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Occupational chemical exposure and risk estimation in process development and design

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A B S T R A C T

Each year more people die from diseases caused by work than are killed in industrial accidents. Therefore, methods are needed to evaluate occupational health hazards as early as possible when the process is still under development. A method for estimating inhalative exposures and risks in petrochemical and related plants is presented. The method is simple and suffices with the limited data availability during the early design stages.

The steps of the method, which utilizes preliminary process flow diagrams are as follows: first the fugitive emissions and process plot areas are estimated based on precalculated process modules representing the typical process sections (such as a distillation unit). Chemical concentration in the air is then calculated based on the wind velocity probability and the estimated process cross-sectional area. For this purpose a typical wind velocity distribution in the area is used. The worker risk of exposure to chemicals is evaluated either based on the concentration in air by using the hazard quotient method or calculating the carcinogenic chemicals intake and the resulting risk of cancer. The values are compared to the benchmarks.

As a result the process route health characteristics such as fugitive emissions rate, critical wind speed, chemical concentration in air and intake amount as well as the corresponding risk of exposure are produced. By using statistical meteorological data, health risks of occupational exposure can be estimated more realistically as probabilities. The approach is capable of comparing alternative processes to select the concept which is inherently occupationally healthier. Using this method, the exposure problems of a process can be identified earlier and proper decisions can be made early in process development or predesign stage.

The concentration-based method is demonstrated by a case study of six competing manufacturing routes for methyl methacrylate (MMA). The C3 is found to be the most harmful alternative to health. Both concentration-based and intake-based methods are applied. The study indicates that the intake-based risk estimation benchmark is stricter than the exposure limit-based benchmark for carcinogens.

Keywords: Worker exposure; Risk assessment; Inherent safety; Occupational health; Process design

Abbreviations: ACGIH, American conference of governmental industrial hygienists; ACH, acetone cyanohydrin based route; COSHH, control of substances hazardous to health; C2/MP, ethylene via methyl propionate based route; C2/PA, ethylene via propionaldehyde based route; C3, propylene based route; EASE, estimation and assessment of substance exposure model; ECHA, European Chemicals Agency; EHI, environmental hazard index; EL, exposure limit; EMKG, easy-to-use workplace control scheme for hazardous substances; EPA, Environmental Protection Agency; HQ, hazard quotient; HQ_{mix}, hazard quotient for chemical mixtures; HTP, concentrations known to be harmful (haitallisiksi tunnetut pitoisuudet); i-C4, isobutylene based route; IETH, inherent environmental toxicity hazard; ISI, inherent safety index; MAK, maximale arbeitsplatzkonzentration; MEL, maximum exposure limit; MMA, methyl methacrylate; NIOSH, National Institute for Occupational Safety and Health; OES, occupational exposure standard; OSHA, occupational safety and health administration; PEL, permissible exposure limit; PFD, process flow diagram; PID, piping and instrumentation diagram; PIIS, prototype index of inherent safety; POEM, predictive operator exposure model; REL, recommended exposure limit; SHE, safety, health, and environment; TBA, tertiary butyl alcohol based route; TLV, threshold limit value; TRA, targeted risk assessment.

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List of notations

A	process cross-section area
b	line's intercept
C	concentration of chemical
C_{ELi}	occupational exposure limit
CDI	chemical daily intake
F	Weibull cumulative distribution function
i	chemical substance
m	fugitive emission rate
P	probability in % of time v is below v_c
v	wind speed
v_c	critical 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

1. Introduction

The interest on safety, health, and environmental (SHE) performance of a process has been increasing after Kletz introduced the concept of inherent safety (Kletz, 1984). It professes that potentially arising process hazards should be identified as early as possible, starting from the process development and design phases. Various methods have been developed for inherent safety assessment namely the prototype index of inherent safety; PIIS (Edwards and Lawrence, 1993) and inherent safety index; ISI (Heikkilä et al., 1996), as well as for inherent environmental assessment such as the environmental hazard index; EHI (Cave and Edwards, 1997) and inherent environmental toxicity hazard index; IETH (Gunasekera and Edwards, 2006).

Unlike for process and environmental safety, there are only a very limited number of methods available for evaluating occupational health hazards during chemical process design (Hassim and Hurme, 2008; Hassim and Edwards, 2006). This is somewhat surprising since more people die from diseases caused by work than are killed in industrial accidents. The difference between process safety and occupational health is that the former concerns with major accidents while the latter deals with long-term effects resulting from work. However, the importance of occupational health assessment has been gradually recognized, especially among chemical industries.

