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Inherent occupational health assessment during basic engineering stage

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ABSTRACT

Each year more people die from work-related diseases than are killed in industrial accidents. Therefore it is essential to evaluate occupational health aspect during the process design. Early evaluation of safety, health, and environmental (SHE) performance is advantageous, since the opportunities to make the process inherently benign are greater and the cost therefore lower. The methods for occupational health assessments need to be tailored to specific design stages, since the data availability is changing as the design proceeds. In this paper, an index-based method called the Occupational Health Index (OHI) is presented for the basic engineering stage. The OHI is the final of the three methods in series proposed for health assessment in development and design stages. The OHI is based on the information available in piping and instrumentation diagrams (PIDs) and the plot plan. Four health aspects are considered; chronic inhalation risks to noncarcinogens and carcinogens, acute inhalation risk, and dermal/eye risk. The index is demonstrated on separation system of a toluene hydrodealkylation process. The assessment results allow the level of occupational health risks to be evaluated, the sources of exposures be detected, and corrective actions taken in a focused way.

1. Introduction

Society demands and voluntary initiatives such as IPPC, REACH, and Responsible Care (Hook, 1996) strive chemical industries to improve safety, health, and environmental (SHE) performance. This goal can be achieved either by inherent way or by add-on systems. A well-known example of the former principle is the inherent safety. The concept of inherent safety was first introduced in the 1970s as an idea of improving process safety through the elimination or reduction of hazards (Kletz, 1984). Not only the risk is reduced, but it is also possible to remove the risk altogether e.g. by substituting dangerous chemical by a safer one. The advantage of inherent concept is to build in the desirable principles into the process instead of introducing add-on systems (such as controls) to correct an originally risky process concept.

In general, inherent principles can be applied throughout a process lifecycle (Hurme & Rahman, 2005). However, the best results will be achieved, if it is implemented during the earlier stages of process development, since many of the decisions are conceptual and fundamental. Assessment of a process when it is still 'on paper' allows an inherently better designs to be implemented before the changes become costly.

Since the idea of the inherent approach is to eliminate risks proactively rather than control them retrospectively, the principle is applicable to health and environmental aspects as well. This was also suggested by Kletz (1984), who originally disseminated the idea of inherent safety. Since then mainly inherent safety and some inherent environmental research have been conducted, but inherent health studies have been neglected. This is surprising since much more people die from occupational diseases than are killed in industrial accidents. According to ILO statistics (ILO, 2005) there are an estimated 159 000 fatalities every year that are attributable to work-related diseases, of which 74 000 may be linked to workplace exposure to hazardous substances in EU27 countries. Therefore, the aim has been to develop a series of methods for evaluating inherent occupational health hazards for the early phases of the process lifecycle; process development (Hassim & Hurme, 2010), process pre-design, and detailed process design/basic engineering. This paper presents the method for the last stage – basic engineering, which involves mostly process design.

Abbreviations: AHI, Atmospheric Hazard Index; CMA, Chemical Manufacturers Association; EHI, Environmental Hazard Index; *HQ,* Hazard Quotient; HQI, Health Quotient Index; IETH, Inherent Environmental Toxicity Hazard; IOHI, Inherent Occupational Health Index; IPPC, Integrated Pollution Prevention and Control; ISI, Inherent Safety Index; OHHI, Occupational Health Hazard Index; PFD, Process flow diagram; PID, Piping and instrumentation diagram; PIIS, Prototype Inherent Safety Index; PRHI, Process Route Healthiness Index; R&D, Process research and development; REACH, Registration, Evaluation, Authorization and Restriction of Chemicals; SHE, Safety, health, and environment; WAR, Waste Reduction Algorithm.

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Nomenclatures

A	Process cross-section area downwind
A_s	Surface area of skin available for contact
C	Chemical concentration
C_{DEL}	Dermal exposure dose limit
C_{EL}	Occupational exposure limit
C_{eq}	Equilibrium vapour concentration
EL	Exposure limit
f	Number of events per day
FE	Fugitive emissions
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
m	Fugitive emission rate
mix	Chemicals mixture
m_a	Dermal absorbed dose rate
m_{CDI}	Chemical daily intake
m_d	Quantity deposited on the skin per event
m_{SF}	Slope factor
Q	Total vapour volume rate
V	Inhaled air volume (m^3/day)
ν	Wind speed
w_i	Individual chemical's weight rate
x_a	Fraction of applied dose absorbed through the skin during the event
x_m	Individual chemical's vapour molar composition
x_w	Weight fraction of the substance in the mixture

