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DEVELOPMENT OF A METHODOLOGY FOR ASSESSING INHERENT OCCUPATIONAL HEALTH HAZARDS

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In the preliminary stages of chemical plant design, selecting the chemical process route is one of the main design decisions. Previously, the most important factor in selecting the best chemical process route was economics. Now safety, environmental and occupational health issues have become important considerations.

Health risks to workers could be reduced by better selection of the chemical process route during the initial stages of process design. The chemical process route may be defined as the raw material(s) and the sequence of reactions that converts them to the desired product(s). In order to choose the 'healthiest' one from a number of alternative routes, the potential health hazards must be quantified. Ranking of alternative chemical process routes based on the severity of potential health effects to the workers exposed could provide an assessment method for avoiding potential harm to humans.

The Process Route Healthiness Index (PRHI) has been developed to quantify the health hazards that might arise from chemical processes; the higher the index, the higher the hazards. The PRHI is influenced by the health impacts due to potential chemical releases and the concentration of airborne chemicals inhaled by workers.

The index has been applied to six alternative routes to methyl methacrylate (MMA). The resulting ranking is compared to those obtained from an Inherent Safety Index, an Environmental Hazard Index and production cost estimates for the same chemical process routes.

Keywords: inherent occupational health; conceptual design stage; index; assessment method.

INTRODUCTION

Inherent means that which is intrinsic to something. In order to achieve an inherently safer, healthier and environmentally friendlier (ISHE) plant, the critical step is the selection of the 'best' chemical process route, that is inherently less hazardous and less harmful to health and the environment. The chemical process route, or simply 'route', may be defined as the raw material(s) and the sequence of reactions that converts them to the desired product(s) (Edwards and Lawrence, 1993). In order to avoid accidents or hazardous events, it is better to design the plant to be ISHE, rather than installing systems to control hazards.

Occupational health is nowadays one of the most important factors to be considered when designing chemical plants, ranking alongside safety and environmental issues. The inherent safety, health and environment (ISHE) concept is a development of inherent safety, which was introduced by Trevor Kletz (1991). ISHE recognizes that occupational health should be considered and given high priority when selecting the chemical process route.

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The earlier the 'healthiness' of a proposed plant is considered, the greater are the benefits. The ISHE approach teaches that hazards that might arise in the possible routes to a product should be identified early, that is when the plant is still 'on paper'. This is because, the choice of route fixes the chemicals present in the plant and hence the actual and potential exposure of the workers. As the project proceeds through the project stages, there are progressively less opportunities for implementing inherently healthier design features. In addition, the cost of ignoring inherent healthiness factors and making retrospective changes increases.

Research on adopting ISHE principles in process design has been growing. Typical work is that reported by Edwards and Lawrence (1993) and Heikkilä (1999) who developed inherent safety indices, for ranking alternative process routes by inherent safeness. A method to assess routes for environmental friendliness has been proposed by Cave and Edwards (1997).

Occupational Health

Occupational health, or simply health, is concerned with the two-way relationship between work and health. An occupational health hazard has a potential to cause harm to human's health. Each year, more people die from diseases caused by work than are killed in industrial accidents (Wenham, 2002). Health differs from safety in terms of the time for the effect to appear. Safety deals with acute, that is serious short-term, events. Whereas, health is a chronic matter, because it takes some time before the effects on people's health can be identified and the impact might persist over a long time. This time factor compounds the task of assessing the occupational healthiness of chemical plants.

In this project, a methodology is developed for analysing new processes, which have not yet been implemented, aiming to foresee the health hazards that might arise. It is intended that all the candidate process routes for the process are ranked by their potential occupational healthiness. However, the same methodology can also be applied to existing processes.

Existing Assessment Methods

ISHE concept can be incorporated at any stage of process design or operation. However, the best results will be achieved if it is implemented at the earliest phase of process design. Among safety, health and environmental aspects, safety issue draws the most attention from researchers in academia as well as in the industries. Various qualitative and quantitative methods were developed for the assessment of chemical process safety. Among others (besides those mentioned previously) are by Khan and Abbasi (1998a) (RRABD), Khan *et al.* (2001) (SweHI), Mansfield (1997) (INSET), Palaniappan *et al.* (2002a, b) (*i*Safe) and Gupta and Edwards (2003) (Graphical Method).

Occupational health aspect, on the other hand, has received limited attention as compared to process hazards. Nevertheless, there are still quite a number of existing methods addressing this area. The examples of these methods include; by Koller *et al.* (1999, 2000) (EHS), Shah *et al.* (2003, 2005) (SREST), Khan and Abbasi (1998b) (HIRA) and by Sheng and Hertwich (1998) (HHS). However, all of the above-mentioned methods attend to health aspect only as part of the other main aspects. For instance, in EHS and SREST methods, they addressed health issue alongside safety and environmental issues. Meanwhile, HIRA considered only a small part of health aspect (as HIRA main objective is to assess safety problems) and HHS evaluated health hazards as part of the environmental assessment activity. Available researches particularly addressing occupational health aspect were carried out by Johnson (2001) (OHHI) and Hellweg *et al.* (2005). Hellweg's work concentrated on adapting occupational health effects in the existing life-cycle assessment (LCA) method. The aim is to prevent overlooking key environmental-health aspects in LCA. As for Johnson, she initiated the work of assessing primarily occupational health hazards in chemical plants with the final objective of ranking the alternative process routes in term of the 'healthiness' level, to aid the process of making decision during design stage. This is the area in which the author is interested in, hence in this paper, the new method for assessing occupational health hazards in particular, is presented. Johnson's work and how it differs from the method presented in this paper are further described in the next section.

COMPARISON WITH PREVIOUS METHODOLOGY

Previously in 2001, Johnson developed a methodology to assess the occupational health of alternative process routes for proposed chemical plant. Her index was described as the Occupational Health Hazard Index (OHHI). Whereas, in this project, an index called the Process Route Healthiness Index (PRHI) is developed. The OHHI has the same objectives as the PRHI, that is to rank the process routes based on the health hazards to the workers who are exposed in the workplace. However, there are several differences between the approaches taken by the OHHI and PRHI. As in the OHHI, the PRHI takes into account the potential of activities and process conditions to cause harm to workers. However, the PRHI considers more possible activities and process conditions for a more complete assessment.

The PRHI only ranks the material in each step of the chemical process route in terms of its inherent health hazard properties based upon its National Fire and Protection Agency (NFPA) Ranking, without including the flammability and the reactivity characteristics whereas the OHHI included all these three properties in the assessment. The reason for doing this is to assess the inherent material health hazards solely by their ability to cause typical occupational disease.

Another difference between the OHHI and PRHI methodologies is the way the worker exposure concentration is estimated. Worker exposure concentration is an estimate of the chemical concentration that is potentially inhaled by the workers in the workplace. This includes airborne contaminants generated both from small leaks and fugitive emissions. The OHHI considered only fugitive emission from one sample connection as a source of worker exposure whereas in the PRHI, all possible sources are taken into consideration. All reaction steps are assumed to have the possibility of generating airborne contaminants via gaseous releases, liquid flash or evaporation from a liquid pool, depending upon the process conditions. In addition, fugitive emissions from various sources are also considered by the PRHI.