The first step in enhancing safety or occupational health is the risk assessment. For health hazards it involves four steps: (1) hazard identification, (2) toxicity assessment, (3) exposure assessment, and (4) risk characterization. The task of performing these procedures is more challenging for a proposed plant, due to the lack of actual process data. From the occupational health context, exposure assessment is a very critical evaluation step. It may be defined as the determination or estimation of the magnitude, frequency, duration, and route of exposure to a chemical (Lipton and Lynch, 1994). The aim is to estimate the concentrations and intakes (dosages) of chemicals to the population at risk. According to Lees (1996), exposure assessment should cover all exposure modes and exposure sources due to leaks as well as activities. However, at the beginning of process development, much process information is not yet available. Therefore, this paper focuses on the estimation of worker inhalative exposure to chemicals released into air using the information available in the early process development and design phases. The release mechanism of interest is fugitive emissions, which are the main source of origin of the continuous background exposure to workers in the oil refineries and petrochemical plants. The majority of large process plants are built outdoors and hence chemicals released to the atmosphere are diluted by natural wind before being in contact with the workers in the process area. Skin contact is also another common route of exposure in chemical plants, especially those that deal with heavy and less volatile substances. Even though skin effects, either absorptive or corrosive, can be very severe they are usually confined to a very short distance from the release point compared to inhalation effects. Here skin route of exposure is not considered. Many of the existing assessment methods include only inhalation route when evaluating health hazards from chemical plants e.g. toxicity hazard index (Tyler et al., 1996). The aim of this paper is to estimate the potential worker exposure risk to chemical releases in a proposed chemical plant as a result of fugitive emissions. The exposure is evaluated based on simple process flow diagrams and annual wind distribution data to include the local meteorological conditions.

1.1. *Effect of wind flows on chemical concentration*

Meteorological factors are well known to be important contributions to air quality. For example, serious pollution episodes in the urban environment often result from unfavorable meteorological conditions, which diminish the ability of the atmosphere to disperse and dilute the pollutants (Ziomas et al., 1995). The variability in the concentrations of airborne chemicals is influenced not only by surface wind speed, but also other parameters, such as ambient air temperature (Elminir, 2005). However, several analyses made on this subject show that the concentrations are strongly correlated with wind speed, but weakly correlated with temperature (Hargreaves et al., 2000; Wehner and Wiedensohler, 2003; Gupta et al., 2004; Turalioglu et al., 2005). Wind speed will affect the rate of build up of chemicals in a given area and will also partly determine people's exposure to outdoor chemicals (Koop and Tole, 2004).

Numerous studies have been conducted to investigate the relationships between meteorology and air pollution for agents such as ozone (Comrie, 1990; Eder et al., 1994), SO_2 (Kalkstein and Corrigan, 1986), and NO_2 (Davis and Kalkstein, 1990). Such studies on releases from chemical plants, in particular the low-level, continuous fugitive emissions are missing especially for processes under development. This paper presents how chemical exposure assessment of process plants under development can be conducted using wind distribution data and fugitive emissions estimation methods. The results can be used further to determine the risk of exposure and to compare the health performance of different design concepts.

2. Wind speed distribution

For estimating a long-term wind speed distribution, a minimum of 12 months of monitoring data is needed (Salmon and Walmsley, 1999). Based on the wind speed data and fugitive emissions estimate, the yearly chemical exposure of workers can be predicted.

2.1. Weibull distribution

Wind speed is influenced by the weather system, the local terrain, and the height above the ground surface. The wind speed variations over the period can be described by a probability distribution function. The best density function that can be used to describe the wind speed frequency curve is the Weibull distribution (Patel, 1999). Generally, the Weibull cumulative distribution function can be described as:

$$F = 1 - e^{-(v/\alpha)^{\beta}} \quad (1)$$

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

Eq. (1) can be transformed into a linear form:

$$\ln(-\ln(1-F)) = \beta \ln v - \beta \ln \alpha \quad (2)$$

In order to estimate the Weibull parameters of α and β, a linear regression can be done. The Weibull β parameter is the line's slope. The estimate for the α parameter is calculated by Eq. (3):

$$\alpha = e^{-(b/\beta)} \quad (3)$$

where b is the intercept.

The value of β, which determines the shape of the curve, is typically ranging from 1.5 to 2.5. Meanwhile, the α (scale parameter) value for most wind sites is normally between 5 and 10 m/s (Patel, 1999).

2.2. Wind speed variation with height

Wind speed depends on distance from ground (height). An equation is required to predict the wind speed at one height in terms of the measured speed at another height. The wind speed data is typically measured high above ground level. However, for occupational exposure assessment, it is necessary to know the wind speed at workers' breathing level. The average workers' breathing zone is typically between 1 and 1.5 m high (Chen et al., 2003). 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. (4) (Patel, 1999):

$$v = v_0 \left(\frac{z}{z_0}\right)^{\gamma} \quad (4)$$

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 – low for smooth terrain and high for rough ones, ranging from 0.10 to 0.40 (Patel, 1999).

3. Exposure risk assessment

A variety of different approaches exist for quantifying human exposures. Direct methods involve measurements of exposure at the point of contact at the moment it occurs, e.g. personal monitoring and biomonitoring. These are impossible during process design stage. Indirect methods involve extrapolating exposure estimates from other measurements and existing data (Nieuwenhuijsen, 2003). Existing data are not always available for all the type of chemical industry and they do not reflect the age of the plant or the level of engineering. Therefore, a wide variety of exposure models are currently employed for health risk evaluations. Specific models have been developed for chemical exposure assessment by government, industry, and academia (Fryer et al., 2006). Examples of the methods are discussed below.

3.1. Occupational exposure models in literature

In a workplace, workers may become exposed to a range of substances, which are likely hazardous to their health. For assessing the magnitude of such exposures, occupational exposure models have been in use since the early 1990s, which are direct contact-based (Paustenbach, 2000). In the UK, among the models currently used are the estimation and assessment of substance exposure (EASE) model (HSE, 2000) and the predictive operator exposure model (POEM) (PSD, 1992).