2. Existing assessment methods

While there is abundant design guidance and standards for chemical plants on reduction of fire and explosion hazards and environmental discharges, relatively little has been published on techniques for controlling health risks (Money, 1992). The same also applies to assessment methods – various index-based methods have been developed for inherent safety assessment (Abedi & Shahriari, 2005; Khan, Sadiq, & Amyotte, 2003; Koller, Fischer, & Hungerbühler, 2001; Rahman, Heikkilä, & Hurme, 2005) and inherent environmental evaluations (Adu, Sugiyama, Fischer, & Hungerbühler, 2008; Hassim, Grönlund, & Hurme, 2008; Hertwich, Pease, & McKone, 1998; Koller, Fischer, & Hungerbühler, 2000a) during chemical process design. However for occupational health hazards in chemical plant industries, majority of assessment approaches target for existing processes e.g. the method developed by the Health and Safety Commission's Advisory Committee on Toxic Substances (Russell, Maidment, Brooke, & Topping, 1998). Among the earliest methods assessing health hazards in chemical plants comprehensively is the Dow Chemical Exposure Index, CEI (Dow Chemicals, 1998). However, it does not meet the 'occupational' hazard assessment criteria because it evaluates the acute health risk to people as a result of loss of containments, and not the long-term effects on workers from normal operation. For process development stage, the methods developed earlier are the Occupational Health Hazard Index (Johnson, 2001) and Process Route Healthiness Index (Hassim & Edwards, 2006). These methods are additive-type indexes, which can be used to rank alternative reaction chemistry pathways to a desired product by their inherent health hazard level. Even though they were originally developed for process research and development stage, they require massive process data, hence making their practical applicability low. Health features of the process at the end of design phase when more detailed process data is available (e.g. piping details and manual operations) are not comprehensively and accurately assessed. Therefore both methods are not sufficient to evaluate the inherent occupational health hazards of process designs during basic engineering stage.

There are also several works by e.g. INSIDE Project (2001); Koller, Fischer, and Hungerbühler (1999, 2000b); and Srinivasan and Nhan (2008) that address all the SHE aspects altogether. These methods intend to cover all the SHE aspects, however health is often not as well assessed as the other two. In the INSET Toolkit (INSIDE Project, 2001), health hazards are assessed simply based on R-phrases and brief scoring system called Leak Factor to estimate the fugitive release rate in the process. In the EHS (Koller et al., 1999, 2000b) and IBI (Srinivasan & Nhan, 2008) methods, only chemical health effects are assessed (based on e.g. exposure limit values and NFPA ranking) without considering the chemical exposure aspect. However a proper risk assessment requires both the chemical exposure and the effect to be evaluated (Tielemans, Marquart, de Cock, Groenewold, & van Hemmen, 2002). Also, most of the time health is evaluated from environmental perspective and not from occupational health point of view; e.g. the IBI method assesses chronic health hazards using the WAR algorithm approach.

These methods are not satisfactory for assessing the inherent occupational health of process concepts because of the minimal focus given on the health compared to the safety and environmental aspects. Therefore methods specifically for health risks are needed to identify and assess inherent health hazards comprehensively. Details about the available health assessment methods and their shortcomings for process development and design phases application are discussed by Hassim and Hurme (2010).

3. Assessment stages

For risk assessment of chemicals, it is necessary to quantify both the exposure levels and hazards encountered in the workplace (Tielemans et al., 2002). The objective of the research is to develop a set of occupational health assessment methods for assessing these aspects during the first stages of chemical process lifecycle.

The stages discussed are; process research and development (R&D), preliminary process design, and basic engineering. Since information available varies in these stages the methods are tailored for each stage to suffice for the data available.

In R&D stage only reaction chemistry data and the properties of the chemicals are available. An index called the Inherent Occupational Health Index; IOHI (Hassim & Hurme, 2010) was developed. It utilizes data on chemical properties and process conditions from the reaction chemistry. Eight subindexes are used to calculate the IOHI – six are to describe the exposures propensity (process mode, temperature and pressure, material phase, volatility and corrosiveness) and two for health effects following chemical exposures (exposure limit value and R-phrase). Each subindex is assigned with penalty; higher penalty indicates higher tendency of exposures and more severe effects.

In the preliminary process design stage, process flow diagram (PFD) is generated. This allows health risks of process routes to be estimated more quantitatively. A method called the Health Quotient Index (HQI) was created for quantifying the process' health risks. The HQI is calculated based on average toxicity of chemicals present in a process. The index estimates long-term risk

of inhalation exposure due to fugitive emissions, which are estimated by a process module based method. Two levels of estimation are provided to quantify fugitive emissions at this stage; based on simple PFD or detailed PFD. Basically, simple PFD consists of process sketch and process descriptions only (without exact material balance), which can be found in patents and encyclopaedias. From detailed PFD data on mass and energy balances is available, thus more accurate fugitive emissions estimates are produced. Chemicals concentrations in air are calculated using the estimated fugitive emissions, process cross-sectional area calculated from the estimated process plot area, and the wind velocity (Hassim, Pérez, & Hurme, submitted for publication). The HQI is calculated by dividing the estimated chemical concentration by the respective exposure limit either for an individual chemical or a chemicals mixture.

A plant construction project starts with basic engineering, which mainly involves detailed process design. The main task in this stage is to produce the piping and instrumentation diagrams (PIDs). Final flow sheets, equipment process datasheet, operating instructions and preliminary layout are also produced (Hurme & Rahman, 2005). In basic engineering, no pipeline or instrumentation design is made, neither equipment diagrams. These are tasks in the later stage of detailed engineering. In basic engineering stage, further process data such as the piping and equipment details and points for manual operations, is available from the PID. This information can be utilized to identify health hazards and to quantify risks to workers more comprehensively and to propose changes in process design before the engineering stage is finished and the process enters procurement and construction phases. For this basic engineering stage, which consists mostly of detailed process design, a method called the Occupational Health Index (OHI) is proposed in this paper. This is the most detailed method developed for the early process lifecycle phases, following the IOHI and HQI developed for process research & development and preliminary process design stages, respectively (Hassim & Hurme, 2010). The aim of the research is to provide a set of methods that can be used at different stages and which are tailored to suffice for the data available.

