with the existing computer aided design tools. This is attractive since CAPE tools are commonly used in design. The integration can be done through a spreadsheet tool or in the PFD level by incorporating the index calculation into a flowsheeting program. New databases are needed; health property database and fugitive emissions database (for standard modules and PID components). The integration is quite straightforward except in the PID stage where more elaborate CAPE tool integration is needed.

The correlation between different stage indices was studied. It was found out that the HQI correlates well with IOHI ($R^2 = 0.85$) even though they are designed for different stages. The correlation however depends much on how the additive aspect of indices is considered.

Also a correlation between SHE criteria was analyzed to find out, if any interdependency exists between SHE characteristics at inherent level. It was found out that safety & health and safety & environmental criteria were correlated more than health & environmental criteria. Since the SHE index methods are very much based on the same parameters, a feasibility for a universal index, which is capable of evaluating all the SHE properties, was studied. It was found out that the health index IOHI can substitute the safety and environmental indices (ISI and IETH) with 95% correlation. Also ISI can substitute the others well. It has to be kept in mind however that IOHI is only a partial expression of health since it does not include fugitive emissions directly.

Finally an overall approach for health evaluation in process development and design was proposed. It includes the three indices for the R&D, PFD, and PID stage evaluation. The presented approaches allow an early analysis of process routes, concepts, and designs. Potential hazards can be foreseen in each design stage so that proactive, rather than retrospective actions can be taken. This will potentially reduce both costs and health risks, since the health related selections can be done early when there are more degrees of freedom left. This will decrease the need for expensive later modifications and excessive investments on add-on protective systems. The health level is enhanced on an inherent level by reducing the health hazard potential itself. By doing so, protection load is transferred from the protective layers into the inherent process related selections.

By using the methods proposed, the legal requirements of choosing the safest chemicals and process concepts can be brought into a more systematic practice in process R&D and design.

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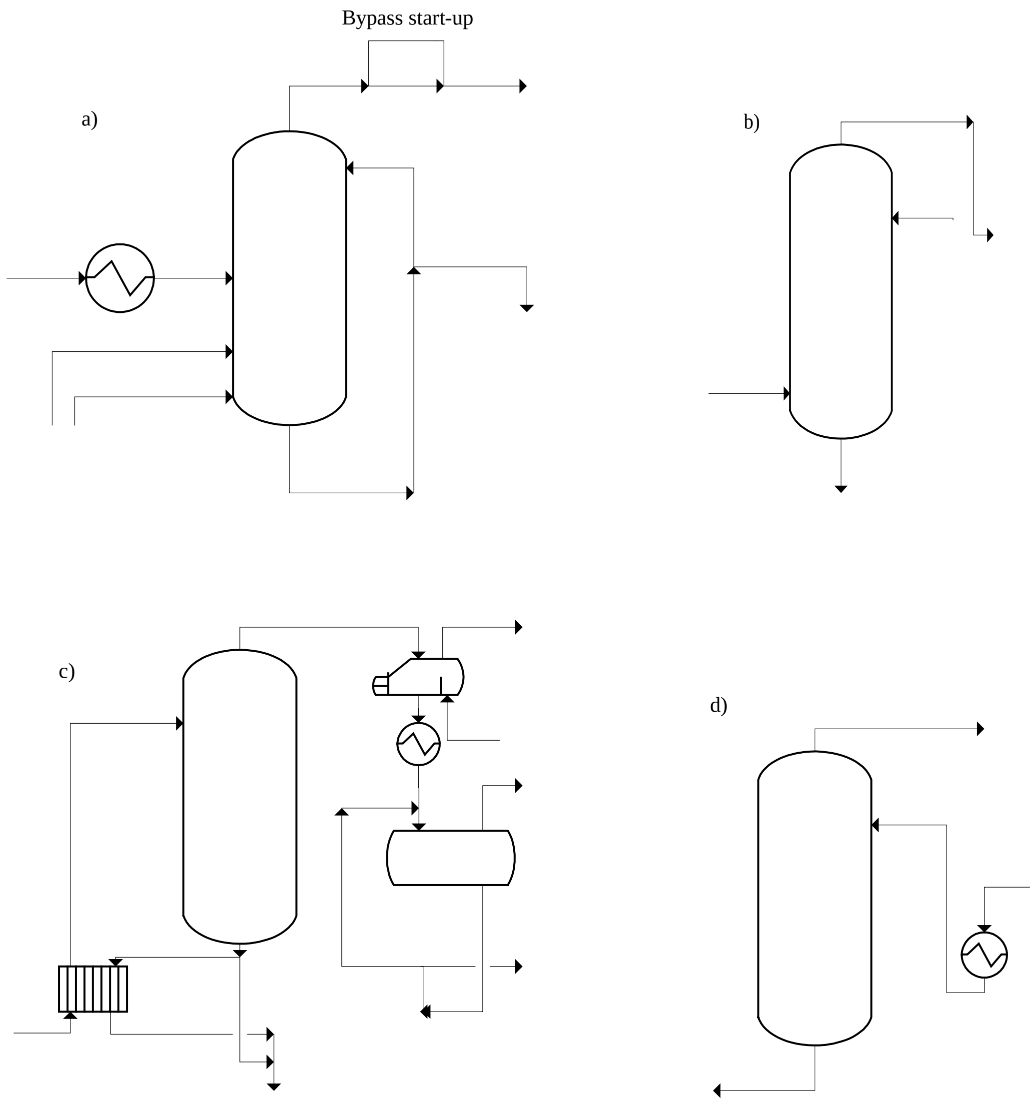
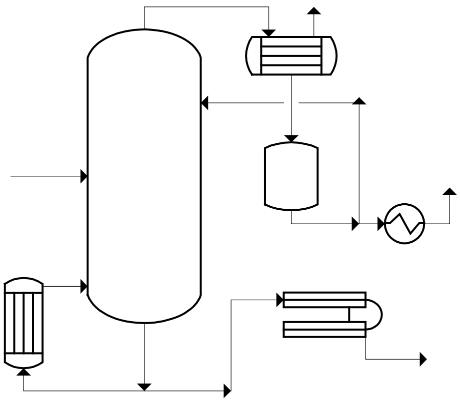
APPENDIX 1:

Process streams considered in fugitive emissions quantification for a) absorber; b) liquid-liquid extractor; c) stripper; d) flash; e) distillation; f) ion exchanger; g) tubular reactor; h) stirred tank reactor; i) compressor.



e)



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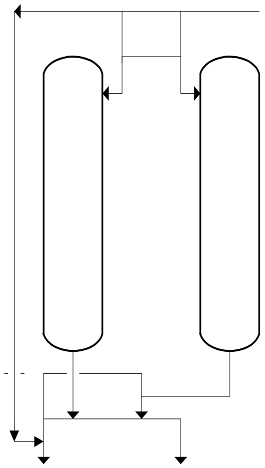

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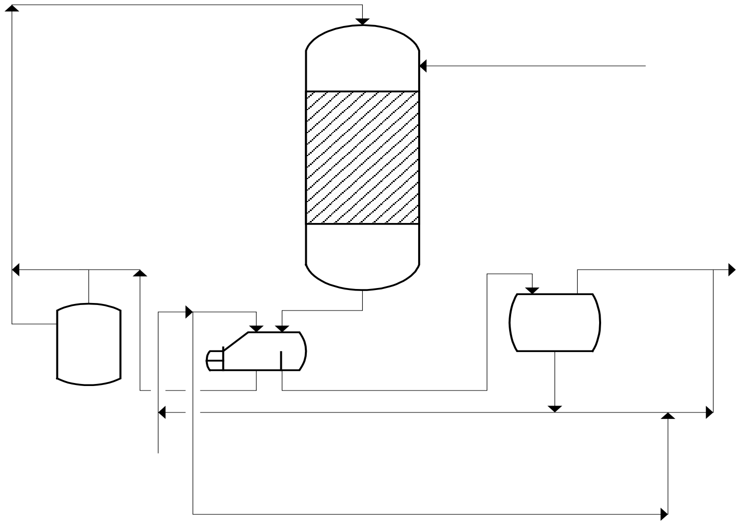

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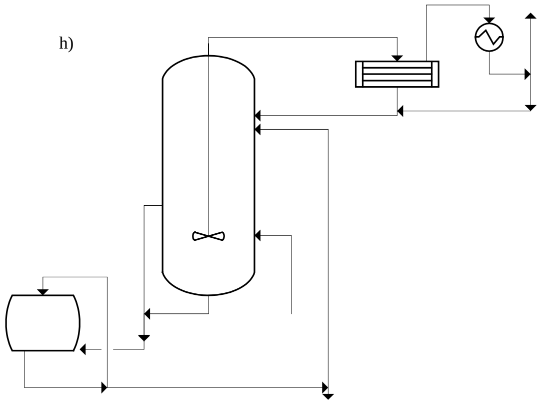

i)