The EASE model can predict exposure levels for a broad range of occupational situations. It requires knowledge of the physical properties of the substance under consideration, its pattern of use, the processes being undertaken in the workplace, and any control measures that are in place (HSE, 2000). Exposure estimation is made for solids and volatiles using matrix-like system that combines the above-mentioned information. The EASE model established the exposure values based on historical exposure data from enforcement activities in known problem areas, rather than the normal operations that are required for more routine risk assessment contributing to over-prediction of exposure in many cases (ECHA, 2008).

Meanwhile POEM is designed for pesticides preparation and application for UK conditions so it has very limited scope. The POEM model is based on national database and statistic, whereas in EUROPOEM which is the European version, exposure data obtained in European countries is combined (van Drooge et al. (2001)).

Recently, the European Chemicals Agency (ECHA) has proposed several models for estimating occupational exposures (ECHA, 2008):

(a) *For Tier 1*: the models discussed are the ECETOC Targeted Risk Assessment (ECETOC TRA) and the easy-to-use workplace control scheme for hazardous substances (EMKG). The ECETOC TRA aims to assess the health and environmental risks from the supply and use of chemicals. The calculated basis of the approach is a modified version of the EASE model version 2.0 (HSE, 2003). The easy-to-use workplace control scheme for hazardous substances (EMKG) is a generic model that can be used to derive a Tier 1 inhalation exposure value for the workplace. It may be used as the first step in the exposure assessment and it should be seen as an approach for filtering the rather non-risky workplace situations from those requiring detailed attention. The model is mainly based on the COSHH Essentials (HSE, 1999). The EMKG can be used in cases where the more specific ECETOC TRA cannot be used. Both require information on control strategies.

(b) *For Higher Tier*: currently there are no validated higher Tier exposure models (ECHA, 2008). However, many algorithms that have been developed for specific purposes may be used, e.g. the ConsExpo and the EUROPOEM. In the USA, the Environmental Protection Agency (EPA) and several institutions for EPA have developed many models, which may contain useful approaches for higher Tier exposure.

The difference between Tier 1 and higher Tier approaches is the first Tier exposure estimations are meant to be conservative and may be well above the actual exposures. Meanwhile the higher Tier estimations are much more specific and require more detail for the estimation parameters and exposure determinants.

Several other exposure assessment models are discussed by Fryer et al. (2006), van Drooge et al. (2001), and European Commission DG Enterprise and Industry (2008).

3.2. Exposure risk assessment during chemical process design

The occupational exposure models discussed above are direct contact-based and not suitable for large plants located outdoors. They are more appropriate for indoor facilities and are task-oriented. Also detailed information on the nature of work activities is required, making the models best applicable on existing plants. Therefore new exposure models are needed for plants under development and design.

In petrochemical plants, process materials are well contained most of the time. The inhalative exposures come from fugitive emissions. Even though the quantity is small, the releases are continuous and mostly uncontrolled. The need of such exposure estimation methods is emphasized by the new reports pointing out that exposure to workplace agents at levels previously thought to be safe can produce adverse health effects (Unnikrishnan and Hedge, 2006).

Based on the above criteria a more general method has been developed for estimating exposure risks in chemical processes. The method only requires limited process information accessible at the process development or design stage. The exposure estimating approach is based on the data on fugitive emissions, the process area, and the wind speed distribution.

3.3. Estimation of fugitive emissions

To estimate fugitive emissions, three methods have been developed basing on the information available in specific process development or design phases; simple process flow diagram (PFD), detailed PFD, and piping and instrumentation diagram (PID) stage.

For the *simple* (*i.e. preliminary*) *PFD stage* the details of the process are still unknown, the method uses precalculated fugitive emissions for standard process modules, which represent typical operations in chemical plants such as distillation and reactor systems. The database of precalculated emissions for process modules 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 (Hassim et al., in press). Since the exact material balance is not known, the calculation is based on the assumption that the streams are 100% of the 'worst' component, which is the most toxic substance.

In *detailed PFD* the emission estimate is based on real stream compositions because of the availability of mass balance data. This makes the estimate more accurate compared to the simple PFD case.

The *PID stage* provides more exact fugitive emissions estimate by utilizing the real number of piping and equipment components from PID and basing the emissions estimation on the real types of the components (e.g. valve or pump seal type).

The process area dimensions needed for chemicals air concentration calculations are determined by utilizing precalculated area estimates of standard process modules for the PFD stages. Actual process area measured from plot plan is used for the PID stage. The methods for estimating fugitive emissions and process area are discussed in detail by Hassim and co-workers (Hassim et al., in press; Hassim and Hurme, 2008).

3.4. Estimation of chemical concentrations in air

Concentrations of chemicals in air can be estimated in PFD stages by using the fugitive emissions and process cross-section area calculated from the estimated process plot area by assuming a square plot (Hassim et al., in press). By assuming the average height of main unit operations' leak sources in petrochemical plants is below 7 m (Mecklenburgh, 1985), chemical releases are assumed to be diluted and fully mixed by wind flow within the process area. The average chemical concentration (C) in air at the downwind edge of the plot area is (Hassim et al., in press):

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

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

Wind speed distribution within the studied area gives a more realistic concentrations estimate compared to using only a single average wind speed value in the calculation.