4. Goal of the Occupational Health Index development

The goals of the OHI are to: 1) identify occupational health problems of chemical processes based on information available from the PID; 2) estimate the risk of health hazards to workers; and 3) give quantitative and qualitative background for analyzing occupational health problems to support risk elimination or reduction. Unlike the IOHI and the HQI methods presented earlier for R&D and conceptual design phases, it is not the main aim of OHI to compare and rank alternative processes, but to assess in a more comprehensive manner the process selected in earlier stages. The method is aimed for a process for which the PID and plot plan documents are under design or already available. Therefore the method can be used to evaluate the effect of process detail selections (such as the pump or valve type) on the health risk. The OHI can be applied not only to the overall plant, but also on sub process or specific equipment. For process safety assessment, such methods are already available; e.g. the Dow Fire & Explosion Index (AIChE, 1994) and Mond Index (Tyler, Thomas, Doran, & Grieg, 1994), but methods for occupational health are still missing.

5. Development of the Occupational Health Index

The OHI comprises of four subindexes, each representing one health aspect considered in the assessment. The aspects are categorized under chronic and acute exposure risks: the *chronic* inhalation risks to 1) noncarcinogens and 2) carcinogens and the 3) *acute* inhalation risk and 4) dermal/eye risk. These four aspects were selected based on adverse health impacts that could be experienced by workers upon performing routine work activities. The main intended application area for the index is petrochemical plants, oil refineries, and related processes with volatile substances. Therefore the main route of exposure is the inhalative through fugitive emissions, since the plants are mostly handling gases and volatile liquids that typically vaporized upon being leaked to the atmosphere. Airborne enters human body more significantly through inhalation. Gases and vapours can pass through the skin only to some degree, therefore dermal contact is mostly from liquids and solids (Lipton & Lynch, 1994). In chemical processes, continuous dermal/eye contact to liquids and solids is uncommon, because the plants mainly involve well-contained process materials. Therefore chronic dermal/eye exposure is not included in the index, but is still briefly discussed in Section 5.4.

The assessment will result in four indicators on the occupational health risks of the process; risk estimations of the three inhalation-based exposures give numerical results, meanwhile the dermal-based exposure risk is presented non-numerically.

5.1. Chronic inhalative exposure risk: noncarcinogens

The common way to estimate the risk of chronic exposure to chemicals is using the exposure limits, which are defined as health-based standards that are established following a rigorous evaluation of the available toxicological data (Brooke, 1998). They are used to determine an airborne level to which people may be exposed repeatedly (8 h, 5 days, 11 months per annum), without experiencing adverse health effects.

Exposure risk to chemicals is commonly assessed based on the widely accepted concept of hazard quotient (*HQ*). The *HQ* is the ratio of the estimated chemical concentration to the reference exposure limit (Roach, 1994). Since chemical processes are rarely handling a single substance but rather chemicals mixture, exposure risk is either calculated for individual substances, if no additive effect is considered or for mixture by assuming the chemicals have additive effects (worst-case) (Eq. (1)). According to Calamari and Vighi (1993), this is the simplest assumption that can be made for assessing the overall impact due to a mixture of chemicals.

$$HQ_{nc-mix} = \sum \frac{C_i}{C_{ELi}} \tag{1}$$

where $HQ_{nc\text{-}mix}$ = hazard quotient index for long-term exposure to mixture of noncarcinogens, C_i = concentration of chemical i, C_{ELi} = occupational exposure limit of compounds.

Since the plant emissions monitoring data does not exist during design, the chemical concentrations in the air need to be estimated.

5.1.1. Fugitive emission and concentration estimation

From the context of occupational health in the chemical industries, fugitive emissions are the major sources of worker exposure. Despite being very small and mostly invisible to the eye, fugitive emissions are the main sources of origin of the continuous background exposure to workers (Lipton & Lynch, 1994). Therefore for this particular $HQ_{nc\text{-}mix}$ subindex, chemical health risk from exposure to fugitive emissions is the interest. The airborne chemical concentrations estimation requires data on the fugitive emissions rate, the process area, and the wind speed in outdoor facilities.

For quantifying the fugitive emissions, three methods have been developed that utilize data from the three types of process design documents: simple process flow diagram (PFD), detailed PFD,

and piping and instrumentation diagram (PID) (Hassim et al., submitted for publication). This paper discusses the basic engineering stage, which includes mainly detailed process design. Therefore the PID based fugitive emission estimation method is used. The estimation of fugitive emissions in this stage is more precise than in the preliminary design that is PFD-based because actual piping and component number and type data from PIDs is available. The types of leak sources are also known in more detail. Not only traditional leak sources such as valves, flanges, pumps, compressor seals, relief valves, sampling connections, process drains, and open-ended lines are considered, but also others which have not traditionally been treated as fugitive emissions leak sources, e.g. heat exchanger heads, sight glasses, bolted manways/hatches, caps/plugs, and compression fittings.

