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# ASSESSING INHERENT HEALTH HAZARD FOR PROPOSED PLANTS

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**Abstract.** Proper selection of chemical process route is one of the main design decisions during the preliminary stages of chemical plant design. Previously, the most important factor for selecting the best chemical process route was only the economics. But now, safety, environmental and health issues have become important factors to be considered. Health risks on workers could also be reduced by proper selection of chemical process route. However, the health hazards needed to be quantified in order to choose the 'healthiest' route. Process Route Healthiness Index (PRHI) has been developed to foresee the potential health hazards from chemical processes. PRHIP ranks process routes in terms of their occupational healthiness. The higher the index, the higher is the hazard. PRHI is influenced by the health impact due to chemical releases and the concentration of airborne chemicals inhaled by workers. In this article, PRHI has been applied on six alternative routes for Methyl Methacrylate (MMA). The results of the ranking was compared to the Inherent Safety Index, Environmental Hazard Index and production costs for the six alternative chemical process routes.

*Keywords*: Occupational health hazard, assessment method, ISHE, ranking index

**Abstrak.** Di peringkat awal reka bentuk loji kimia, keputusan paling penting dan kritikal yang perlu dibuat adalah ketika pemilihan proses kimia yang bakal digunakan untuk penghasilan produk yang dikehendaki. Sebelum ini, ekonomi merupakan faktor yang diberi keutamaan dalam pemilihan proses kimia yang terbaik. Sebaliknya kini, faktor kesihatan, keselamatan serta alam sekitar merupakan isu penting yang menjadi tumpuan dan amat dititikberatkan dalam pengoperasian sesebuah loji. Risiko ke atas kesihatan para pekerja di kawasan loji berikutan terdedah kepada bahan-bahan kimia di tempat kerja dapat dikurangkan melalui pemilihan proses kimia yang betul. Proses yang paling 'sihat' dapat dikenal pasti dengan menjumlahkan ancaman ke atas kesihatan manusia. Dalam projek ini, PRHI telah diperkenalkan untuk menjangka potensi ancaman proses kimia ke atas kesihatan pekerja. Proses alternatif yang wujud bagi menghasilkan produk yang sama akan disusun berdasarkan tahap kesihatan yang dihasilkan oleh setiap proses. Lebih tinggi nilai indeks yang diperolehi, maka lebih berbahayalah sesuatu proses itu. Nilai PRHI dikira berdasarkan pelepasan bahan kimia serta kuantiti bahan kimia yang dihidu oleh pekerja. Indeks yang telah dibangunkan dalam projek ini diaplikasikan ke atas enam proses kimia alternatif yang wujud bagi menghasilkan metil metakrilat (MMA). Keputusan bagi pengiraan PRHI ini kemudiannya dibandingkan dengan *Inherent Safety Index* (ISI), *Environmental Hazard Index* serta kos penghasilan produk bagi kesemua enam proses alternatif.

*Kata kunci*: ISHE, teknik penilaian keselamatan loji

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## 1.0 INTRODUCTION

A chemical process route can be defined as a system involving raw material(s) and the sequence of reactions that converts them to the desired product(s)[1]. To avoid any undesirable accidents or hazardous events from occurring, it is better to design a new plant which is inherently safe, rather than to install control systems for an existing plant.

Nowadays, health issue has been taken as one of the most important factors to consider when designing a chemical plant apart from safety and environmental issues. Industrialists have seriously taken into consideration the importance of health effects to the workers exposed. Introduction of Inherent Safety, Health and Environment (ISHE) concept by Trevor Kletz [2] underlines the need to consider health factor as one of the most important priority when selecting chemical process route.

The earlier the healthiness of a proposed plant is taken into account, the greater would be the benefits. Based on the ISHE concept, the potential hazards from all the alternative production routes could be identified early. This is indeed crucial since the choice of a process route fixes the chemicals present in a plant, and hence, its healthiness.

## 2.0 DEFINITION OF PRHI

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

(1) The type of chemical substance present
(2) The amount of chemicals released

The PRHI for each route is calculated using the basis stated above, by evaluating the exposures and effects of each chemical in each route. In this report, chemical exposure is defined as the amount of chemicals released due to pipe leakage. Calculations of chemical concentration being inhaled by workers is one of the most critical steps in PRHI. This is due to the fact that some chemicals are harmless in a small quantity but can be very hazardous if they exist in a large quantity. Paracelsus wrote, 'All substances are poison. There is none which is not poisonous. The right dose differentiates a poison from a remedy' [3].