BASIS OF THE PRHI

Chemical plants are threats to human health because they expose workers in plants as well as the people living near the plant to chemicals, many of which are hazardous to health. For example, one of the incidents involving chemical exposures to workers thus resulting severe health impacts occurred in the Coalite TCP plant at Bolsover, UK in 1968. The plant produced 2,4,5-trichlorophenol (TCP), which was used for herbicides and antiseptics. On the day of the accident, a reaction runaway occurred which blew the top off the reactor and released flammable vapors that exploded and killed the shift chemist (Lees, 1996).

The explosion event itself is not within our area of interest, but the attention is on the health impacts of the plant workers exposed. The workers who were in the building during the explosion were affected but they appeared to recover after 10 days. The undamaged part of the plant was thoroughly cleaned and brought back into use while the damage part was sealed off. Some weeks later, chloracne (acne-like skin effect caused by chemicals) symptoms appeared not only among those who were in the plant at the time of the accident but also among others who had worked in the building occasionally after it had been cleaned. Within 7 months, they were 79 cases of chloracne. It is believed that the cause of the disease was not TCP itself but an impurity identified as 2,3,7,8-tetrachlorodibenzo-p-dioxin, which is also known as TCDD or dioxin. TCDD is the unavoidable byproduct, formed during the production of TCP. The toxicity of TCDD is reviewed in the Seveso Report and it was reported that TCDD is an ultra-toxic substance. This substance can enter into the body by three major possible routes which are ingestion, inhalation or skin contact. Besides chloracne, TCDD can also causes skin burns and rashes and damage to liver, kidney and urinary system as well as to the nervous system. It appears to have potential to disturb the metabolic processes. There are also various degrees of evidence for carcinogenic, mutagenic and teratogenic properties.

There are several other incident cases reported (Lees, 1996) involving TCDD exposure during plant operation before the Bolsover incident. One of them was the 100 cases of dioxin poisoning at the Rhone-Poulenc TCP plant at Pont de Claix, France in the period of 1953 to 1970.

The PRHI provides an estimate of the worst health effects that might be expected from exposure to chemicals in the workplace. It is calculated using the very limited data available when choosing a chemical process route. Furthermore, in the very early stages of the process design, much data must be estimated. The PRHI is a dimensionless number, which indicates the potential occupational health hazard of a route; higher PRHI values indicate larger hazards. The development of the PRHI takes into account all of the factors that can potentially contribute to health hazards. It assumes that all the airborne material releases are totally inhaled by the workers exposed, regardless of the plume distribution effects.

DEFINITION OF THE PRHI

The level of health hazard posed by a chemical plant is influenced by two basic factors:

(1) The chemical substances present.
(2) The amount of chemical released.

The PRHI for the possible routes that might be considered for a new plant is calculated, by evaluating the exposure to and effects of each chemical in each route. Exposure can be defined as any feature of the environmental and organizational context of the work or non-work situation that can be seen as external to individuals and might affect their health (Consensus Reports, 2001). The effects of a chemical are assessed by using the value assigned by the NFPA Ranking for Health, which indicates its inherent level of hazard to health.

In this report, chemical exposure is defined as the amount of chemical that might be released due to pipe leakage. The potential exposure is evaluated by identifying work activities and conditions that might lead to a release of the chemicals thus causing harm to health. The calculation of chemical concentration being inhaled by the workers is one of the critical steps in the PRHI method. The reason is that some chemicals are harmless in small quantities but can be very hazardous in a large quantity. Paracelsus wrote, 'All substances are poisons: there are none which is not poison. The right dose differentiates a poison and remedy' (Health and Safety Commission, 1992).

The PRHI for each route is calculated by:

$$\mathrm{PRHI} = \mathrm{ICPHI} \times \mathrm{MHI} \times \mathrm{HHI} \times \frac{WEC_{\max}}{OEL_{\min}} \qquad (1)$$

The detail steps for calculating the PRHI are listed below.

(1) Identify and penalize work activities and conditions that are potentially harmful to health. The sum of these penalties gives a number called the Inherent Chemical and Process Hazard Index (ICPHI).
(2) Penalize the chemicals based on inherent ability to cause typical occupational disease. This is called the Health Hazard Index (HHI).
(3) Rank material at each stage of the process by healthiness, based on the NFPA Ranking for Health. This gives the Material Harm Index (MHI).
(4) Identify and estimate quantifiable sources of material entering the workplace through small leaks and fugitive emissions.
(5) Estimate the Worker Exposure Concentration (WEC), which is the likely concentration of chemicals in the workers' immediate environment.
(6) Obtain or estimate the Occupational Exposure Limit (OEL) for the chemicals in the process route.
(7) Calculate the Process Route Healthiness Index (PRHI).

METHODOLOGY

The objective of this paper is to develop a methodology that enables new plants, which have not yet been built, to be assessed with respect to their potential occupational health hazards.

The methodology was designed and developed to take into account the possible factors that might affect human health in the workplace. To make it more meaningful, the methodology was developed in such a way that all the factors considered in the assessment are presented as a number, described as an index. The index equation has been developed to include all the factors that may contribute to occupational health hazards. The terms in the equation are arranged in a way that higher index values are obtained for processes with larger hazards. For example, the value of the ICPHI term will increase as the hazards become larger.

Potentially Harmful Activities and Process Conditions: Inherent Chemical and Process Hazard Index (ICPHI)

Activities that are likely to cause process materials to enter the workplace, either by normal operating or maintenance activities are identified. This step is very important in assessing the occupational health hazard of a route, because different routes may involve different activities that might expose workers to chemicals more or less frequently and in larger or smaller quantities. For the purposes of assessment, each activity is assigned a penalty; a higher penalty indicates a higher hazard posed by the activity. Penalties have been assigned based on the probability of the releases that will be caused by the activities or the process conditions. The higher the probability of the release, the higher the penalty will be. The activities are classified by type of process operation in Table 1.

Harmful conditions could potentially arise as a result of the inherent chemical and physical properties of the materials. Similarly to the activities, the process conditions and material properties are also given a penalty based upon their severity. The chemical and physical properties selected for the PRHI give an indication of the likelihood of increased maintenance or the creation of harmful conditions. The process conditions, material properties and penalties are shown in Table 2. The total penalties for activities (AP) found from Table 1, and the total penalties for conditions and properties (CP) found from Table 2, are then added to give the value of the ICPHI.

$$\mathrm{ICPHI} = \mathrm{AP} + \mathrm{CP} \tag{2}$$

Ability to Cause Typical Occupational Diseases: Health Hazard Index (HHI)

All the chemicals involved in each process route are evaluated for their ability to cause typical occupational diseases. The Occupational Safety and Health Administration (OSHA), Health Code (HC) and Health Effects (HE) list the principal effects of exposure to each substance. Health codes are used in determining whether a violation of an air contaminant standard is serious or other-than-serious. These are based on guidelines in the Field Operations Manual, OSHA Instruction CPL 2.45B, Chapter IV, 1989 (U.S. Department of Labor, 1989). The HE values range from 1 to 20, with 1 representing the most severe health effects and the effect becoming less severe as the values increase up to 20. The penalty assigned to chemicals for their ability to cause typical occupational health is termed the HHI. In order that our penalty system is consistent, in that a high value indicates the more severe situations, the OSHA penalties are inverted. A value of HHI = 21 − (HE code) is used. The value of HHI is then scaled so that the penalty assigned is consistent with the other penalties; minimum 0 and maximum 5. The scaling is done by dividing the value of HHI = 21 − (HE code) for each disease with a maximum ranking value of 20 and then multiplying it with a maximum scale of 5. Table 3 shows the penalties assigned for each health effect.

$$\text{Scaled penalty} = \frac{21 - (\text{HE code})}{20} \times 5 \tag{3}$$

Table 1. Summary of penalties for activities or operations.

