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Inherent occupational health assessment during preliminary design stage

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ABSTRACT

Chemical process routes can already be assessed as early as in the development and design phases. Process screening should not look at economic and technical aspects only, but also the safety, health, and environmental performances. In this paper, a method called the Health Quotient Index (HQI) is presented for the preliminary process design phase. The HQI provides a simple approach to quantify workers' health risk from exposure to fugitive emissions e.g. in petrochemical plants. The method utilizes process data from flow sheet diagram, which is already available at the preliminary design stage. Since the mechanical details of the process are still unknown, a database of the precalculated fugitive emissions for typical operations in chemical plants was created to simplify the assessment. The HQI can be used to rank alternative process concepts or to quantify the risk level of processes. As a case study, six process routes for producing methyl methacrylate are discussed. Three health indexes are compared in the case study. The HQI is able to highlight the difference of hazard levels between the routes better as a result of more detailed assessment of the exposures.

1. Introduction

Growing concern among the public and the workforce about the issue of chemical exposures seems to be the trend. Estimation of workers' health risk in petrochemical plants due to chemical exposure is complex, since many chemicals may be involved and each may have multiple toxic effects. Although research on occupational health and development of related tools are progressing well, the adoption and application are relatively slow. The reason is, majority of the methods are too elaborate, making them unattractive to industries, which prefer a simpler and faster method (Gupta & Edwards, 2002). Nevertheless, occupational exposure to hazardous chemicals has shown considerable decrement during the past few decades due to greater risk perception (Ahlberg, 1999).

There is also a demand to make risk assessment exercise even more transparent and intelligible (Ahlberg, 1999). To achieve simple but thorough assessment, different methods are needed for different points of the lifecycle since the amount of information available varies. An assessment method claiming to be applicable during the whole rather than at a specific point of the process neither has a fixed balance region nor a fixed viewpoint (Koller, 2000). Even though process improvement can be done at any process design and operation, the opportunities and the costs are more attractive at development and design stages, especially for incorporating inherent safety features.

The concept of inherent safety points out that hazards should be avoided rather than controlled (Kletz, 1984). Inherent occupational health can be achieved by reducing the quantity of harmful chemicals and the number of unhygienic operations in the plant, which can be done especially during process concept development. Early assessment may help to reduce the risk and improve health quality of a process.

The aim of the research has been to develop a series of inherent occupational health hazards assessment methods for the research and development (R&D) (Hassim & Hurme, 2010a), preliminary design, and basic engineering (Hassim & Hurme, in 2010b) stages. This paper presents the method for the preliminary process design. Hazards evaluation at this stage is important because degree of freedom for applying changes and incorporating inherently healthier design features is high and the associated cost is lower.

Abbreviations: HTP, concentrations known to be harmful (haitallisiksi tunnetut pitoisuudet); IOHI, inherent occupational health index; ISI, inherent safety index; MAK, maximale Arbeitsplatzkonzentration; OEL, occupational exposure limit; OHHI, occupational health hazard index; OHI, occupational health index; PEL, permissible exposure limit; PFD, process flow diagram; PIIS, prototype inherent safety index; PRHI, process route healthiness index; REL, recommended exposure limit; TLV, threshold limit value.

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Nomenclature

A_i	floor area of process module i
A_n	process cross-section area
A_t	total process floor area
C	chemical concentration
C_{EL}	occupational exposure limit
i	individual chemical substance
m	fugitive emission rate
mix	chemicals mixture
Q	air volumetric flow rate
s	process side length
v	wind speed

Generally, there are two types of health effects; the acute and chronic effects due to the short-term and prolonged exposure, respectively. From occupational health context, chronic exposure is more common because it deals with normal, day-to-day operations and working activities. Acute exposure may also occur but rarely, mainly as a result of periodic emissions. Periodic emissions arise from the need to open up or enter the 'system' occasionally, or to perform works manually. Acute exposure due to catastrophic accidents or loss of containment is out of the scope since they are discussed by process safety methods.