In the PFD stage, average component emission values (EPA, 1988) were used to give an estimate on the safe side. In PID stage, the maintenance and environmental policy of the plant is known better, so the decision is made on which type of valves etc. are used.

From the flowsheet, the chemicals present in each process stream and their weight compositions are determined. From the PID specific piping components in each stream are identified, e.g. rising-stem valve. Emission factors for the components are presented by Schroy (1979), Carson and Mumford (1985), EPA (1995), and TCEQ Publication RG-360 (2006). The rates for dusts refer to total dust emissions. Values should be halved for an estimate of the respirable dust release (King & Hirst, 1998). After the piping components' rates are totalled up for each stream, the stream rate is multiplied with the respective chemical weight fraction of that particular stream. For an integrated plant, emission rates for the same chemical substance are aggregated from the whole plant.

The emission dispersion calculation is based on the wind velocity and the process cross-section area, which is calculated from the plot dimension (length of plot edge) and the height below which majority of the fugitive emission sources reside. This height depends on the design but is typically about 7 m for petrochemical plants as can be concluded from the layout guidelines given by Mecklenburgh (1985). For the maximum concentration estimate, the shorter width of the plot area is used. Chemical emissions are assumed to be diluted and fully mixed by wind flow over the process cross-section area downwind. If available, wind distribution data in the location should be used to simulate realistic workers exposure conditions (Hassim & Hurme, submitted for publication). Alternatively, the local average wind velocity can be utilized. For outdoor facility the typical value is 4 m/s (CCPS, 2000). From these data, the average chemical concentration (C) in the air at the downwind edge of the plot area can be calculated as follows:

$$C = \frac{m}{\nu A} \tag{2}$$

where m = fugitive emission rate, ν = wind speed, A = process cross-section area downwind.

To characterize the risk, the calculated $HQ_{nc\text{-}mix}$ value is compared to a benchmark. HQ value < 1 is often considered to indicate acceptable risks for noncarcinogens although values $HQ < 1$ are not risk free. The HQ based risk benchmark is however influenced by other factors as well, such as the harmfulness of the substances. More elaborate HQ based risk classifications are discussed by Hassim and Hurme (submitted for publication) in more detail.

5.2. Chronic inhalative exposure risk: carcinogens

The risk estimation approach from exposure to carcinogens are similar to those for noncarcinogens. However the HQ is calculated for individual carcinogenic substances (Eq. (3)) rather than for a mixture.

$$HQ_{c-i} = \frac{C_i}{C_{ELi}} \tag{3}$$

where $HQ_{c\text{-}i}$ = hazard quotient index for long-term exposure to carcinogen i.

For carcinogens a stricter risk benchmark should be exercised as they pose more severe chronic health effects than noncarcinogens. Roach (1994) mentioned that even below the threshold limit, there is still a risk that some employees may be adversely affected, when exposure is greater than 10% of the exposure limit. The safety margin however depends on the carcinogens, but since it is straightforward to use a single safety margin, the 10% value is often used as the benchmark ($HQ < 0.1$) (Hassim & Hurme, submitted for publication).

It is also possible to quantify carcinogenic exposure risk based on intake. The daily chemical intake can be calculated from the chemical concentration estimated and the inhalation rate and exposure time. If actual data is lacking, typical values of these variables can be used as discussed by Hassim and Hurme (submitted for publication). In principle the intake based risk can be estimated for both carcinogens and noncarcinogens. However the intake reference limits known as reference dose (mg/kg day) are not available for many noncarcinogens making this approach less applicable for them. For carcinogens the risk is calculated using slope factor, m_{SF} (kg day/mg) as follows:

$$Risk = m_{CDI} \times m_{SF} \tag{4}$$

where m_{CDI} = chemical daily intake (mg/kg day).

The risk term is expressed as the probability of risk for producing cancer effect within a certain time. One cancer case per a million persons (1×10^{-6}) for public in 70-year lifetime (Watts, 1997) and one cancer case per a ten thousand persons (1×10^{-4}) for occupational environment in 45-year worktime (Chan, Shie, Chang, & Tsai, 2006) are the common benchmarks.

5.3. Acute inhalative exposure risk

From occupational health perspective, health hazards risk may present as a result of both chronic and acute exposures. Although long-term exposure is more important occupationally, the health risk due to large exposure within short-term duration cannot be neglected. The sources of acute exposure in a chemical plant may be involved in manual operations such as sampling, filter changing, gauging, etc. Only acute exposure sources due to normal process operations are considered here. Loss of containment type of accidents are covered by safety indices such as Dow Chemical Exposure Index. Neither tasks such as maintenance are beyond the scope of the study.

The HQ based risk assessment approach is utilized again here. The subindex can be calculated for both individual chemicals and mixture of chemicals ($HQ_{a\text{-}mix}$) as earlier. Similarly for mixture an additive-type effect is used as the worst-case assumption.

To estimate the acute inhalative risk, the equilibrium vapour concentration, C_{eq} (mg/m^3 or ppm) of the exposed chemical or mixture is needed. This can be calculated by adiabatically flashing the stream at atmospheric pressure. This corresponds to a situation where pressurized liquid stream is discharged, e.g. for emptying the system or sampling. Part of the stream is flashed and the operator is exposed to it. Based on the composition of the vapour outlet stream from the flash, the C_{eq} for individual chemical is calculated:

$$C_{eq}(mg/m^3) = \frac{w_i}{Q} \tag{5}$$

where w_i = individual chemical's weight rate, Q = total vapour volume rate.