The PRHI of each route is given by:

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

## 3.0 METHODOLOGY

### 3.1 Potentially Harmful Activities and Process Conditions

Different routes may involve different activities that could possibly expose workers to chemicals more frequently. For the assessment purpose, each activity is assigned a penalty. Higher penalty indicates higher hazards posed by the activity performed (*See* Table 1).

**Table 1** Summary of penalty for activities or operations

| Activities or operations | Range | Penalty |
|---|---|---|
| Transportation | Pipes | 1 |
| | Bag | 2 |
| | Drums | 3 |
| | Vibration | 4 |
| Mode of process | Continuous | 1 |
| | Semi-continuous | 2 |
| | Batch | 3 |
| Sampling | On-line analyser | 1 |
| | Collect from close loop | 2 |
| | Runs volatile liquid on pad | 3 |
| Venting or flaring | Scrub vent effluent | 1 |
| | Above occupiable platform level | 2 |
| | Occupiable platform level | 3 |
| Maintenance works | No | 0 |
| | Yes | 1 |
| Others | Extrusion | 3 |
| | Air open mixing | 3 |
| | Solid handling | 2 |
| | Size reduction | 2 |
| | Agitation | 1 |
| | Others | 1 |

**Table 2** Summary of penalty for proses conditions

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

Potentially harmful conditions will arise as a result of the inherent chemical and physical properties, which are intrinsic in the materials involved. Like activities, these process conditions are also given a penalty based on their severity. (*See* Table 2)

## 3.2 Ability to Cause Typical Occupational Diseases

Occupational Health and Safety Association (OSHA), Health Code (HC) and Health Effects (HE) list principal effects of exposure of each substance, which is based on guideline in their Field Operations Manual, OSHA Instruction CPL 2.45B, chapter IV, 1989 [4]. The HE values range from 1 to 20, with 1 representing the most severe health effects. The effects become less severe as the value approaches to 20. To ensure the penalty system is consistant, in that a high value would indicate the more severe situations, the 21-HE code penalty system will be applied for health effects (*See* Table 3).

**Table 3** Ranking matrix for occupational disease

| Diseases | Severity | Ranking Penalty |
|---|---|---|
| Cancer–Currently regulated by OSHA as carcinogen | HE 1 | 20 |
| Chronic (Cumulative) Toxicty–Known or Suspected animal or human carcinogen, mutagen (except Code HE1 chemicals) | HE 2 | 19 |
| Chronic (Cumulative) Toxicity–Long-term organ toxicity other than nervous, respiratory, hematologic or reproductive | HE 3 | 18 |
| Acute Toxicity–Short-term high risk effects | HE 4 | 17 |
| Reproductive Hazards–Teratogenesis or other reproductive impairment | HE 5 | 16 |
| Nervous System Disturbances–Cholinesterase inhibition | HE 6 | 15 |
| Nervous System Disturbances–Nervous system effects other than narcosis | HE 7 | 14 |
| Nervous System Disturbances–Narcosis | HE 8 | 13 |
| Respiratory Effects Other Than Irritation–Respiratory sensitization (asthma or other) | HE 9 | 12 |
| Respiratory Effects Other Than Irritation–Cumulative lung damage | HE 10 | 11 |
| Respiratory Effects–Acute lung damage/edema or other | HE 11 | 10 |
| Hematologic (Blood) Disturbances–Anemias | HE 12 | 9 |
| Hematologic (Blood) Disturbances–Methemoglobinemia | HE 13 | 8 |
| Irritation-Eyes, Nose, Throat, Skin–Marked | HE 14 | 7 |
| Irritation-Eyes, Nose, Throat, Skin–Moderate | HE 15 | 6 |
| Irritation-Eyes, Nose, Throat, Skin–Mild | HE 16 | 5 |
| Asphyxiants, Anoxiants | HE 17 | 4 |
| Explosive, Flammable, Safety (No adverse effects encountered when good housekeeping practices are followed) | HE 18 | 3 |
| Generally Low Risk Health Effects–Nuisance particulates, vapours or gases | HE 19 | 2 |
| Generally Low Risk Health Effects–Odour | HE 20 | 1 |