2. Existing works

Unlike process safety, methods for assessing health hazards during chemical process design are still very much lacking. Most of the existing works assess public community health risk and/or for existing plants. The Dow Chemical Exposure Index, CEI (Dow Chemicals, 1998) is a comprehensive method, but it is not suitable for occupational health assessment because it evaluates acute exposure only due to major chemical releases. Gurjar & Mohan (2003) developed an integrated risk analysis method for both acute and chronic exposures. The assessment is not for occupational settings, but focuses on general populations, living in the nearby industrial area. Health and Safety Commission's Advisory Committee on Toxic Substances established a work called COSHH Essentials for evaluating the effects of chemicals exposure to employees (Maidment, 1998). The method however, is developed for existing small and medium enterprises. The National Institute for Occupational Safety and Health (NIOSH) developed a model to compute index numbers expressing the relative health risk of occupational groups due to their potential chemical exposures (Pedersen & Hornung, 1986). It ranks different industrial types by their health risks. The function of the model is more towards publishing a statistic on health risks in different industry titles rather than assessing occupational health hazards of a process in detail. A comprehensive study was designed to evaluate workers' potential risks in Taiwan's petrochemical complex retrospectively (Chan, Shie, Chang, & Tsai, 2006) by measuring air toxic concentrations over 3 years. The procedure is meant for existing plants, hence restricting its applicability on process design.

There are also existing methods which integrate the assessment of health, safety, and environmental aspects altogether, e.g. the EHS method (Koller, Fischer, & Hungerbühler, 2000), INSET Toolkit (INSIDE Project, 2001), SREST (Shah, Fischer, & Hungerbühler, 2005), and IBI (Srinivasan & Nhan, 2008). However health is always the minor focus and most of them evaluated the health effects only, with the exposure factor being neglected due to the limited process data.

The early methods particularly assessing occupational health aspect during process development and design phases are the OHHI (Johnson, 2001) and the PRHI (Hassim & Edwards, 2006). The PRHI is an improvement of the OHHI – both were developed for the R&D stage. The PRHI is complex because it includes many factors in the assessment and it requires ample process information. With reaction chemistries and block diagrams as the only available information at this stage, the assessment becomes tedious. The index also has the disadvantage of assessing several factors repeatedly. Nevertheless, the PRHI offers a lot of benefits such as enabling the properties of inherent health hazards to be quantified and alternative process concepts to be ranked by the health level, which are helpful for decision making during process screening. Also it is the first methodology, formally published on inherent occupational health assessment of chemical processes.

3. Background of the Health Quotient Index (HQI) method

Because of the lack of design oriented occupational health assessment methods, the overall scope of the research is to develop approaches for the first three stages of plant lifecycle – this paper discussing the second stage, i.e. preliminary design.

For the R&D stage, a method called the Inherent Occupational Health Index, IOHI was developed based on process reaction chemistries and the properties of compounds present (Hassim & Hurme, 2010a). The method qualitatively evaluates both health effects and exposure to hazards of chemical processes based on the penalty values assigned to eight selected subindexes. The assessment results are used to rank alternative process routes for the synthesis of the desired product.

For the basic engineering stage, the Occupational Health Index, OHI is proposed using information on piping details as well as working procedures based on piping and instrumentation diagrams (PIDs) (Hassim & Hurme, 2010b). The method assesses four aspects of: chronic inhalation risks to noncarcinogens and carcinogens, acute inhalation risk, and dermal/eye risk. For inhalation based exposures the results are in quantitative form, whereas for dermal-based exposure, the result is in qualitative form.

This paper focuses on health evaluation of preliminary process design stage. In this stage the flow sheets (PFDs) are developed for the basic process concept created in R&D stage. A method called the Hazard Quotient Index (HQI) is proposed for this stage based on information available from process flow sheets. 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 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 HQI is developed based on the following assumptions:

(1) Inhalative exposures from fugitive emissions are the only exposure source considered; this is a valid first assumption for large-scale continuous plants with few manual operations.
(2) The emission rate is constant with time; the method does not consider level of maintenance but employs 'average' leak rates.
(3) All chemical concentrations inhaled by the exposed workers are absorbed by the body (worst-case scenario).
(4) 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.

4. Development of the Health Quotient Index (HQI) method

4.1. Assessment steps

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

(1) *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 sheets or mass balances. Leak points are analyzed from the process diagrams.

(2) *Exposure assessment* basically 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 because of limited data to evaluate working practices as causes of occupational exposure to periodic emissions at this stage. Besides, fugitive emissions are the main source of background exposure to workers in chemical processes (Lipton & Lynch, 1994). Also, only inhalation exposure is assessed due to insufficient information on manual operations as sources of dermal/eye exposure. Inhalation route is a very important source of exposure occupationally (Lipton & Lynch, 1994) especially in petrochemical industries, which are mostly dealing with airborne chemicals. Both periodic emissions and other routes of exposures are included in the next stage method.