Table 1
Risk matrix for dermal/eye exposure.

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*

In case liquid is below atmospheric boiling point, the equilibrium concentration in air can be calculated similarly through the bubble point at process temperature. Alternatively as a simplification, the C_{eq} can be estimated based on the atmospheric vapour pressure of individual chemicals at 20 °C as approached by many index-based methods for evaluating acute toxicity risk, such as the Vapour Hazard Index (Pitt, 1982), Substance Hazard Index (API, 1990), and Safety Factor (Martel, 2004).

The risk is quantified by comparing the calculated *HQ* value to a common benchmark value 5000 for acute toxicity risk when involving equilibrium concentration. *HQ* value $<$ 5000 implies acceptable risks in this case (Lipton & Lynch, 1994).

5.4. Dermal and eye contact risks

The adverse effects caused by skin exposure can occur locally within the skin or systemically due to absorption through the skin and distribution over body system (Cherrie & Robertson, 1995). Local effects are caused primarily by liquids (e.g. acids, alkalies, organics) or solids causing irritating or corrosive effects. Systemic effects can be caused by gases, liquids, and solids. However according to van Hemmen and Brouwer (1995), for most gases and vapours, uptake via skin is negligible as the area of skin is much smaller than lung (1.8 m^2 and 90 m^2, respectively).

5.4.1. Dermal/eye occupational exposure risk assessment in chemical plants

In larger scale industry, long-term skin contact is not common because of protective clothing and small number of manual operations because of automation. However if protective clothing is not properly used, there is an inherent risk on dermal and eye exposure. Contact times vary depending on the frequency of contact-related operations and how seldom contact areas (e.g. hands) are washed. Generally dermal/eye effects are local when exposure to hazardous agents are large and within a short period of time. This normally concerns liquids and solids. Meanwhile systemic effects develop following continuous exposure which commonly involve vapours or gases. For airborne chemicals the most important systemic exposure route is the inhalation. This has been considered already earlier by the inhalative exposure index. Potential rather than actual exposure is used here as the worst-case assumption. This is a common approach taken when initial exposure assessment is conducted under uncertainty as in process predesign (Mulhausen & Damiano, 1998).

5.4.2. Quantitative risk assessment

Quantitative dermal risk assessment requires data on the amount of skin contact. Dermal exposure can be estimated using Eq. (6) (Mulhausen & Damiano, 1998):

$$m_a = A_s m_d f x_a x w \tag{6}$$

where m_a = dermal absorbed dose rate (mg/day), A_s = surface area of skin available for contact (cm^2), m_d = quantity deposited on the skin per event (mg/cm^2-event), f = number of events per day, x_a = fraction of applied dose absorbed through the skin during the event, x_w = weight fraction of the substance in the mixture.

The skin surface area (A_s) for various parts of the body has been measured by several researchers e.g. U. S. Environmental Protection Agency (EPA, 1985) and can be used as default values in predicting dermal dose. Hands generally receive the highest exposure in occupational environment (EPA, 1996). Surface areas of hand skin susceptible for contact in different work activities are given by Lipton and Lynch (1994) and Mulhausen and Damiano (1998). They also provide default values for the other variables, such as the amount of contaminant retained on the skin per event. For chemicals with unknown dermal penetration properties, the conservative assumption is to consider any material in contact with the skin to be completely absorbed ($x_a = 1$) (Mulhausen & Damiano, 1998).

The predicted dermal exposure (m_a) is compared to the dermal exposure dose limit. However nearly all chemical exposure limits (C_{EL}) are established in units of airborne concentration. The airborne concentration based exposure limits can be converted into dermal exposure dose limits (Mulhausen & Damiano, 1998):

$$C_{DEL} = C_{EL} \times V \tag{7}$$

Table 2
Probability and frequency of dermal/eye exposure.

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 worker 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 3
Summary of the subindexes.

Subindex	Exposure duration	Exposure source	Calculation approach	Application	Benchmark of acceptable risk
HQ_{nc} (noncarcinogen)	Long-term	Fugitive emissions	Hazard quotient	Individual chemical, Mixtures	<1
HQ_c (carcinogen)	Long-term	Fugitive emissions	Hazard quotient	Individual chemical	<0.1 (concentration) <10^{-4} (intake)
HQ_a	Short-term	Manual operations	Hazard quotient	Individual chemical, Mixtures	<5000
Dermal/eye risk	Short-term	Manual operations	Qualitative	Individual chemical	Qualitative risk level

where C_{DEL} = dermal exposure dose limit (mg/day), C_{EL} = occupational exposure limit (mg/m^3), V = inhaled air volume (m^3/day).

Although worker's respiration rate depends on activity, the typical breathing volume is about 10 m^3 of air in a workday (Dutch, 1982; Chan et al., 2006). However this approach is valid only for substances that pose their toxicity as a systemic effect. For such chemicals with potential skin absorption property, Sk notation is the label assigned. For chemicals with local dermal effect (such as acids and alkalies), the methodology described above is not appropriate, since their effects are often very acute such as skin corrosion and their effects cannot be presented as a body dose basis.