Activity	Operation	Penalty
Transport	Pipe	1
	Bag	2
	Drum	3
	Vibration	4
Mode of process	Continuous	1
	Semi-continuous/Semi-batch	2
	Batch	3
Venting or flaring	Scrub vent effluent	1
	Above occupiable platform level	2
	Occupiable platform level	3
Maintenance works	No	0
	Yes	1
Others	Agitation	1
	Others (for example: sieving, filtering, and so on)	1
	Solid handling	2
	Size reduction	2
	Extrusion	3
	Air open mixing	3

Table 2. Summary of penalties for process conditions and material properties.

Condition	Range	Penalty
Temperature (°C)	Low	0
	High (>92°C)	1
Pressure (atm)	Low	0
	High (>68 atm)	1
Viscosity (cp)	Low (0.1–1 cp)	1
	Medium (1–10 cp)	2
	High (10–100 cp)	3
Ability to precipitate	No	0
	Yes	1
Density difference (sg)	Low (0–1 sg)	1
	Medium (0–1.5 sg)	2
	High (0–2.5 sg)	3
Ability to cause corrosion	No	0
	Yes	1
Volume changes (%)	Low (>25%)	1
	Medium (25–32%)	2
	High (33–50%)	3
Solubility	No	0
	Yes (50%)	1
Material state	Gas	0
	Liquid	1
	Slurry	2
	Granules	3
	Powder	4

Material Harm Index (MHI)

The NFPA assigns values ranging from 1 to 4 to chemicals according to reactivity, flammability and ability to cause health hazards. In this, 1 indicates the least hazardous condition whereas 4 indicates the most hazardous condition. For the purpose of assessing the occupational health hazard, the NFPA value for health is taken as the Material Harm Index. The MHI is obtained by summing up the NFPA values for all chemicals present in each process route. Table 4 shows the criteria used to determine the NFPA value for health.

ESTIMATING WORKPLACE CONCENTRATION

One of the critical values that must be estimated for the PRHI calculation is the concentration of chemicals inhaled by the exposed employees. There are two possible quantifiable sources of chemical emissions into the workplace; small leaks and fugitive emissions.

A literature survey indicates that workplace general ventilation rates are normally between 0.2 and 30 mixing air changes (ACH) per hour (Michael, 1997).

The average level of ventilation is not known. A guess that the average value might be halfway between 0.2 and

Table 3. Ranking matrix for occupational disease.

Diseases	Severity	21-HE	Scaled penalty
Cancer—currently regulated by OSHA as carcinogen	HE 1	20	5
Chronic (cumulative) toxicity—known or suspected animal or human carcinogen, mutagen (except Code HE1 chemicals)	HE 2	19	4.8
Chronic (cumulative) toxicity—long-term organ toxicity other than nervous, respiratory, hematologic or reproductive	HE 3	18	4.5
Acute toxicity—short-term high risk effects	HE 4	17	4.3
Reproductive hazards—teratogenesis or other reproductive impairment	HE 5	16	4.0
Nervous system disturbances—cholinesterase inhibition	HE 6	15	3.8
Nervous system disturbances—nervous system effects other than narcosis	HE 7	14	3.5
Nervous system disturbances—narcosis	HE 8	13	3.3
Respiratory effects other than irritation—respiratory sensitization (asthma or other)	HE 9	12	3.0
Respiratory effects other than irritation—cumulative lung damage	HE 10	11	2.8
Respiratory effects—acute lung damage/edema or other	HE 11	10	2.5
Hematologic (blood) disturbances—anemias	HE 12	9	2.3
Hematologic (blood) disturbances—methemoglobinemia	HE 13	8	2.0
Irritation: eyes, nose, throat, skin—marked	HE 14	7	1.8
Irritation: eyes, nose, throat, skin—moderate	HE 15	6	1.5
Irritation: eyes, nose, throat, skin—mild	HE 16	5	1.3
Asphyxiants, anoxiants	HE 17	4	1.0
Explosive, flammable, safety (no adverse effects encountered when good housekeeping practices are followed)	HE 18	3	0.8
Generally low risk health effects—nuisance particulates, vapours or gases	HE 19	2	0.5
Generally low risk health effects—odour	HE 20	1	0.3

Taken from OSHA web page, http://www.osha-slc.gov/dts/chemicalsampling/field.html.

30 is unwise, because an average level of ventilation calculation requires technical data such as air movement and air velocity. So in this project, air change rates of 0.2 and 30 were used for dilution of the concentration as worst-case and best-case scenarios respectively.

The ventilation rate, Q ($m^3\ h^{-1}$) is given by:

$$Q = \text{ACH} \times (\text{room volume}) \tag{4}$$

A hypothetical worker will respire at a rate of 20 l per minute, equating to 10 m^3 of air inhaled in an 8-h workday (Nolan *et al.*, 1995). Studies show that this corresponds to an average-sized man working at a moderate rate (Dinman, 1991). Chemicals from small leaks are assumed to diffuse into a 10 m^3 volume of air. So, the concentration of chemicals inhaled by exposed workers is actually the chemicals that have been diluted by this 10 m^3 volume of air, not the concentration at the leakage point. The ventilation rate plays a role in diluting dispersed material. In addition, the workers will not be exposed to the dispersed chemicals for the whole 8-h of a normal working shift. So, it is important to know the length of time during which workers are in the exposure area. However, as we do not know the exact exposure time, an estimate of 6 h exposure is used based upon the standard worker exposure time for maintenance personnel in industry.

Table 4. NFPA health rating criteria.

Criteria	Rating
Materials which upon very limited exposure could cause death or major residual injury even though prompt medical treatment is given, including those which are too dangerous to be approached without specialized protective equipment. This degree should include: • materials which can penetrate ordinary rubber protective clothing; • materials that under normal conditions or under fire conditions give off gases that are extremely hazardous (i.e., toxic or corrosive) through inhalation or through contact with or absorption through the skin.	4
Materials which upon short-term exposure could cause serious temporary or residual injury even though prompt medical treatment is given, including those requiring protection from all bodily contact. This degree should include: • material giving off highly toxic combustion products; • materials corrosive to living tissue or toxic by skin absorption.	3
Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given, including those requiring use of respiratory protective equipment with independent air supply. This degree should include: • materials giving off toxic combustion products; or materials giving off highly irritating combustion products; • materials, which either under normal conditions or under fire conditions, give off toxic vapours lacking warning properties.	2
Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given, including those which require use of an approved type of gas mask. This degree should include: • materials, which under fire conditions would give off irritating combustion products; • materials, which on the skin could cause irritation without destruction of tissue.	1
Materials that on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.	0

Determining the Airborne Quantity Resulting from Small Leaks

There are three possible small leak sources of airborne material that might be inhaled by the workers in the workplace.