(3) *Toxicity assessment* involves the acquisition and evaluation of toxicity data for each chemical. Dose–response curve provides the best data, but it is available only for very limited chemicals (Watts, 1997). Therefore threshold exposure limits are used because it is easily available for a wide range of chemicals (international, e.g. TLV, OEL, REL, and PEL; or local, e.g. MAK in Germany and HTP in Finland). Here, HTP 8-h values are used since the study concerns continuous exposures to fugitive emissions.

(4) *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).

4.2. Estimating input data for the assessment

The exposure risk calculation requires data on chemical concentrations in the air of working area. In large-scale continuous plants this originates mostly from fugitive emissions. Since the plant emissions monitoring data does not exist during design, the chemical concentrations in the air need to be estimated, which requires data on the fugitive emissions rate and the dilution rate, which can be estimated from the process area and the wind speed in outdoor facilities. Here the estimation uses data from the PFDs.

4.2.1. Estimating fugitive emissions

For preliminary design stage, two methods were developed to estimate fugitive emissions from a chemical process; based on simple and detailed PFDs. Since the process piping and equipment details are still unknown, the methods are based on precalculated fugitive emissions for standard process modules, which represent typical operations in chemical plants such as distillation, absorber, etc., systems (Hassim, Pérez, & Hurme, in press). The precalculated emissions database was created based on the U.S. Environmental Protection Agency (EPA) emission factors (EPA, 1988) for different process stream services, e.g. gas/vapor, light liquid, and heavy liquid. The equipment and piping considered in each module's fugitive emissions estimate are summarized in Table 1.

In *simple PFDs*, the stream service is determined briefly from process descriptions. If the stream is in a gas/vapor phase, it is a gas service. For a liquid stream, if the stream mainly contains highly volatile chemicals, it is in light liquid service. Otherwise, it is a heavy liquid. Since the exact material balance is unknown, the calculation assumes the streams are 100% of the 'worst' component, which is the most toxic substance in the stream. For the plant, fugitive emission rates from all streams that contain the same 'worst' chemical are totaled up.

In *detailed PFDs*, the service of the stream is identified from the mass balances. For a liquid stream under operating conditions, the vapor pressure at 20 °C of individual chemicals in the mixture is determined. For those with vapor pressure >0.3 kPa, their weight compositions are summed up. If the weight composition is ≥20 wt%, the stream is in a light liquid service; or else, it is a heavy liquid. The emission estimation uses actual stream compositions data, making the estimate more accurate compared to the simple PFDs case. Similar to the simple PFDs, the emission rates of the same chemical substance are totaled up from the whole process (Hassim et al., in press).

4.2.2. Estimating air volumetric flow rate

For indoor process, ventilation is employed to maintain the air quality in the workplace environment. However, most petrochemical plants are outdoor facilities. Siting of plant in the open air rather than in a building is often the most effective means of ventilation, since small leaks will be dispersed by wind (Lees, 1996).

Here, air-flow rate within the process is estimated from process area dimensions and wind speed. The process plot area dimensions are determined by utilizing precalculated area estimates of standard process modules (Hassim et al., in press). Total process floor area is calculated summing up the floor area of the modules in the process, A_t:

$$A_t = \sum A_i. \tag{1}$$

where A_i is floor area of module i. The process side length is calculated by assuming a square plot, s:

$$s = (A_t)^{1/2} \tag{2}$$

By assuming the average height of main unit operations' leak sources in petrochemical plants is below $h = 7$ m (Mecklenburgh, 1985), the process cross-section area, A_n is calculated as:

$$A_n = hs \tag{3}$$

Finally, the area is multiplied by the wind speed, v to produce the air volumetric flow rate, Q:

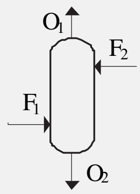
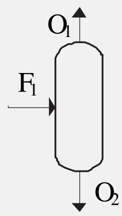
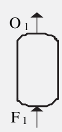
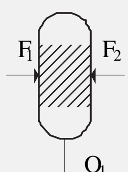
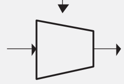
$$Q = vA_n \tag{4}$$

The local average wind speed should be used. If this is not available, the typical wind speed of 4 m/s can be used (Baldwin & Maynard, 1998). The method is discussed by Hassim et al. (in press) in more detail.

4.2.3. Estimating airborne chemical concentration

Chemical releases are assumed to be diluted and fully mixed by wind flow within the process area. The average chemical

Table 1
The number of piping components considered in estimating fugitive emissions.