5.4.3. Qualitative risk assessment

Due to the constraints of the quantitative dermal assessment e.g. nearly all the variables in Eq. (7) are unknown in design stage, a qualitative risk evaluation approach is proposed using matrix based on the data on chemicals' dermal harmfulness and the likelihood or frequency of exposure (Table 1). The assessment starts with the identification of the source for acute dermal exposure in the process. R-phrases are used to determine chemicals with dermal/eye effects. The likelihood/frequency of exposure is categorized using descriptive terms (Table 2) as also approached by Lipton and Lynch (1994) and Mulhausen and Damiano (1998).

5.5. Summary of the Occupational Health Index method

Overall there are four subindexes produced for this index method: hazard quotient index for long-term inhalative exposure to 1) noncarcinogens (HQ_{nc}) and 2) carcinogens (HQ_c), as well as 3) hazard quotient index for short-term inhalative exposure (HQ_a) and 4) risk level of dermal/eye exposure. Summary of the subindexes is given in Table 3.

6. Application to case study

A product distillation system of toluene hydrodealkylation (HDA) process is used as a case study to demonstrate the method. Apart from noncarcinogens, the process also includes carcinogenic and dermal toxic compounds as well as an acute exposure source, allowing the calculation of all the four subindexes. In the HDA process, toluene is reacted with hydrogen to produce benzene and methane. The reaction takes place at 630 °C and 23 bar (Turton, Bailie, Whiting, & Shaeiwitz, 1998).

$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4 \quad (8)$$

Majority of methane and hydrogen in the reactor's product stream are flashed off before being fed to a distillation unit. Sketch of the HDA process is shown in Fig. 1. To demonstrate the method, the product distillation system was considered (Fig. 2).

For *chronic exposure risk assessment*, fugitive emissions are first estimated by analyzing the number of leak points from the column's PID (Fig. 2). Leak points in utility or inert streams are excluded from the calculation. Piping component types assumed for the process are low rating rising valve, heat exchanger head with two flanges, pump with single mechanical seal, gasketed flange, and sampling point. The number of each leak point source is given in Table 4. The total fugitive emissions estimate in each stream is then multiplied with the stream's weight composition to obtain the emission rate of each chemical substance in this process. Their concentrations are then calculated using Eq. (2) by assuming the average wind speed 4 m/s. Plot area of the distillation system is 96 m^2. For a square plot the edge length is 9.8 m. Process cross-section area of the system, which is required to calculate the concentrations, is therefore 69 m^2 if maximum height of 7 m for emission points is assumed (as discussed in Section 5.1.1). The results are shown in Table 5. The risks are quantified separately for noncarcinogens and carcinogens. The HQ values for methane and

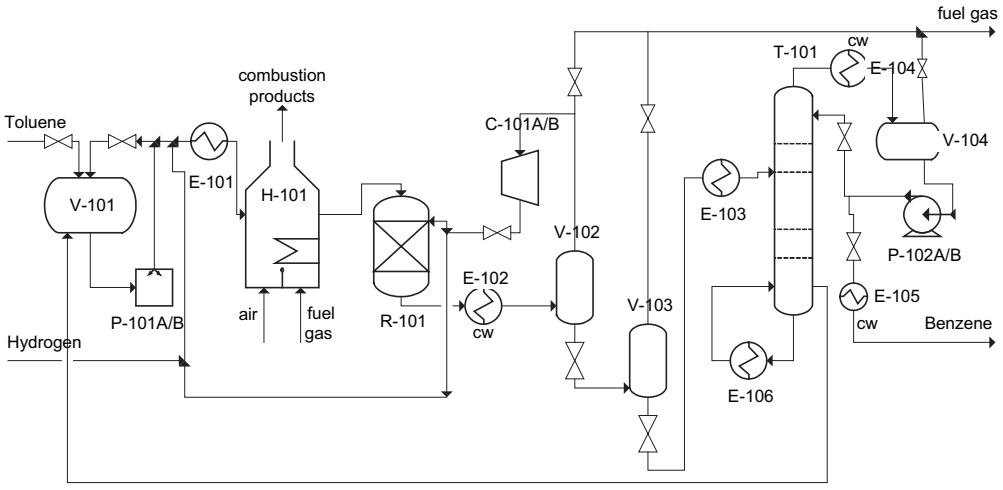

Fig. 1. Sketch of the toluene hydrodealkylation (HDA) process.