3.5. Concentration-based risk assessment

Exposure risk assessment can be based on chemical concentrations or intakes. The results may be expressed in terms of a potential chemical exposure and its distribution in a year. The most common approach for assessing exposure risk to chemicals is using the hazard quotient (HQ). The HQ is simply the ratio of the exposure concentration estimate to the reference exposure limit (Chan et al., 2006; Mower, 1998; Roach, 1994). The value is used for evaluating the potential health risk in human from chemical exposures. The HQ approach is widely used, as it is a simple and quick calculation. It is also very easy to communicate the results, since risk acceptability is based solely on the comparison of the calculated HQ value to a single critical value: HQ value < 1 does not always indicate acceptable risks. Below the threshold limit, there is still a risk that some employees may be adversely affected, when exposure is greater than 10% of the limit (Roach, 1994). Especially for carcinogens often any concentration is a risk (Watts, 1997).

HQ based exposure risk assessment methods have been presented by Mulhausen and Damiano (1998), Bullock and Ignacio (2006) (AIHA methods), Pääkkönen and Rantanen (2001) and FIOH (2009) (FIOH method). In the AIHA method, the HQ benchmarks were first categorized into four and later five ratings (Table 1). BS8800 (2004; 1996) presents a qualitative risks classification into five classes in terms of harmfulness of chemicals and level of exposure. However, no HQ benchmarks were given. FIOH extended the method by including HQ benchmarks to describe the exposure and R-phrases to describe the harmfulness (Table 2).

For carcinogens, the safety factor on the exposure limit depends on the carcinogenic substance. It is not feasible however to establish different safety factors for different car-

Table 1 – AIHA exposure ratings (Bullock and Ignacio, 2006; Mulhausen and Damiano, 1998).

Exposure rating	1998 HQ	2006 HQ	Control zone description
0	–	≤1%	–
1	≤10%	1–10%	Highly controlled
2	10–50%	10–50%	Well controlled
3	50–100%	50–100%	Nominally controlled
4	>100%	>100%	Poor controlled

Table 2 – Simple classification of health risks from chemical exposure (FIOH, 2009; Pääkkönen and Rantanen, 2001).

Consequence/benchmark	Slightly harmful (irritation etc.) R20, 21, 22, 36, 37, 38	Harmful (long-term etc.) R23, 24, 25, 33, 34, 40, 43, 48, 62, 63, 64	Consequence/ benchmark	Extremely harmful (toxification, cancer etc.) R26, 27, 28, 35, 39, 41, 42, 45, 46, 49, 60, 61, 65
<50% HTP	Insignificant risk	Small risk	<10% HTP	Moderate risk
50–100% HTP	Small risk	Moderate risk	10–50% HTP	Significant risk
>HTP	Moderate risk	Significant risk	50–100% HTP	Unbearable risk

cinogens, because this would require laborious studies. In practice 10% of the threshold limit is often used as the standard for carcinogens (HQ < 0.1). This is also supported by the guideline given by Roach (1994). FIOH (Table 2) assigns 'moderate risk' to such exposure condition on carcinogens.

The hazard quotient approach provides a fast method for identifying various classes of risk. For example for harmful chemicals HQ > 100% poses a significant risk which necessitate actions. For extremely harmful chemicals the corresponding range is 10% < HQ < 50% whereas range 50% < HQ < 100% presents unbearable risk requiring immediate action (FIOH, 2009; Pääkkönen and Rantanen, 2001).

The hazard quotient approach is based on the exposure limits data for the chemicals published by regulatory bodies and organizations e.g. MAK (Germany), MEL and OES (UK), TLV (ACGIH), PEL (OSHA), REL (NIOSH), and HTP (Finland).

The HQ can be calculated based on chemical concentration or dose estimate. However in this research, the HQ calculation is performed based on the estimated concentration. The concentration is compared to the 8 h reference limit value, which represents a typical day-to-day workplace exposure. The HQ can be applied for both single chemicals and chemical mixtures. For the latter case, if the mixtures are assumed to have additive effects, the hazard quotient for mixtures (HQ_{mix}) is expressed by Eq. (6):

$$HQ_{mix} = \sum \frac{C_i}{C_{ELi}} \quad (6)$$

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

3.6. *Critical wind speed*

Since fugitive emissions are diluted by the wind, a new occupational health concept, critical wind speed, can be defined. It refers to the minimum velocity of air necessary to maintain the level of chemicals in exposure limits (HQ ≤ 1) in local wind conditions. The critical wind speed may already provide an idea about the relative exposure level of the process concepts studied. The higher the calculated critical value, the higher the wind speed required to keep the chemicals below exposure limits, thus implying the greater relative exposure risk.