Module	Sketch	A (m^2)	Stream	HEX	Valve	Pump	Flange	Sample pt.	Comp.	Agitat.
Absorber		82	F_1	1	-	-	5	1	-	-
			F_2	-	13	-	33	-	-	-
			O_1	-	9	-	22	1	-	-
			O_2	-	21	2	53	1	-	-
Liquid extractor		48	F_1	-	23	2	48	1	-	-
			F_2	-	6	-	13	-	-	-
			O_1	-	5	-	11	1	-	-
			O_2	-	10	-	23	1	-	-
Stripper		147	F_1	-	11	-	28	-	-	-
			O_1	2	44	2	113	1	-	-
			O_2	1	17	-	41	1	-	-
Flash		72	F_1	1	5	-	15	-	-	-
			O_1	-	2	-	5	-	-	-
			O_2	-	33	2	67	-	-	-
Distillation		129	F_1	-	4	-	11	-	-	-
			O_1	2	32	4	95	1	-	-
			O_2	2	17	2	49	1	-	-
Ion exchanger		28	F_1	-	5	-	12	-	-	-
			O_1	-	12	-	28	-	-	-
PFR		108	F_1	1	12	-	35	1	-	-
			F_2	-	6	-	15	-	-	-
			O_1	-	48	2	112	1	-	-
CSTR		95	F_1	-	10	-	23	-	-	-
			F_2	-	11	-	24	-	-	-
			O_1	-	50	2	141	3	-	1
Compressor		182	Total	3	18	-	65	-	1	-

A: Average floor area; HEX: Heat exchanger; Comp: Compressor; Agitat: Agitator; F: Feed stream; O: Outlet stream.

concentration (C) in air at the downwind edge of the plot area is:

$$C = \frac{m}{Q} \tag{5}$$

where m is fugitive emission rate; Q is air volumetric flow rate within the process facility as calculated by Eq. (4).

4.3. Health Quotient Index formulation

The Hazard Quotient Index (HQI) is formulated based on the widely accepted concept of hazard quotient, which is the ratio of the estimated chemical concentration (C_i) to the reference exposure limit (C_{ELi}) (Roach, 1994).

$$HQI_i = \frac{C_i}{C_{ELi}} \tag{6}$$

The calculated HQI is a dimensionless number. The hazard quotient can be applied to individual chemical as well as chemicals mixture.

Real world exposures to process materials in petrochemical plants are rarely to single chemicals but rather to mixture. Exposure of humans to chemicals mixture is the rule rather than exception, and therefore health risk assessments should focus on mixtures and not on single chemicals (Feron, Cassee, Groten, & van Vliet, 2002). The health risk assessment should be affected by the total toxicity of those chemicals. I.e. full risk evaluation must consider the potential of combined health impact of multiple chemicals (Chan, Shie, Chang, & Tsai, 2006). The chemicals may be hazardous as a mixture, even if the individual substances are at concentrations below their acceptable toxicity limits, especially if there are additive effects (e.g. solvents).

The health risk for mixture, HQI_{mix} is calculated by assuming the chemicals have additive effects (worst-case). This is the simplest assumption that can be made for assessing the overall impact due to a mixture of chemicals (Calamari & Vighi, 1993).

$$HQI_{mix} = \sum \frac{C_i}{C_{ELi}} \tag{7}$$

Chemicals with no exposure limit data are excluded from the index calculation (Chan et al., 2006).

To characterize the risk, index value <1 is often considered to indicate acceptable risks because the figure suggests that the receptors are exposed to concentrations below the threshold limits. The quantified risk from the HQI does not provide a value for the probability of harm as the result of exposure. Instead, it appraises the absence or presence of effects from exposure to chemicals even though values HQ < 1 are not risk free. In comparing alternative processes, the higher the index value, the greater the risk. More detailed benchmarks for acceptable HQ values are discussed by

Hassim & Hurme (in press-a). The steps for calculating the HQI_{mix} index are summarized in Fig. 1.

5. Case study

The HQI index is demonstrated by six process routes to manufacture methyl methacrylate (MMA). Each route differs from the process complexity (number of subprocess), technology (unit operations), and chemistry (raw materials, yield, intermediates, by-products). The routes discussed are:

(1) Acetone cyanohydrin based route (ACH)
(2) Ethylene via propionaldehyde based route (C2/PA)
(3) Ethylene via methyl propionate based route (C2/MP)
(4) Propylene based route (C3)
(5) Isobutylene based route (i-C4)
(6) Tertiary butyl alcohol based route (TBA)

Only those subprocesses related to the actual production of MMA are included in the assessment. The ones related to the production of raw materials and the disposal of by-products are excluded. This especially concerns with the ACH-based process – out of the six subprocesses in this route, only three of them are considered. Details about the selection of subprocesses for the assessment are further discussed by Hassim & Hurme (2010a). Simple PFDs for the routes are compiled by Rahman, Hekkilä, & Hurme (2005).