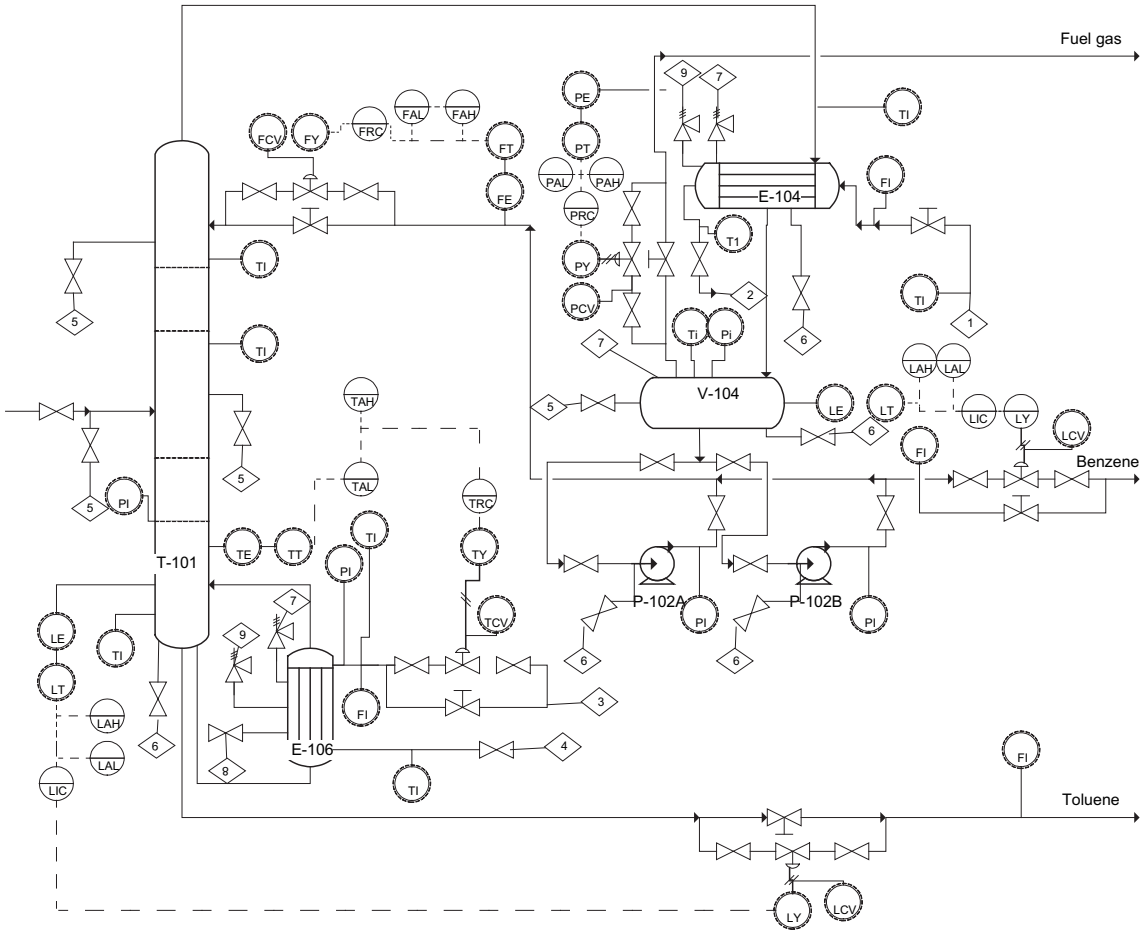

Fig. 2. PID of the product distillation tower – 1. cooling water; 2. cooling water return; 3. steam; 4. condensate; 5. sample port; 6. chemical sewer; 7. vent to flare; 8. clear sewer; 9. vent to atmosphere.

toluene are totalled up to give $HQ_{nc\text{-}mix}$ (Eq. (1)) of 0.00034 (<1). The value is way below the benchmark of 1, hence suggesting the risk of exposure to mixture of chemicals in the case study as acceptable. Hydrogen is excluded from the subindex calculation because the substance is only a simple asphyxiant.

For chronic assessment of carcinogen, the $HQ_{c\text{-}i}$ for benzene is then calculated by comparing its fugitive concentration (0.23 mg/m^3) to the long-term exposure limit (8-h) of 3.25 mg/m^3 (HTP Values, 2007) – resulting to $HQ_{c\text{-}i}$ (Eq. (3)) value of 0.07 (<0.1). The result indicates the exposure risk to benzene is acceptable, but as much as reasonably possible, exposure to such carcinogen should be avoided.

For the risk-based approach the benzene's daily intake rate is then calculated by assuming 1632 working hours per year for a worker exposed to the process area air for the full working time (Hassim & Hurme, submitted for publication) – the result is 0.0184 mg/kg day. The risk of getting cancer is calculated using benzene's slope factor (Eq. (4)) (0.029 kg day/mg) and the result is 5.3 cancer cases per 10 000 persons (>1 × 10^{-4}) per 45-year worktime. The calculated risk implies that excess cancer cases will be about 5 times greater than the common goal of 1 case per 10 000 persons for occupational environment and is therefore unacceptable. The result is somehow expected since the intake risk-based benchmark

Table 4
Data on leak points in the HDA process case study.

Type of leak point	Number of leak points	Emission factor (mg/s)	Total rate (mg/s)
Rising valve (low rating)	32	1.7	54.4
Heat exchanger head	4	0.111	0.44
Pump single mechanical seal	2	1.7	3.4
Gasketed flange	102	0.056	5.71
Sampling point	4	4.17	16.7

Table 5
HQ calculation for chemicals in the HDA process case study.

Chemical	Rate (mg/s)	Concentration (mg/m^3)	*HQ*
Hydrogen	0.01	0.00004	Simple asphyxiant
Toluene	17.8	0.06	0.00034
Benzene	62.5	0.23	0.07
Methane	0.32	0.0012	0.000002

Table 6
Exposure risk to benzene before and after design improvement.