3.7. *Intake-based risk assessment*

The chemical intake is most commonly expressed as daily chemical intake amount. The intake is influenced by many variables that can be categorized into human-related (e.g. inhalation rate, body weight) and work-related (e.g. exposure time, frequency, duration) variables. Determination of accurate intake is often difficult. For example, exposure time, frequency, and duration vary among individuals. Site-specific information is the most reliable information source. Unfortunately, this is not yet available for non-existing plants, but needs to be estimated. The worker's average daily exposure is calculated based on local work duration; e.g. in Finland typical working hours in chemical industry is 1632 h per year (8 h per shift, 204 shifts per year). The working duration is assumed to be 45 years. In reality, exposure duration is shorter than working duration. However, due to data unavailability during the design stage, it is assumed that the exposure takes place all over the whole working time. It is also assumed that respiration rate is 10 m^3 per day at work, which is one-half of one person's respiration rate in 1 day (Chan et al., 2006; Dutch, 1982).

Different reference values are established for noncarcinogens and carcinogens. Reference dose (mg/kg-day) is used to estimate noncarcinogenic risk, which has the same calculation approach and result definition as the hazard quotient discussed earlier, but based on intake rather than concentration.

$$HQ = \frac{CDI}{\text{reference dose}} \quad (7)$$

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

For carcinogens the risk is estimated using slope factor. Slope factor (kg-day/mg) is derived from the slope of a carcinogenic dose–response curve (Watts, 1997). The intake-based risk for carcinogens can be calculated as follows:

$$\text{risk} = CDI \times \text{slope factor} \quad (8)$$

Compared to the concentration-based limits, the intake-based reference limits provided by the EPA are available only for a limited number of chemicals. This is especially true for noncarcinogens. In practical occupational health assessment,

Table 3 – List of the number of standard modules in each route.

Standard module	C2/MP	C2/PA	C3	i-C4	TBA	ACH
Liquid–liquid extractor	0	2	1	2	2	1
Flash	2	3	0	2	2	0
Distillation	7	8	8	5	5	4
Stripper	0	1	0	1	1	1
Compressor	1	1	1	0	0	0
Absorber	0	1	0	1	1	0
Stirred tank reactor	0	2	1	1	1	3
Tubular reactor	3	2	3	2	2	0

intake concept is rarely used. Instead, concentration of a chemical is used for risk estimation. The issue of limited chemical toxicity information often hinders risk assessment being performed based on the intake estimation. The risk term is expressed as the probability of risk for producing cancer effect (per 10^4 or 10^6 persons in a certain time). It is the quantitative result in risk assessment calculations. The common value of acceptable risk level or the benchmark for public is one cancer case per a million persons in 70-year lifetime (Watts, 1997) and for occupational environment one cancer case per 10,000 people per 45-year worktime (Chan et al., 2006).

4. Case study for chemical exposure assessment

As a case study an assessment of six competing process routes for manufacturing methyl methacrylate (MMA) is presented. The routes are acetone cyanohydrin based route (ACH), ethylene via propionaldehyde based route (C2/PA), ethylene via methyl propionate based route (C2/MP), propylene based route (C3), isobutylene based route (i-C4), and tertiary butyl alcohol based route (TBA). For more details about the processes, see Rahman et al. (2005).

4.1. *Analysis on wind distribution data*

For estimating the worker potential exposure at real wind conditions, wind distribution data in a seaside location in Finland was used in the case study. The data for 2007 consisting of almost 9000 measurements at 25 m height from surface. The highest probability of the wind speed in that year falls between 3 and 4 m/s at 25 m. First, the wind speeds at 1.5 m above ground level are estimated based on the data at 25 m height. The friction coefficient value of 0.20 is applied in Eq. (4). Then, using Eqs. (1)–(3) the Weibull parameters were estimated by regression; the shape parameter β was found to be 2.29 and the scale parameter α is 2.1 m/s at 1.5 m height. The annual wind distribution at 1.5 m height is shown in Fig. 1. The corresponding cumulative distribution is presented in Fig. 2.

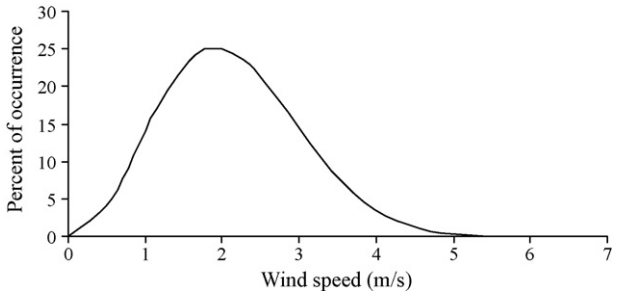

Fig. 1 – Annual wind probability distribution at 1.5 m height in the case study.

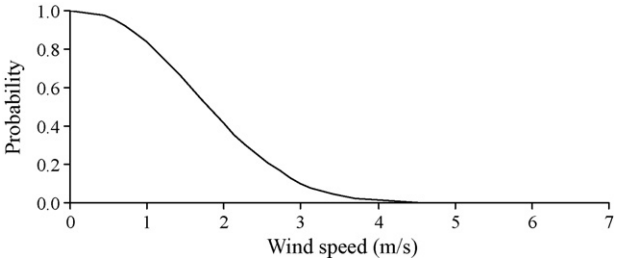

Fig. 2 – Cumulative probability of the wind speed at 1.5 m height in the case study.