The HQI is calculated for the six MMA processes by using the simple PFD approach. The number of standard modules involved in each MMA process as well as the area of the process plot is presented in Table 2. The HQIs calculated for the 'worst' chemical in the stream (Eq. (6)) and mixtures in the route (Eq. (7)) are presented in Tables 3 and 4. Results in Table 3 show that none of the chemicals in the routes have concentrations exceeding their threshold limits ($HQI < 1$). This indicates the exposure risk to any of the chemicals is in acceptable level in all the processes. The same finding is also obtained from the HQI_{mix} for the combined impact.

Table 4 shows that the C2/MP route posses the lowest chemical exposure risk compared to the other five routes. The i-C4 and TBA routes have a low HQI value also. It is not surprising for these two processes to receive about the same HQI_{mix} value, since they are similar, except for the primary reactants which are however quite safe. The ACH route presents a moderate level of hazard among the processes evaluated based on the routes ranking. The dangerous substances hydrogen cyanide and acetone cyanohydrin present a health risk in the ACH-based route. The emission rate of hydrogen cyanide is very low. Therefore acetone cyanohydrin is the main

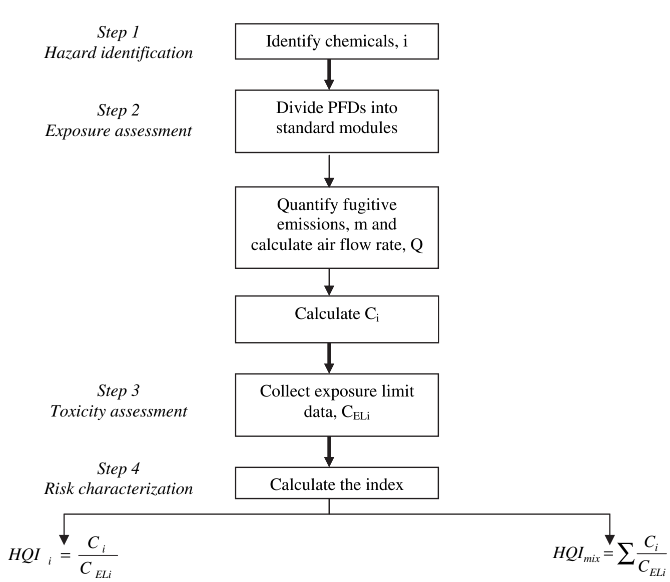


Fig. 1. Flow chart of the overall assessment steps.

Table 2
The number of process modules in the MMA routes and the estimated plot area.

Module	ACH	C2/MP	C2/PA	C3	i-C4	TBA
Absorber	–	–	1	–	1	1
Stripper	1	–	1	–	1	1
Flash	–	2	3	–	2	2
Distillation	4	7	8	8	5	5
PFR	–	3	2	3	2	2
CSTR	3	–	2	1	1	1
Liquid extractor	1	–	2	1	2	2
Ion exchanger	–	–	–	–	–	–
Compressor	–	1	1	1	–	–
Plot area (m^2)	997	1556	2164	1684	1426	1426

Table 3
Summary of the HQI calculation.