Airborne material from gaseous release

The following equation, based on the sonic gas flow rate equation, is used to estimate the airborne quantity for a gas release (Dow Chemicals, 1998). All the symbols used are defined in the notation section at the end of this paper.

$$AQ_g = 4.751 \times 10^{-6} D^2 P_a \sqrt{\frac{MW_{avg}}{T + 273}} \quad (5)$$

Airborne material from flashing liquids

This is possible when the leak in the plant is liquid rather than gaseous. The amount of liquid spilled must be quantified. The liquid leak rate can be determined as follows (Dow Chemicals, 1998).

$$L = 9.44 \times 10^{-7} D^2 \sqrt{1000 P_g \rho_l} \quad (6)$$

The value of the diameter, D in the equation can have a maximum value of 0.25 inch (0.635 cm). This is because this hole size formation is possible in various types of process equipment (Johnson, 2001). The total liquid release is calculated by assuming that the pool reaches its final size after 15 min (Dow Chemicals, 1998).

$$W_P = 900 \text{ L} \quad (7)$$

If the liquid is stored at a temperature above its boiling point, a portion will flash into a vapour. This flashing portion is estimated by assuming that the vaporization process is adiabatic.

$$AQ_f = \left(\frac{C_p}{H_v}\right)(T_s - T_b) \times L \quad (8)$$

Airborne material evaporation from the surface of a pool

In this case, the first step is to estimate the size of the puddle as it spreads out on the ground. Since the contours of the ground cannot be known, the maximum surface area is calculated by using a typical value of spill thickness which is 1 cm (Dow Chemicals, 1998).

$$A_P = 100 \frac{W_p}{\rho_l} \quad (9)$$

The airborne quantity evaporated from the pool surface, AQ_p is given by (Dow Chemicals, 1998):

$$AQ_p = 9.0 \times 10^{-4} \left(A_p^{0.95}\right) \frac{(MW_{avg}) P_v}{T + 273} \quad (10)$$

Fugitive Emission

Fugitive emissions are 'leaks' that occur wherever there are discontinuities in the solid barrier that maintains containment. They can also be defined as emissions that cannot be caught by a capture system (Lipton and Lynch, 1987). The Environmental Protection Agency has developed four approaches to quantify fugitive emissions, which are

(1) Average Emission Factor Approach
(2) Screening Ranges Approach
(3) EPA Correlation Approach
(4) Unit-Specific Correlation Approach

Screening data is required when estimating emissions for all the approaches except Approach 1. A screening value is a measure of the concentration in the ambient air of leaking compounds that reflects the leak rate from a piece of equipment. It is measured in units of parts per million by volume, ppmv. This value can be measured by using a portable monitoring instrument to sample air near to potential leak sources on a single piece of equipment. Hence, screening values cannot be measured for new processes; so, Approach 1 is used to estimate fugitive emissions. The equation below is used to estimate total organic carbon (TOC) mass emissions from all of the equipment in a stream.

$$\text{FE} = F_A \times N \quad (11)$$

The Workplace Concentration (WC) is estimated using the values calculated above. The quantity of airborne material produced from small leaks in each stream is called SM whereas the quantity of airborne material produced from fugitive emission is called FE. SM and FE are added to estimate the minimum and maximum WC.

$$\text{WC}_{max} = \frac{(\text{SM} + \text{FE})}{Q_{min}} = \frac{(\text{SM} + \text{FE}) \text{ kg h}^{-1}}{2 \text{ m}^3 \text{ h}^{-1}} \quad (12)$$

$$\text{WC}_{min} = \frac{(\text{SM} + \text{FE})}{Q_{max}} = \frac{(\text{SM} + \text{FE}) \text{ kg h}^{-1}}{300 \text{ m}^3 \text{ h}^{-1}} \quad (13)$$

The values of Q_{min} and Q_{max} are obtained by multiplying the ACH by the room volume of 10 m^3.

DETERMINING WORKER EXPOSURE CONCENTRATION (WEC)

Finally, in order to obtain the WEC, it should be corrected with the estimated exposure time, EET_j for the *j*th workgroup compared to their normal average work time (AWD) of 8 h per day. The WEC is calculated for minimum or maximum workplace concentration, *i*, and for different groups of workers, *j*, including process operators, maintenance personnel, laboratory/instrument technicians, research and development scientists.

$$WEC_{max} = WC_i \times \frac{EET_j}{AWD} \quad (14)$$

ESTIMATING OCCUPATIONAL EXPOSURE LIMIT (OEL)

OELs are useful as a reference standard against which to compare the concentrations of the chemicals to which workers are exposed. The standards for exposure limits act as a simple indicator of hazards if limit values are exceeded. For material with no OEL or threshold limit value (TLV) available, the values must be estimated

Table 5. Summary of results.

Process route	AP	CP	ICPHI = AP + CP	HHI	MHI	WEC_{max}	OEL_{min} (kg m^{-3})	PRHI
ACH	19	43	62	73.1	39	1.33	1×10^{-6}	2351
C2/PA	12	28	40	57.0	26	34.54	21×10^{-6}	975
C2/MP	6	17	23	45.5	16	35.84	293.2×10^{-6}	21
C3	13	33	46	64.8	24	54.84	16.04×10^{-6}	2446
i-C4	9	20	29	53.8	15	0.72	14.51×10^{-6}	12
TBA	9	23	32	53.0	15	0.89	53×10^{-6}	4

AP, Penalties for Activities; CP, Penalties for Conditions; ICPHI, Inherent Chemical and Process Hazard Index; HHI, Health Hazard Index; MHI, Material Harm Index; WEC_{max}, Worker Exposure Concentration; OEL_{min}, Minimum Occupational Exposure Limit.

based on the steps outlined in the Annex. The collected OEL values for each compound are then used to calculate the average OEL for the main sources (output streams from each main reaction stage).

$$OEL_{avg} = \sum_i OEL_i \times MF_i \tag{15}$$

In the equation above, the 'partial' occupational exposure limit for an individual chemical, *i*, in each reaction step (output stream) is calculated based on its mass fraction in the stream. The total of the partial occupational exposure limit values for the chemicals in the stream equals the OEL_{avg}. The lowest OEL_{avg} among all the reaction steps of a route, OEL_{min}, is used to calculate the PRHI for the route. This is because, the lower the OEL value is, the more hazardous the effect of the chemical to human's health is. OEL_{min} is used to represent the process route in PRHI calculation as it interprets the worst-case scenario.