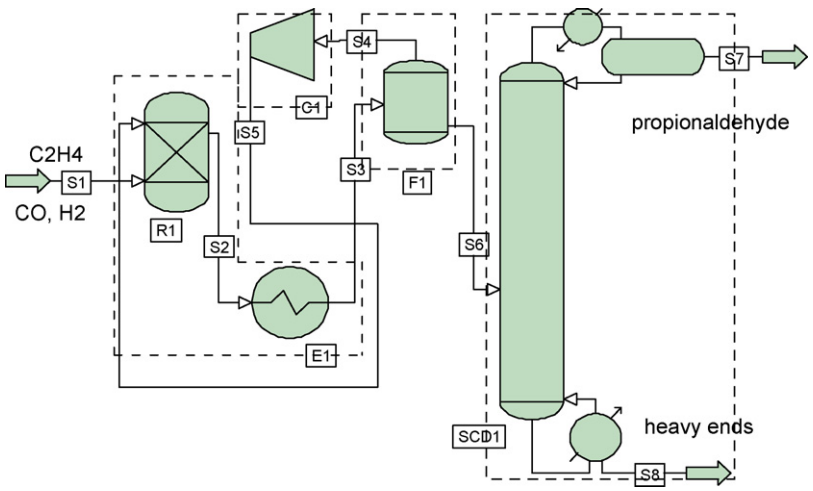

Fig. 3 – Example of simple PFD on the first subprocess of C2/PA route with the division of precalculated modules (tubular reactor, compressor, flash, distillation).

Table 4 – Fugitive emissions and process area estimates for MMA processes.

Route	Substance	Fugitive emission/route (g/s)	Process plot area (m^2)	Process cross-section area (m^2)
C2/MP	Carbon monoxide	0.16	1556	276
	Methyl propionate	0.40		
	Methanol	0.47		
	Methyl methacrylate	0.31		
	Methylal	0.04		
C2/PA	Carbon monoxide	0.19	2164	326
	Propionaldehyde	0.42		
	Methacrolein	0.37		
	Methacrylic acid	0.24		
	Hexane	0.42		
	Acetic acid	0.17		
	Methyl methacrylate	0.38		
	Methanol	0.17		
	Formaldehyde	0.04		
C3	Hydrogen fluoride	0.26	1684	287
	Isobutyl fluoride	0.25		
	Isobutyric acid	0.26		
	Methacrylic acid	0.15		
	Methyl methacrylate	0.49		
	Methanol	0.17		
	Propylene	0.11		
i-C4	Isobutylene	0.02	1426	264
	Methacrylic acid	0.18		
	Hexane	0.42		
	Acetic acid	0.20		
	Methyl methacrylate	0.38		
	Methanol	0.17		
	Methacrolein	0.14		
TBA	Tertiary butyl alcohol	0.02	1426	264
	Methacrolein	0.14		
	Methacrylic acid	0.19		
	Hexane	0.42		
	Acetic acid	0.17		
	Methyl methacrylate	0.38		
	Methanol	0.17		
ACH	Hydrogen cyanide	0.03	997	221
	Acetone cyanohydrin	0.29		
	Methacrylamide	0.18		
	Methanol	0.17		
	Methyl methacrylate	0.54		
	Acetone	0.02		

4.2. *Estimation of fugitive emissions and process area*

Fugitive emissions from the six MMA production routes are quantified using the simple PFD-based estimation method (Hassim et al., in press; Hassim and Hurme, 2008). The emission rate calculation based on simple PFDs utilizes pre-calculated standard submodules representing subprocesses in the route (Table 3). Example of standard module determination

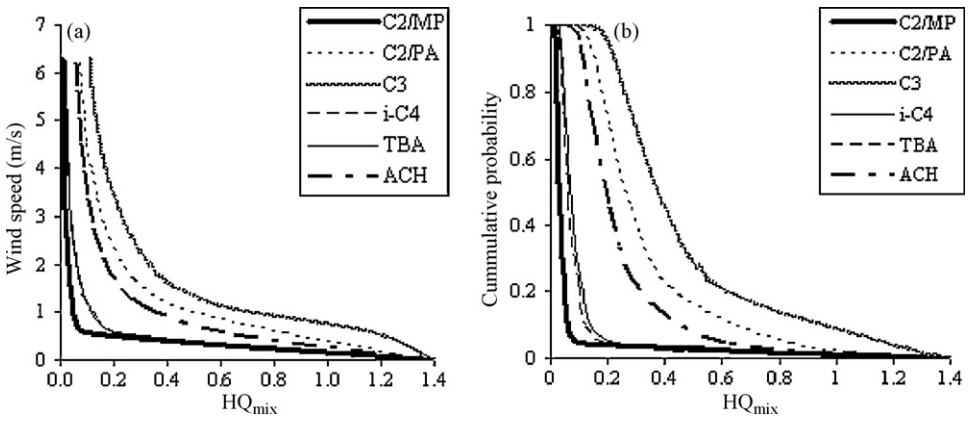

Fig. 4 – The health index of chemical mixtures for MMA processes based on: (a) wind speed (b) wind speed probability over year.

Table 5 – Critical wind speed analysis of MMA process routes.