	Before	After
Leak source type	Low rating valve Normal sample point	High rating valve Closed sampling point
Emission factor (mg/s)	Valve: 1.7 Sample point: 4.17	0.03 0 (negligible)
Benzene rate (mg/s)	62.5	8.6
Intake (mg/kg day)	0.0184	0.0025
Risk (cancer case per 10 000 persons)	5.3	0.7

Table 7
Summary of results from occupational health assessment.

Aspect	Subindex	Results	Benchmark	Conclusion	Action
Chronic exposure risk (noncarcinogen)	$HQ_{nc\text{-}mix}$	0.00034	<1	Acceptable risk	–
Chronic exposure risk (carcinogen)	$HQ_{c\text{-}i}$	0.07	<0.1	Acceptable risk	–
	Risk	5.3×10^{-4}	$<10^{-4}$	Non-acceptable risk	High rating valves needed
Acute exposure risk (inhalation)	$HQ_{a\text{-}mix}$	212 000	<5000	Non-acceptable risk	Closed sampling needed
Acute exposure risk (dermal)	Risk	Toluene:Low toxicity Benzene:Moderate toxicity	Qualitative risk level (Table 1)	Minor risk Moderate risk	Closed sampling needed

is stricter than the *HQ* based benchmark. An in depth discussion on the different risk benchmarks is given by Hassim and Hurme (submitted for publication).

Benzene emissions in the process come mainly from low rating rising valves and sampling points. There are four sampling points in the case study. Generally in chemical plants a lot of sampling points are installed throughout the process. However most of them are not used to take sample, but fugitive emissions does still occur continuously. If high rating valves and closed sampling system are used instead, which are inherently healthier due to the lower emission factors (high rating valve: 0.03 compared to low rating valve: 1.7 mg/s and closed sampling point: negligible (assume 0) compared to normal sampling point: 4.17 mg/s), the risk can be greatly reduced to 0.7 cases per 10 000 persons (see Table 6).

For *acute exposure risk assessment*, manual sampling point in the overhead drum V-104 of the distillation column (Fig. 2, item 5) is the acute exposure source to workers. The other three sample points are not in use. For inhalative exposure, the sampling is simulated with adiabatic flash to quantify the acute airborne concentrations (C_{eq}) of the chemicals resulting from sampling without cooling. The concentrations are then compared to the chemicals' short-term exposure limits (15-min). The $HQ_{a\text{-}mix}$ is calculated to be 212 000 (>5000). The risk value is considerably larger than the acceptable risk benchmark, which is implying that acute inhalative chemicals exposure as a result of manual sampling is the major health problem. Therefore, safer and healthier means of taking sample, e.g. using sample cooler to prevent vaporization or closed sampling system is necessary.

The same sampling point is also a potential *dermal/eye exposure* risk. Based on the R-phrases, benzene (R36/38, R48/23/24/25) may cause irritation to eyes and skin (local effect) and serious health damage by prolonged exposure (systemic effect). Toluene (R38) may irritate the skin (local effect). A qualitative category of exposure frequency/probability is determined from Table 2. For manual open sampling activity, the most appropriate category is possible/daily contact. The risk matrix classifies the dermal/eye risk of benzene as moderate and therefore measures are needed. The dermal/eye risk of toluene is evaluated to be minor (no action). Since the sampling point is also a dermal/systemic risk in addition to acute exposure risk as discussed before, a closed sampling system might be the best alternative to avoid both problems.

The results of the assessment of the case study are summarized in Table 7 and the emission values and evaluation results for the improved design are presented in Table 6.

7. Conclusions

The Occupational Health Index method has been proposed for assessing occupational health risk of chemical processes with volatile components (e.g. petrochemical plants). The method was designed for implementation during the basic engineering stage. This is the last design phase, where it is still possible to apply modifications at reasonable cost and the opportunity to incorporate inherently better designs is still high. The index requires PID and process plot plan as information sources. The method is an extension of the two earlier indexes, the IOHI and the HQI, which are intended for earlier design phases and require only reaction chemistry and PFD, respectively as information source. Due to the availability of more precise data, the OHI is expected to be more comprehensive and reliable. The method uses four criteria to evaluate the occupational health; chronic inhalative exposure to noncarcinogens and carcinogens, acute inhalative exposure, and dermal/eye exposure. Four risk assessment results are obtained; three in numerical form (the inhalation-based exposures) and one is non-numerical form (the dermal-based exposure). The chronic inhalative exposures are based on the fugitive emissions calculations.

The index has been demonstrated on the benzene-toluene separation system in toluene hydrodealkylation process. The results indicated that long-term inhalative exposures to both noncarcinogens (methane and toluene) and carcinogen (benzene) present no risk based on the calculated *HQ* values. The intake based assessment for benzene inhalative exposure however, shows that the cancer risk benchmark is exceeded. The difference of the results is contributed by the fact that the slope factors are stricter than the exposure limits. The cancer risk can be reduced below the benchmark by installing high rating valves. Exposures due to manual sampling activity are estimated to be risky for both acute inhalation and dermal/eye contact routes. This source can however be improved by installing a closed sampling system.

The case study shows that the OHI method can be used in basic engineering to evaluate the level of occupational health of design and to locate where corrective actions are needed to reduce occupational exposures. The effect of the actions can also be estimated.

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