CASE STUDIES

The PRHI index has been tested on six process routes to produce MMA (Edwards and Lawrence, 1993). 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)
- Tertiary butyl alcohol based route (TBA)

Results and Discussion

The values for the index calculated by equation (1) are very large numbers because the PRHI formula includes division by the lowest OEL, selected from amongst all the average OELs, calculated for each reaction step, in the process route. Thus, the absolute index is divided by 10^8 to get a smaller number. This is an interesting choice of number because it is also used in calculating Fatal Accident rates; 10^8 h is equivalent to a group of 1000 workers, each with a 40-years working life. A summary of the PRHI for the case study process routes is presented in Table 5. The AP and CP in the table refer to the total penalties for activities and total penalties for conditions and properties respectively. In order to make the index values more presentable and to facilitate comparison, the PRHI values are then scaled with reference to the largest number is given a value of 100. The scaled values are listed in Table 6.

$$PRHI_{scaled} = \frac{PRHI_{unscaled}}{PRHI_{max}} \times 100 \tag{16}$$

The C3 process route has the highest Process Route Healthiness Index out of the six routes assessed. The boiling point of all materials in reaction step 1 of the C3 based process route is less than 0°C, resulting in a very high quantity of airborne material generated from a flashing liquid. The PRHI for the C3 route is therefore the highest.

However, the PRHI value calculated for the ACH process route does not demonstrate so much difference from the C3s. It has the highest penalty for activities and conditions, the highest Health Hazard and Material Harm Index values and the lowest occupational exposure limits. This is partly due to the ACH route having the largest number of reaction steps and the involvement of many materials in the process. Many of these chemicals are potentially harmful to human health. Hence, it can be concluded that both C3 and ACH process routes pose the highest potential hazard to human's health in producing MMA.

A high operating pressure of 350 atm and a large number of reaction steps in the C2/PA route are the two main causes of the high PRHI calculated. However, the PRHI for the C2/MP route is very low compared to the other three routes, with higher rank. This is a consequence of the small number (2) of reaction steps involved.

The i-C4 process route is more or less the same as the TBA route in terms of the process conditions and the materials involved. The only significant difference is the usage of tert-butyl alcohol as a raw material in the TBA process route and isobutylene in the i-C4 process route, which poses a greater health hazard to humans than the tert-butyl alcohol.

Table 6. Scaled Process Route Healthiness Index.

Process route	Scaled PRHI	Ranking
ACH	96.0	2
C2/PA	40.0	3
C2/MP	0.86	4
C3	100.0	1
i-C4	0.49	5
TBA	0.16	6

1–Posses the worst case.

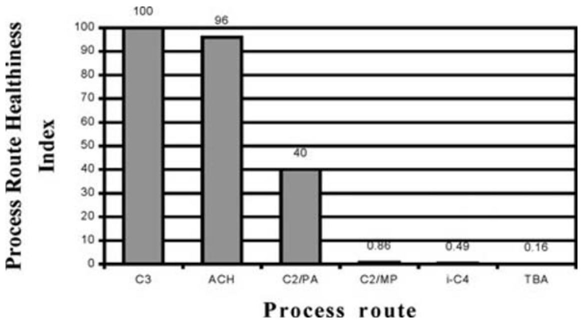

Figure 1. Process Route Healthiness Index for MMA process routes.

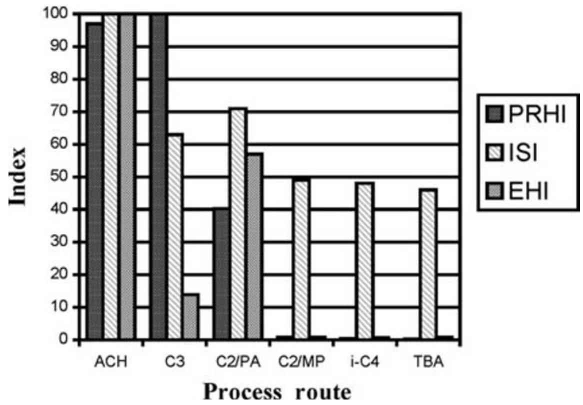

Figure 2. Comparison of index for the MMA process.

COMPARISON WITH INHERENT SAFETY INDEX, ENVIRONMENTAL HAZARD INDEX AND COST OF PRODUCTION INDEX

The same six MMA process routes have been assessed by Edwards and Lawrence (1993) in terms of their inherent safety and this was compared to plant capital cost and cost of production (COP) estimates. The index used to rank the MMA process routes for inherent safety is known as the Inherent Safety Index (ISI). The COP economics for the six process routes for MMA were estimated on the basis of producing 150 000 tonnes per year with a return on investment of 20%.

Another index that has been tested on these six MMA process routes is called the Environmental Hazard Index (EHI), developed by Cave and Edwards (1997). The EHI is a dimensionless number that indicates the potential environmental hazard of a route; the higher the EHI, the higher the environmental hazard.

The ISI defines the hazard as the potential loss of human life due to explosiveness and toxicity. The EHI defines the hazard as the loss of life of species in the ecosystem due to toxicity. The PRHI defines hazard as the health effects on humans due to chemical exposure in the workplace. The rank positions of the routes by these three indexes are tabulated below.

Based on this comparison the ACH based process route is the route that should not be considered when looking for the best process for producing MMA. Even though the ACH route ranks the second worst process ion PRHI calculation, however as mentioned before, the difference between index values calculated for C3 and an ACH route is very small. From the ranking shown in Table 7, the ACH route is potentially the least safe, healthy and environmentally friendly process with the highest cost of production. The ranking order of the routes by the ISI is very similar to that obtained by the PRHI. The 'best' three routes as ranked by the PRHI; C2/MP, i-C4 and TBA correspond perfectly with the ISI ranking. The only difference in the rankings is in the order of C3, ACH and C2/PA. However, the EHI shows significant differences in the ranking order against the PRHI except for the position of C2/MP. Although no routes are ranked radically differently.

The route rankings by the PRHI differ from those for the ISI and EHI because both these indexes are based on the chemical inventories of the routes, whereas the PRHI does not consider inventory in the assessment. This is because, in calculating PRHI, chemical inventory is not the crucial factor that could contribute to occupational health hazards among workers exposed significantly. The similarity of calculation method of the ISI and EHI resulted in a good correlation between the ISI and EHI rankings. However the PRHI is estimated based on different methods from the ISI and EHI. Comparison between PRHI, ISI, and EHI values is shown in Figure 2.

Table 7. Comparison of safety, health, environmental and cost indexes.

Order	COP	ISI	EHI	PRHI
Worst process	ACH	ACH	ACH	C3
↑	C2/PA	C2/PA	C2/PA	ACH
	i-C4	C3	C3	C2/PA
	C3	C2/MP	C2/MP	C2/MP
Best process	TBA	i-C4	TBA	i-C4
	C2/MP	TBA	i-C4	TBA

CONCLUSION

A Process Route Healthiness Index has been developed for assessing process plant occupational health hazards in the early project stages. The index has been tested on six routes to MMA. According to the case study results, several operating conditions play a major role in influencing the level of health hazard posed by a process route as assessed by the PRHI. The operating pressure, as well as the material boiling points are two parameters that affect the value of the PRHI. Equation (5) indicates the effect of absolute operating pressure on the quantity of airborne for gas releases where high pressure resulted in high airborne quantity. On the other hand, the effect of material boiling points on airborne quantity is shown by equation (8) where the lower the boiling point, the higher the airborne quantity released. Significantly, the number of reaction steps and the materials involved also have a large influence on the index values.