Process route	Critical speed (v_c) m/s	Probability ($v < v_c$) %	Time ($v < v_c$) h/a	Healthiness rank
C2/MP	0.05	0.02	2	1
C2/PA	0.48	3.34	293	5
C3	0.67	7.11	623	6
i-C4	0.13	0.16	14	3
TBA	0.12	0.13	12	2
ACH	0.35	1.63	142	4

1 indicates the lowest risk.

is shown in Fig. 3 for the first subprocess of the C2/PA route. This subprocess comprises of the following submodules: tubular reactor, compressor, flash system, and distillation. Since exact mass balance data is still unavailable at this earliest design stage, the most toxic chemical in each process stream is determined to represent the stream emission rate. Fugitive emissions of each substance throughout the route are added up. Also the process areas are estimated based on the number of standard modules involved in the route. The estimated fugitive emissions and process areas are summarized in Table 4.

4.3. *Concentration-based estimation of exposure risk*

The concentration of chemicals in each MMA route is calculated by Eq. (5) using the estimated fugitive emissions, process cross-section areas (Table 4), and wind velocity at worker level (Eq. (4)). The estimation is based on the annual probability distribution of the wind speed (Fig. 2). Subsequently, the mixture hazard quotient (Eq. (6)) is calculated for the components in the route. HQ_{mix} considers additive health effects of the chemicals.

The HQ_{mix} indicates how close the concentration estimate is to the exposure limit; the higher the HQ_{mix} value, the greater the risk. In this study, the HTP values (HTP Values, 2007) are used as the exposure limits. It is often assumed that the risk is acceptable if the concentration estimate is less than the exposure limit. For carcinogens, a safety factor of 10% is used as a guideline as discussed in Section 3.5.

Fig. 4(a) presents that the HQ_{mix} value is larger at lower wind speeds and it decreases gradually as the speed is getting higher. This is due to better dilution. The corresponding plot based on the yearly cumulative wind speed probability at working level is presented as Fig. 4(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 C3 route is the worst option because the process exhibits large harmful material of hydrogen fluoride fugitive emissions, which contributes to significantly higher HQ value compared to the other routes. The same trend is shown by the critical wind speed analysis presented in Table 5.

The wind velocity at $HQ_{mix} = 1$ corresponds to the critical wind speed in Fig. 4(a). Fig. 4(b) represents the probability and Table 5 summarizes the number of hours in a year for the wind velocity to be below the critical wind speed. The whole year corresponds to 8760 h. The C3 is the least inherently occupational healthy process route among the alternatives. It exhibits significant exposure risk ($HQ > 1$) for around 623 h in a year (7.1% of time) whereas the best process C2/MP has only 2 h/a (0.02% of time) chemical concentrations above the threshold limit value at this location (Table 5). In fact a risk distribution (% of time the process is in small, moderate or significant risk area) can be produced. The information can obviously be used to compare different process concepts.

4.4. *Intake-based estimation of exposure risk*

Since slope factors are available only for carcinogens, only the intake of carcinogens is estimated here. C2/PA is the only MMA process route containing a carcinogenic substance (formaldehyde). The intake of formaldehyde is calculated using the annual probability distribution of wind speed (Fig. 1), assuming 1632 working hours per year for a worker and the worker is exposed to the process area air for the full working time. The probability of carcinogenic risk is determined by multiplying the daily intake by the slope factor of formaldehyde (0.045 kg-day/mg) (Watts, 1997) (Eq. (7)). Fig. 5(a) shows the cumulative probability of getting cancer from the exposure to formaldehyde in a location with these annual wind distributions. One in 10,000 persons (1×10^{-4}) in 45-year worktime

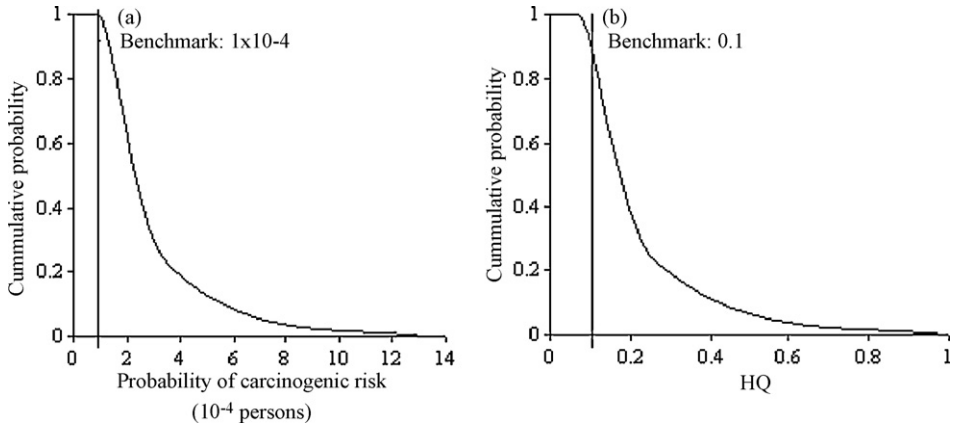

Fig. 5 – Risks of formaldehyde exposure and the benchmarks for the C2/PA route estimated based on: (a) intake (b) concentration.

Table 6 – Comparison of concentration exposure benchmark for some chemicals.