Process	Worst chemical[a]	Total m	Q	C_i	C_{ELi}	HQI_i
		mg/s	m^3/s	mg/m^3	mg/m^3	C_i/C_{ELi}
ACH	Hydrogen cyanide	29	884	0.03	5	0.007
	Acetone cyanohydrin	290		0.33	5	0.066
	Methacrylamide	178		0.20	NA	–
	Methanol	174		0.20	270	0.001
	Methyl methacrylate	542		0.61	42	0.015
	Acetone	25		0.03	1200	0.00002
C2/MP	Carbon monoxide	155	1104	0.14	35	0.004
	Methyl propionate	402		0.36	300	0.001
	Methanol	467		0.42	270	0.002
	Methyl methacrylate	311		0.28	42	0.007
	Methylal	37		0.03	3200	0.000
C2/PA	Carbon monoxide	185	1302	0.14	35	0.004
	Propionaldehyde	422		0.32	46	0.007
	Methacrolein	365		0.28	24	0.012
	Methacrylic acid	241		0.18	71	0.003
	Hexane	420		0.32	1800	0.0002
	Acetic Acid	168		0.13	13	0.010
	Methyl methacrylate	377		0.29	42	0.007
	Methanol	174		0.13	270	0.0005
	Formaldehyde	37		0.03	0.37	0.077
C3	Hydrogen fluoride	255	1149	0.22	1.5	0.148
	Isobutyl fluoride	246		0.21	NA	–
	Isobutyric acid	261		0.23	28.8	0.008
	Methacrylic acid	152		0.13	71	0.002
	Methyl methacrylate	490		0.43	42	0.010
	Methanol	174		0.15	270	0.001
	Propylene	113		0.10	859	0.0001
i-C4	Isobutylene	16	1058	0.02	NA	–
	Methacrylic acid	179		0.17	71	0.002
	Hexane	420		0.40	1800	0.0002
	Acetic acid	198		0.19	13	0.014
	Methyl methacrylate	377		0.36	42	0.008
	Methanol	174		0.16	270	0.001
	Methacrolein	136		0.13	24	0.005
TBA	Tert-butyl alcohol	16	1058	0.02	303	0.0001
	Methacrolein	136		0.13	24	0.005
	Methacrylic acid	186		0.18	71	0.002
	Hexane	420		0.40	1800	0.0002
	Acetic acid	168		0.16	13	0.012
	Methyl methacrylate	377		0.36	42	0.008
	Methanol	174		0.16	270	0.001

[a] Chemical refers to 'worst chemical' based; m: Fugitive emission rate; Q: Air volumetric flow rate; C: Chemical concentration; C_{ELi}: Threshold limit; HQI: Health Quotient Index; i: Chemical substance.

Table 4
Summary of the HQI for the combined effect of chemicals.

Process	HQI_{mix}	Normalized index	Rank order
ACH	0.09	4.77	4
C2/MP	0.01	0	1
C2/PA	0.12	6.89	5
C3	0.17	10	6
i-C4	0.03	1.16	3
TBA	0.03	1.03	2

6: Posses the worst case.

contributor to the greater health risk than in the C2/MP, TBA, and i-C4 processes.

Both the C2/PA and C3 routes receive the highest index values due to the presence of harmful species of formaldehyde and hydrogen fluoride, respectively. Even though formaldehyde is more hazardous to health (indicated by its lower threshold limit), its concentration is much lower than the hydrogen fluoride's. The HQI_i for hydrogen fluoride (0.148) is almost double of the value calculated for formaldehyde (0.077). This is among the reasons why the C3 route receives a higher index value than the C2/PA route. Even though the concentrations of both species are below their threshold limits, the concentrations however, are much closer to the benchmark ($HQI_i = 1$) compared to the other species in the processes.

6. Comparison with the PRHI and IOHI

Table 5 presents the normalized index values calculated for three methods to assess the inherent health hazards; the IOHI (Hassim & Hurme, 2010a), which is based on material properties and reaction conditions data only; the PRHI (Hassim & Edwards, 2006), which evaluates additional factors including operational aspects and material releases; and the HQI_{mix} discussed in this paper. For consistency, the additive-type IOHI index values are utilized, similar to those calculated in the additive-type PRHI method.

The values of the indexes (see Fig. 2) are correlated pairwisely by linear regression. Linear regression is considered appropriate, since the index-based methods are mathematically linear (Hassim, Grönlund, & Hurme, 2008). The coefficient of determination, R^2 acts as an indicator of the correlation between the methods compared; the higher the R^2 value, the stronger the correlation. Coefficient of determination describes, which amount of the dependency of one variable is explained by the other variable (Whitehead and Whitehead, 1993). The comparison shows that correlation between the results of the HQI_{mix} and PRHI is poorer ($R^2 = 0.77$) than that between the HQI_{mix} and IOHI ($R^2 = 0.85$). The PRHI and IOHI methods have the worst correlation ($R^2 = 0.51$). This indicates that the HQI_{mix} and IOHI correlate the best among the indexes. This is understandable since these methods are developed for subsequent design phases.

Table 5
Comparison of occupational health indexes (normalized).

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}.