The PRHI cannot be and is not intended to be precise, because at the route selection stage much data is lacking and must be estimated. Without full plant specifications, no measure could give a definitive assessment. Rather the PRHI is intended as a guide to allow the selection of chemical process reaction routes based on health considerations. The index estimated for six process routes to MMA shows that it is possible to attempt quantification of health hazards in the initial stages of process design. Further work must attempt to correlate the PRHI with measurable indicators of occupational health for operating plant, in order that the index values can have any meaning or utility.

NOMENCLATURE

ACH	air changes per hour
AP	total penalties on activities
AQ_g	mass rate of vapour due to gaseous release, kg s^{-1}
AQ_f	mass rate of vapour due to flashing, kg s^{-1}
AQ_p	mass rate of vapour due to evaporation from the surface of a pool, kg s^{-1}
A_p	pool area, m^2
AWD	average working day (8 h)
CP	total penalties on conditions and properties
C_p	specific heat at constant pressure, kJ kg^{-1} $°C^{-1}$
D	diameter of the hole, mm
EET_j	estimated exposure time (h) for group of workers j
F_A	emission factor, kg h^{-1} $source^{-1}$
FE	flowrate due to fugitive emissions, kg h^{-1}
HC	health code
HE	health effects
HHI	health hazard index
H_v	heat of vaporization of the liquid, kJ kg^{-1}
i	minimum, or maximum ventilation rate
ICPHI	Inherent Chemical and Process Hazard Index
j	workgroup of process operator, maintenance personnel, laboratory/instrument technician, research and development scientist
L	liquid leak rate, kg s^{-1}
MF_i	mass fraction of chemical i
MHI	Material Harmful Index
MMA	methyl methacrylate
MW	molecular weight of the material
MW_{avg}	average molecular weight for materials in each process route
N	number of pieces of equipment of applicable equipment type in the stream
NFPA	National Fire and Protection Agency
OEL_i	occupational exposure limit for chemical i
OEL_{min}	minimum occupational exposure limit, kg m^{-3}
OEL_{avg}	average occupational exposure limit, kg m^{-3}
OSHA	Occupational Safety and Health Administration
PRHI	Process Route Healthiness Index
P_a	absolute pressure $= (P_g + 101.35)$ kPa
P_g	gauge pressure, kPa gauge
P_v	vapour pressure of the liquid, kPa
Q	ventilation rate, m^3 h^{-1}
SM	flowrate due to small leaks, kg h^{-1}
T	operating temperature, °C
T_b	normal liquid boiling point, °C
T_s	storage or operating liquid temperature, °C
TLV	threshold limit value
TOC	total organic carbon
WC_i	workplace concentration (kg m^{-3}) of minimum or maximum ventilation rate i
WEC_{max}	worker exposure concentration
W_p	total mass entering the pool, kg
ρ_l	liquid density, kg m^{-3}

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APPENDIX

(1) Estimating occupational exposure limit (OEL) or threshold limit value (TLV) if the values are not available for a chemical in route.

(a) Check for availability of Lethal Concentration LC_{50}, acute toxicity data, and assume that there is a linear relationship of the nature OEL = $(LC_{50})/K$, where K is a dimensionless constant. The value of K is estimated by calculating the average ratio of LC_{50} to OEL for the chemicals in the route where they are known.

(b) If data for the LC_{50} is not available for the compound, then use the occupational exposure limit for a compound, with a similar molecular weight and functional groups.

The assumed relationships to estimate the OEL are

- OEL (interest compound) = LC_{50}(compound)$/K$
- OEL (interest compound) = OEL (similar compound)

(2) Example of PRHI calculations

Tertiary butyl alcohol (TBA) based process route is chosen to illustrate PRHI calculations.

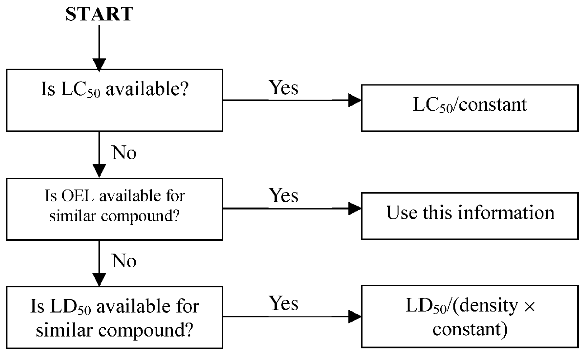

Figure A. Algorithm for estimating OEL.

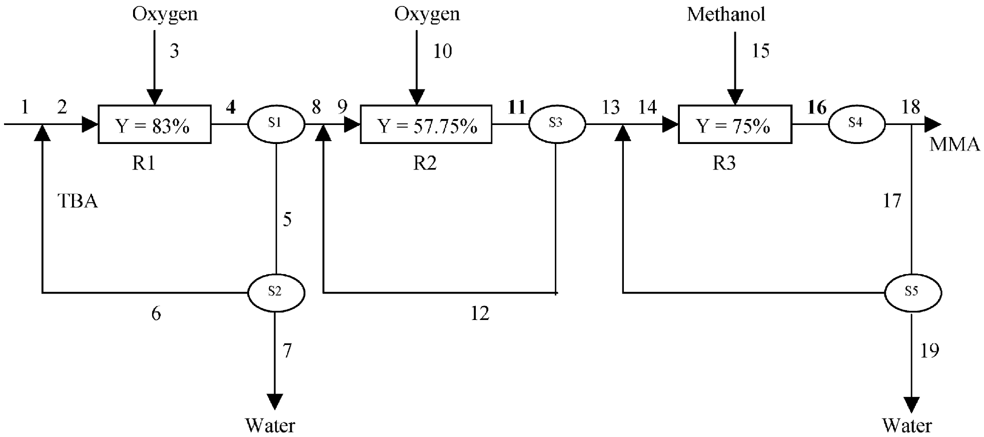

Figure B. Flow diagram of tert-butyl alcohol (TBA) process route.

Table A. Mass fraction.

		Mass fractions		
Material	MW	Stream 4	Stream 11	Stream 16
Tert butyl alcohol	74.20	0.12		
Oxygen	32.00	0.05	0.08	
Methacrolein	70.10	0.54	0.34	
Water	18.02	0.28		0.11
Methacrylic acid	86.09		0.58	0.19
Methanol	32.04			0.07
Methyl methacrylate	100.12			0.63

Table B. Penalties for activities or operations.

	Reaction Step 1		Reaction Step 2		Reaction Step 3	
Activity	Operation	Penalty	Operation	Penalty	Operation	Penalty
Transportation	Pipes—gases	1	Pipes—gases	1	Pipes—liquid	1
Process Mode	Continuous	1	Continuous	1	Continuous	1
Venting	None	0	None	0	None	0
Maintenance	Required	1	Required	1	Required	1
Other	None	0	None	0	None	0
Route total		3		3		3

Total penalties for activities, AP = 3 + 3 + 3 = 9.