Substance	R-phrase	HTP (mg/m^3)	0.1HTP (mg/m^3)	C of 10^{-4} risk (mg/m^3)	10^{-4} risk compares to HQ	0.1HTP compares to risk
Benzene	R45	3.25	0.325	0.043	0.013	7.5×10^{-4}
Formaldehyde	R40	0.37	0.037	0.028	0.075	1.3×10^{-4}
Propylene oxide	R45	12	1.2	0.048	0.004	25×10^{-4}

is usually used as the benchmark risk for occupational exposures (Chan et al., 2006). The benchmark however depends on the local policy and risk perception. In this case, the carcinogenic risk of formaldehyde exposure is larger than 1 in 10,000 for 98.7% of the year – indicating that the cancer risk exceeds the benchmark (Fig. 5(a)). It is also possible to estimate the total annual intake of formaldehyde in the process (1632 working hours) with these wind conditions – the result is 1.1 mg/kg-per person. This corresponds to an average daily intake of 0.0053 mg/kg-day. The associated average risk of getting cancer as a result of exposure to formaldehyde can now be calculated. The result is 2.4×10^{-4} cancer cases per 10,000 persons per 45-year worktime (Eq. (7)) for the wind distribution in question. This exceeds the benchmark (10^{-4}) implying that the C2/PA route may be an unsuitable process option if build with unsophisticated engineering standards. However using better engineering such as leak proof valves and hermetic pumps, the situation may change. But for this a new analysis is needed based on detailed engineering data such as PID, which presents the real number and type of leak points.

4.5. *Comparison of intake and concentration-based approaches*

Since the intake-based risk assessment method requires reference doses and slope factors, its practical application is more limited than the concentration-based approaches because the intake limits are available mainly for carcinogens.

In the above C2/PA case study, the benchmarks of both methods are exceeded: the 10^{-4} intake risk benchmark is exceeded for 98.7% of time and the 0.1HTP value for 87% of time in these wind conditions. In this case the intake-based benchmark is stricter.

A question arises on how the benchmarks generally compare. Table 6 presents a comparison of exposure benchmarks for some carcinogenic or potentially carcinogenic chemicals. It is presented to which hazard quotient the 10^{-4} intake risk benchmark compares and which intake risk the 0.1 hazard quotient corresponds. It can be seen that for these chemicals the risk benchmark for the 0.1HQ concentration is 1.3–25 times larger than the 10^{-4} benchmark. The results however vary since the occupational exposure limits are often based on different criteria than the slope factors. E.g. formaldehyde exposure limit (HTP) is based on irritation but the slope factor on the carcinogenic effect.

As a conclusion it can be said that the intake and concentration-based methods are not generally options since the intake-based method is less frequently applicable. It can be used mainly for evaluating the carcinogenic risk. The concentration-based approach is more widely applicable. The point of view of the methods is however different. Intake-based method mostly reflects the risk of cancer whereas the exposure limit-based method reflects different health risks and nuisances.

5. Discussion

This paper discusses how chemical exposure risk can already be estimated in the PFD stages. The chemical concentration and the intake amount are first calculated using a standard process module based method. In the simple PFD phase, the estimates serve as an indicator of the maximum exposure since the stream compositions are unknown, and they are assumed to consist solely of the most dangerous component. In this stage average emission factors are used, which are based on standard technology resulting in a larger emissions estimate. Furthermore, full working time exposure is also assumed for workers in this stage.

The accuracy of the estimation method in simple PFD phase is related to the unknown compositions of process streams. Meanwhile in both PFD stages, the uncertainties are contributed by the applicability of the standard modules for the particular case studied and the accuracy of plot area estimations. Also the wind speed conversion to lower altitude depends on experimental parameters.

6. Conclusions

A method for estimating inhalative exposures is proposed for occupational health risk evaluation during the development and design stages of chemical processes. The risk evaluation can be performed through chemical concentration or intake-based methods.

Both the exposure concentration and the intake amount can be calculated by standard process module based approach in the PFD stages. To depict the realistic exposure scenario local wind speed distribution is used. The results of the assessment may be used to characterize the exposure risk and to compare the design concepts based on health aspects.

The concentration-based method was tested with six alternative processes for MMA production. The result suggests the C3 as the most harmful route to health, whereas the C2/MP is the best. Data on critical wind speed was produced, from which the percentage of time the exposure is above exposure limit values can be determined. This may already provide an idea about the relative exposure level of the process concepts studied.

Both the concentration- and the intake-based risk assessment approaches were applied on the route containing a carcinogen. The study reveals that the acceptable concentration calculated based on 10^{-4} risk benchmark is smaller than that based on 10% of the exposure limit, indicating the intake-based is stricter than the concentration-based approach. The same trend is apparent for other carcinogenic compounds discussed. This is because of the different background of exposure limit values and slope factors used.

The method developed is simple and flexible for large scale continuous plants involving volatile compounds such as petrochemical plants and oil refineries. The estimation can be

done in any process development or design phase (preliminary PFD, PFD or PID stages). The method of fugitive emission calculation however varies depending on which design stage is considered. The method allows foreseeing the potential exposure risk of competing processes or the risk level of a process already in the development stage. This enables early actions on process route selection or choice of dedicated technology, such as leak proof valves or hermetic pumps, to reduce occupational exposure risks.

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