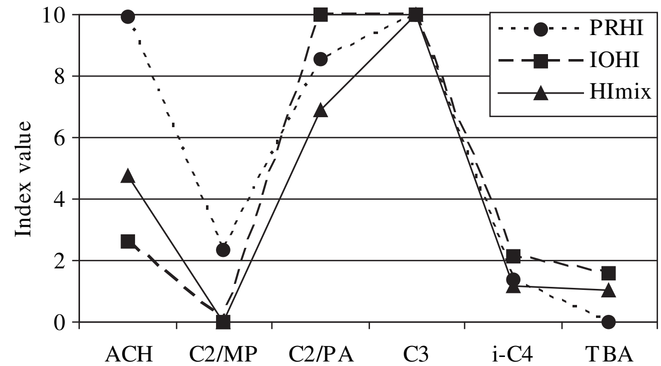


Fig. 2. Normalized index values of the MMA routes.

When looking at the route rankings (Table 5) by HQI_{mix} vs. PRHI, none of the route is ranked at the same position except for the C3 route (the worst route).

The ranking order given by the HQI_{mix} agrees very well to that assigned by the IOHI method. All the MMA synthesis routes have the same ranking position. This satisfying result somehow indicates that both methods developed for different stages are relatively reliable. It also suggests that the IOHI method (R&D stage), despite its simplicity, gives results that are consistent with those given by the more comprehensive method of the HQI_{mix} (preliminary design stage). Compared to IOHI, the HQI_{mix} has the advantage of highlighting additional information on the relative hazard of the worst routes; the C2/PA and C3, which were getting the same IOHI index value in the R&D stage. In fact these routes contain the most hazardous chemicals of all routes; formaldehyde and hydrogen fluoride (exposure limits of 0.37 and 1.5 mg/m^3, respectively). Even the R&D stage method IOHI could detect this. The more elaborate method HQI could quantify the comparison by pointing out that even though formaldehyde is more dangerous, its fugitive emission rate is negligible making the C2/PA healthier than the C3 route, which has a somewhat less dangerous chemical but higher leak rate resulting to higher HQI_{mix} value. Therefore the conclusion is, the HQI_{mix} is capable of disclosing further insight on the process occupational health hazards compared to the IOHI method, because the HQI_{mix} evaluates the workers' exposure aspects in more detail.

7. Conclusions

Occupational health hazard assessment during the preliminary process design stage is vital because the degree of freedom for making process modifications is still high and the costs are low. To make the health assessment of process designs feasible, different method is needed for each design and development stage to be able to utilize the information becoming available as the design proceeds. Earlier, a method called the IOHI was developed for the R&D stage. It was based on material properties of chemicals present and the process conditions (pressure and temperature).

In this paper the HQI method was proposed for assessing inherent occupational health hazards during the preliminary process design stage, which involves the creation of flow sheets. The HQI is a dimensionless risk expression (hazard quotient), which is calculated by comparing the estimated air concentration of chemicals to the threshold limit values. The calculation of the HQI is based on the information available from the PFDs such as the main process equipment present and the material balances. Fugitive emissions are estimated by a module-based approach. Fugitive emissions and process cross-section area estimates were utilized together with wind speed to estimate concentrations of chemicals in the air of process area. The assessment result can be used not only to compare different process concepts, but also to quantify the occupational risk of chemical exposure.

The HQI was demonstrated by a case study of six process concepts for MMA production. The calculated index values suggest that C2/MP is the route with the lowest health risk and the C3 route with the highest risk. This is because of the type of chemicals involved and the rate of fugitive emissions. Comparison with the PRHI and IOHI methods shows that the route ranking order given by the HQI agrees 100% with the order assigned by the IOHI method. The HQI was however able to differentiate the hazard levels between the C3 and C2/PA routes. These routes received the same IOHI index value. More detailed chemical exposure calculation in the HQI_{mix} allowed the more precise risk assessment of the processes compared to the qualitative IOHI method.

Based on the case study presented, the methods IOHI and HQI allow an occupational health risk evaluation of process concepts to be made in a consistent way in process R&D and preliminary process design phase.

References

Ahlberg, R. W. (1999). Risk assessment and risk communication in chemical exposure. *International Archives of Occupational and Environmental Health, 72*(3), M11–M13.

Baldwin, P. E. J., & Maynard, A. D. (1998). A survey of wind speeds in indoor workplaces. *Annals of Occupational Hygiene, 42*(5), 303–313.

Calamari, D., & Vighi, M. (1993). *Scientific basis for the assessment of several chemical substances in combination at low level*. Luxemburg: EEC.

Chan, C.-C., Shie, R.-H., Chang, T.-Y., & Tsai, D.-H. (2006). Workers' exposures and potential health risks to air toxics in a petrochemical complex assessed by improved methodology. *International Archives of Occupational and Environmental Health, 79*, 135–142.