Table C. Process conditions and material properties.

Step	Material	Description of condition								
		Temp (°C)	Pr (atm)	Viscosity (cp)	AP	Density	Cor	VC/MC	Solubility	MS
Step 1	Tert-butyl alcohol	350	4.8	3.355 (30°C)	No	7.86 g l^{-1}	No	1	Water soluble	Gas
	Oxygen	350	4.8	0.02075 (25°C)	No	1.309 g l^{-1} (25°C)	No	1	3.2% in water (25°C), soluble in alcohol	Gas
	Methacrolein	350	4.8	0.291 (69°C)	No	0.8 g l^{-1}	Yes	1	Water soluble: 6 g/100 ml	Gas
	Water	350	4.8	0.86 (86°F)	No	1 g l^{-1}	No	1	Soluble	Gas
Step 2	Oxygen	350	3.7	0.02075 (25°C)	No	1.309 g l^{-1} (25°C)	No	−1	3.2% in water (25°C), soluble in alcohol	Gas
	Methacrolein	350	3.7	0.291 (69°C)	No	0.8 g l^{-1}	Yes	−1	Water soluble: 6 g/100 ml	Gas
	Methacrylic Acid	350	3.7	0.32 (100°C)	No	1.018 g l^{-1} (20°C)	No	−1	Water soluble	Gas
Step 3	Water	70–100	6.8–7.5	0.86 (86°F)	No	1 g l^{-1}	No	0	Soluble	Liq
	Methacrylic acid	70–100	6.8–7.5	0.32 (100°C)	No	1.018 g l^{-1} (20°C)	No	0	Water soluble	Liq
	Methanol	70–100	6.8–7.5	0.59 (20°C)	Yes	0.791 g l^{-1}	No	0	Soluble in water and organic solvent	Liq
	Methyl methacrylate	70–100	6.8–7.5	0.53 (25°C)	Yes	0.944 sg (24°C)	No	0	Water soluble: 1.5 g/100 g	Liq

Temp, operating temperature; Pr, operating pressure; AP, ability to precipitate; Cor, corrosivity; VC/MC, volume/molar changes; MS, material state; Liq, liquid.

Table D. Penalties for process conditions and material properties.

Step no.	Penalty									Step sum
	Temp (°C)	Pr (atm)	Vis	AP	Den	Cor	VC/MC	Sol	MS	
1	1	0	2	0	3	1	1	1	0	9
2	1	0	1	0	2	1	1	1	0	7
3	1	0	1	1	2	0	0	1	1	7

Temp, operating temperature; Pr, operating pressure; Vis, viscosity; AP, ability to precipitate; Den, density; Cor, corrosivity; VC/MC, volume/molar changes; Sol, solubility; MS, material state.
Total penalties for process conditions and material properties, CP = 9 + 7 + 7 = 23.

Table E. Penalties for ability to cause occupational ill health.

Step no.	Material	HE	21-HE	Scaled penalty	HHI for material
1	Tert-butyl alcohol	15 Irritation to eyes, nose, throat and skin	6	1.5	1.5 + 3.3 = 4.8
		8 Narcosis	13	3.3	
	Oxygen	NH	NH	0	0
	Methacrolein	2 Mutagen	19	4.8	4.8
	Water	NH	NH	0	0
Total HHI for step 1 = 4.8 + 0 + 4.8 + 0 = 9.6					
2	Oxygen	NH	NH	0	0
	Methacrolein	2 Mutagen	19	4.8	4.8
	Methacrylic acid	16 Irritation	5	1.3	1.3 + 4.0 + 4.8 = 10.1
		5 Teratogen	16	4.0	
		2 Mutagen	19	4.8	
Total HHI for step 2 = 0 + 4.8 + 10.1 = 14.9					
3	Water	NH	NH	0	0
	Methacrylic acid	16 Irritation	5	1.3	1.3 + 4.0 + 4.8 = 10.1
		5 Teratogen	16	4.0	
		2 Mutagen	19	4.8	
	Methanol	16 Irritation of eyes, nose, throat, skin	5	1.3	1.3 + 3.5 + 3.5 = 8.3
		7 Narcosis	14	3.5	
		7 CNS disorder	14	3.5	
	Methyl methacrylate	16 Irritation	5	1.3	1.3 + 4.0 + 4.8 = 10.1
		5 Teratogen	16	4.0	
		2 Mutagen	19	4.8	
Total HHI for step 3 = 0 + 10.1 + 8.3 + 10.1 = 28.5					

NH, not harmful to health; NE, not established.
Total HHI for TBA route = 9.6 + 14.9 + 28.5 = 53.0.

Table F. Material harmful index from NFPA ranking.

Step no.	Material	NFPA health ranking	Penalty
1	Tert-butyl alcohol	1	1
	Oxygen	0	0
	Methacrolein	3	3
	Water	0	0
Total MHI for step 1 = 1 + 0 + 3 + 0 = 4			
2	Oxygen	0	0
	Methacrolein	3	3
	Methacrylic Acid	2	2
Total MHI for step 2 = 0 + 3 + 2 = 5			
3	Water	0	0
	Methacrylic Acid	2	2
	Methanol	2	2
	Methyl Methacrylate	2	2
Total MHI for step 4 = 2 + 2 + 2 = 6			

Total of MHI = 4 + 5 + 6 = 15.

Determining the Airborne Quantity

Airborne quantity from gas releases
(Step: 1 and 2—gas phases)
The airborne quantity from gas releases is calculated for reaction steps 1 and 2 because these processes are in gaseous phase.

$$AQ_g = 4.751 \times 10^{-6} D^2 P_a \sqrt{\frac{MW_{avg}}{T + 273}} \ (\text{kg s}^{-1}) \qquad (5)$$

where AQ_g is airborne quantity from gas releases; P_a is absolute pressure = (P_g + 101.35); P_g is gauge pressure (kPa gauge); MW_{avg} is average molecular weight $= \sum$ mole fraction$_i$ $\times$ molecular weight$_i$; T is temperature (°C); D is diameter of the hole (millimetres) = 0.25$''$ × 25.4 = 6.35 mm.
Below is an example calculation for reaction Step 1.

$$AQ_g = 4.751 \times 10^{-6} \times 6.35^2 \times 486.2 \times \sqrt{\frac{(74 \times 0.06 + 32 \times 0.06 + 70 \times 0.29 + 18 \times 0.59)}{350 + 273}}$$
$$= 0.023\,\text{kg s}^{-1}$$

A summary of airborne quantity calculation for gas releases is included in the table below.

Airborne quantity from liquid releases
(Step: 3—liquid phases)
The airborne quantity from liquid releases is calculated for reaction Step 3 because this process is in liquid phase.

Table H. Liquid leak rate.