Dow Chemicals. (1998). *Dow's chemical exposure index guide*. New York: AIChE.

EPA (1988). *Protocols for generating unit-specific emission estimates for equipment leaks of VOC and VHAP.* Publication number EPA-450/3-88-070.

EPA (1989). *Risk assessment guidance for Superfund: Environmental evaluation manual.* Publication number EPA/540/1-69/001A, OSWER Directive 9285.7-01.

Feron, V. J., Cassee, F. R., Groten, J. P., & van Vliet, P. W. (2002). International issues on human health effects of exposure to chemical mixtures. *Environmental Health Perspectives, 110*(S6), 893–899.

Gupta, J. P., & Edwards, D. W. (2002). Inherently safer design: present and future. *Process Safety and Environmental Protection, 80*(B3), 115–125.

Gurjar, B. R., & Mohan, M. (2003). Integrated risk analysis for acute and chronic exposure to toxic chemicals. *Journal of Hazardous Materials, A103*, 25–40.

Hassim, M. H., & Edwards, D. W. (2006). Development of a methodology for assessing inherent occupational health hazards. *Process Safety and Environmental Protection, 84*(B5), 378–390.

Hassim, M. H., Grönlund, M., & Hurme, M. (2008). Inherent EHS considerations in process development. *Chemical Engineering Transactions, 13*, 295–302.

Hassim, M. H., & Hurme, M. (2010a). Inherent occupational health assessment during process research and development stage. *Journal of Loss Prevention in the Process Industries, 23*(1), 127–138.

Hassim, M. H., & Hurme, M. (2010b). Inherent occupational health assessment during basic engineering stage. *Journal of Loss Prevention in the Process Industries, 23*(2), 260–268.

Hassim, M. H., Hurme, M. Occupational chemical exposure and risk estimation in process development and design. *Process Safety and Environmental Protection*, in press-a.

Hassim, M. H., Pérez, A. L., Hurme, M. Estimation of chemical concentration due to fugitive emissions during chemical process design. *Process Safety and Environmental Protection*, in press. doi:10.1016/j.psep.2010.01.006.

INSIDE Project. (2001). The INSET toolkit. http://www.aeat-safety-and-risk.com/html/inside.html.

Johnson, V. S. (2001). Occupational health hazard index for proposed chemical plant. Master thesis. Loughborough: Loughborough University.

Kletz, T. A. (1984). *Cheaper, safer plants, or wealth and safety at work*. Rugby: Institution of Chemical Engineers.

Koller, G. (2000). Identification and assessment of relevant environmental, health and safety aspects during early phases of process development. PhD thesis, Zurich: ETH Zurich.

Koller, G., Fischer, U., & Hungerbühler, K. (2000). Assessing safety, health, and environmental impact early during process development. *Industrial & Engineering Chemistry Research, 39*, 960–972.

Lees, F. P. (1996). *Loss prevention in the process industries: hazard identification, assessment & control* (2nd ed.). Oxford: Butterworth–Heinemann.

Lipton, S., & Lynch, J. (1994). *Handbook of health hazard control in the chemical process industry*. New York: John Wiley and Sons.

Maidment, S. C. (1998). Occupational hygiene considerations in the development of a structured approach to select chemical control strategies. *Annals of Occupational Hygiene, 42*(6), 391–400.

Mecklenburgh, J. C. (1985). *Process plant layout*. New York: Halstead Press.

Pedersen, D. H., & Hornung, R. W. (1986). Computerized estimates of potential occupational health risk due to chemical exposure. *Risk Analysis, 6*(2), 259–264.

Rahman, M., Hekkilä, A. -M., & Hurme, M. (2005). *Inherent safety index evaluation of methyl methacrylate process concepts*. In: *Plant design report series 75*. Espoo: Helsinki University of Technology.

Roach, S. A. (1994). On assessment of hazards to health at work. *American Industrial Hygiene Association Journal, 55*(12), 1125–1130.

Shah, S., Fischer, U., & Hungerbühler, K. (2005). Assessment of chemical process hazards in early design stages. *Journal of Loss Prevention in the Process Industries, 18*, 335–352.

Srinivasan, R., & Nhan, N. T. (2008). A statistical approach for evaluating inherent benignness of chemical process routes in early design stages. *Process Safety and Environmental Protection, 86*(B3), 163–174.

Watts, R. J. (1997). *Hazardous wastes: sources, pathways, receptors*. New York: John Wiley and Sons.

Whitehead, P., & Whitehead, G. (1993). *Statistics for business* (2nd ed.). London: Pitman.