Step no.	Operating T & P	Material	Mass fraction	Density (kg m^{-3})	Liquid leak rate
3	Liquid phase	Water	0.11	1000	0.931 kg s^{-1}
	T: 70–100°C = 85°C	Methacrylic acid	0.19	1018	
	P: 6.8–7.5 = 7.2 atm,	Methanol	0.07	791	
	P_g = 7.2–1 = 6.2 atm = 628 kPa	Methyl methacrylate	0.63	944	

T, temperature; P, pressure.

Table I. Average boiling point (T_b).

Step no.	Material	Mass fraction	T_b (°C)	Average T_b
3	Water	0.11	100	109.4°C > T
	Methacrylic acid	0.19	162.6	∴ form liquid pool
	Methanol	0.07	64.6	
	Methyl methacrylate	0.63	100	

Airborne quantity from pool evaporation
(Step: 3—$T_b > T$)
$W_p = 900 \times 0.931 = 837.9$ kg

Pool area (A_p) $= 100 \dfrac{W_p}{\rho_l}$

$$A_p = 100 \frac{837.9}{0.11 \times 1000 + 0.19 \times 1018 + 0.07 \times 791 + 0.63 \times 944}$$
$$= 87.9\,\text{m}^2$$

Table J. Data for Step 3.

Material	Mass fraction	MW	Vapour pressure (kPa)
Water	0.11	18	2.34
Methacrylic acid	0.19	86	0.13
Methanol	0.07	32	13.00
Methyl methacrylate	0.63	100	3.73
Average = $\sum MF_i \times MW_i$ or VP_i		83.56	3.54

MF, mass fraction; MW, molecular weight; VP, vapor pressure.

Table G. Airborne quantity from gas releases.

Step no.	Operating temp and pressure	Material	Molecular weight	Mole fraction	AQ_g
1	Gas phase temp: 350°C	Tert-butyl alcohol	74	0.06	0.023 kg s^{-1}
	P: 4.8 atm = 486.2 kPa	Oxygen	32	0.06	
		Methacrolein	70	0.29	
		Water	18	0.59	
2	Gas phase temp: 350°C	Oxygen	32	0.17	0.024 kg s^{-1}
	P: 3.7 atm = 374.8 kPa	Methacrolein	70	0.35	
		Methacrylic acid	86	0.48	

$$AQ_p = 9.0 \times 10^{-4}\left(A_p^{0.95}\right)\frac{(MW)P_v}{T+273}\,(\mathrm{kg\,s^{-1}}) \qquad (10)$$

$$AQ_p = 9.0 \times 10^{-4}(87.9^{0.95})\frac{(83.56)(3.54)}{85+273} = 0.052\ \mathrm{kg\,s^{-1}}$$

Table K. Estimation of fugitive emission, FE.

Step no.	Process condition	Equipment	Stream emission, *FE*	Total fugitive emission
1	Gas $P = 4.8$ atm	1 pump 1 sample point 1 pressure relief valve 2 valves	0.151	Pump: 3 Sample point: 3 Gas valve: 4 Pressure relief valve: 2
2	Gas $P = 3.7$ atm	1 pump 1 sample point1 pressure relief valve 2 valves	0.151	Total for TBA route $= 3 \times 0.0199 + 3 \times 0.0150$ $+ 4 \times 0.00597 + 2 \times 0.104$ $= 0.337$ kg h^{-1}
3	Liquid $P = 7.2$ atm	1 pump 1 sample point	0.035	

Table L. Estimation of workplace concentration.

Step no.	*SM* (kg h^{-1}) = 3600 × (kg s^{-1})	*FE* (kg h^{-1})	*SM* + *FE* (kg h^{-1})	*WC* (kg m^{-3}) = (*SM* + *FE*)/300	WEC_{max} (kg m^{-3}) = *WC* × 6/8
1	0.023 × 3600 = 82.8	0.151	82.951	0.28	0.21
2	0.024 × 3600 = 86.4	0.151	86.551	0.29	0.22
3	0.052 × 3600 = 187.2	0.035	187.235	0.62	0.46
Total worker exposure concentration (WEC_{max}) =					0.89

Table M. Calculating stream average occupational exposure limit, OEL_{avg}.

Step no.	Material	Mass fraction	OEL (mg m^{-3})	LD_{50} or LC_{50} (mg kg^{-1})	Mass fraction for OEL	OEL_{avg}
1	Tert-butyl alcohol	0.12	303 (ACGIH TLV)	NE	0.12/(0.12 + 0.54) = 0.18	0.18(303) + 0.82(24) =
	Oxygen	0.05	NR	NR	0	74.22 mg m^{-3} =
	Methacrolein	0.54	24	LD_{50}: 364	0.82	74.22 × 10^{-6} kg m^{-3}
	Water	0.28	NR	NR	0	
2	Oxygen	0.08	NR	NR	0	0.37(24) + 0.63(70) = 53 mg m^{-3}
	Methacrolein	0.34	24	LD_{50}: 364	0.34/(0.34 + 0.58) = 0.37	= 53 × 10^{-6} kg m^{-3}
	Methacrylic acid	0.58	70	LD_{50}: 1050	0.63	
3	Water	0.11	NR	NR	0	0.21(70) + 0.08(325) + 0.71(410)
	Methacrylic acid	0.19	70	LD_{50}: 1050	0.19/(0.19 + 0.07 + 0.63) = 0.21	= 331.8 mg m^{-3}
	Methanol	0.07	325 (ACGIH STEL)	LD_{50}: 5628	0.08	= 331.8 × 10^{-6} kg m^{-3}
	Methyl methacrylate	0.63	410	LD_{50}: 5204	0.71	

The lowest OEL value, OEL_{min} that will be used in PRHI calculation is 53 × 10^{-6} kg m^{-3}.

Calculating Process Route Healthiness Index (PRHI)

(1) Inherent Chemical and Process Health Index (ICPHI) = AP + CP = 9 + 23 = 32
(2) Health Hazard Index (HHI) = 53
(3) Material Harmful Index (MHI) = 15
(4) Worker exposure concentration (WEC_{max}) = 0.89 kg m^{-3}
(5) Minimum Occupational Exposure Limit (OEL_{min}) = 53 × 10^{-6} kg m^{-3}

$$\mathrm{PRHI} = \mathrm{ICPHI} \times \mathrm{MHI} \times \mathrm{HHI} \times \frac{WEC_{max}}{OEL_{min}} \qquad (1)$$

$$\mathrm{PRHI} = 32 \times 15 \times 53 \times \frac{0.89\ \mathrm{kg\,m^{-3}}}{53 \times 10^{-6}\ \mathrm{kg\,m^{-3}}} = 4.272 \times 10^8$$

In order to get a manageable number, the PRHI value is divided by 10^8

$$\mathrm{PRHI} = \frac{4.272 \times 10^8}{10^8} = 4.3 \sim 4$$

The index of the TBA based route is then scaled to make it more presentable and to facilitate comparison. This is done by dividing the index by the highest index value calculated for the six MMA process routes that are being compared. From the results, the highest index value obtained is 2446; that is from C3 based process route.

$$\mathrm{PRHI}_{\mathrm{TBA\ Scaled}} = \frac{4}{2446} \times 100 = 0.16$$