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

## 3.3 Material Harmful Index

For assessing occupational health hazard, only value for health was taken as the Material Harmful Index, which ranges from 1 to 4. In order for the penalty system to remain consistent, the penalties were inverted, and a value of $4 - NFPA_{health}$ was used.

$$MHI = 4 - NFPA_{health} \tag{2}$$

# 4.0 ESTIMATING THE WORKER EXPOSURE CONCENTRATION (WEC)

There are two possible quantifiable sources of chemical emissions into workplace; small leaks and fugitive emission. General ventilation rate (Equation (3)) used in the estimation will not likely be less than 0.2 mixing air changes per hour (ACH) and will most likely not be higher than 30 ACH. 0.2 ACH is considered as worst-case scenario whereas 30 ACH is the best-case scenario [5].

$$\text{Ventilation rate, } Q = \text{ACH} \times (\text{room volume}) \tag{3}$$

Hypothetical worker will respire at a rate of 20 liters per minute, which is equivalent to 10 $m^3$ of air inhaled in an 8-hour workday [6]. This corresponds to an average-size man working on a moderate rate [7]. Chemicals from small leakage is assumed to be diffused into a 10-$m^3$ volume of air. However, concentration of chemicals inhaled by exposed workers should have been diluted via the dilution factor, and not by the concentration of materials at leakage point.

## 4.1 Determining Airborne Quantity via a Small Leak

Three possible sources of airborne via small leaks in the workplace that might be inhaled by the workers are:

### (i) *Airborne 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 [8].

$$AQ_g = 4.751 \times 10^{-6} D^2 P_a \sqrt{\frac{MW_{avg}}{T + 273}} \tag{4}$$

### (ii) *Airborne from Flashing Liquids*

This is possible when the leakage in a plant involves liquid instead of gaseous. The amount of liquid spill needs to be quantified first using Equation (5) [8].

$$L = 9.44 \times 10^{-7} D^2 \sqrt{1000 P_g \rho_l} \tag{5}$$

The diameter, D in the equation can have a maximum value of ¼” because hole formation of ¼” size is possible in various process equipment. [4] Part of liquids with low boiling points may instantaneously flash into a vapor. The flashed portion can be estimated via Equation (6) by assuming that the vaporization process is adiabatic.

$$F_v = \left(\frac{C_p}{H_v}\right)(T_s - T_b) \times L \tag{6}$$

### (iii) *Airborne Evaporated from the Pool Surface*

Total liquid releases was calculated by assuming that the pool would reach its final size after 15 minutes [8].

$$W_T = 900 \text{ L} \tag{7}$$

Then, the size of puddle spreading out on the ground was estimated.

$$A = 100 \frac{W_p}{\rho_l} \tag{8}$$

Airborne Quantity evaporated from the pool surface, $AQ_p$ is given by:

$$AQ_p = 9.0 \times 10^{-4} \left( A_p^{0.95} \right) \frac{(MW) P_v}{T + 273} \tag{9}$$

### *Fugitive Emissions*

Fugitive emissions are 'leaks' that occur wherever there are discontinuities in the solid barrier that maintains containment. It can also be defined as emissions that cannot be caught by a capture system [9]. Fugitive emissions are quantified using Average Emission Factor Approach developed by the Environment Protection Agency. Equation (10) is used to estimate TOC mass emissions from all of the equipment in a stream of a given equipment type.

$$E_{TOC} = F_A \times WF_{TOC} \times N \tag{10}$$

Workplace Concentration (WC) can be estimated using Equation (11) based on all the values calculated before.

$$WC_{max} = \frac{(SM + FE)}{Q_{min}} = \frac{(SM + FE) \text{ kg.h}^{-1}}{5 \text{ m}^3\text{h}^{-1}} \tag{11}$$

$$WC_{min} = \frac{(SM + FE)}{Q_{min}} = \frac{(SM + FE) \text{ kg.h}^{-1}}{300 \text{ m}^3\text{h}^{-1}} \tag{12}$$

In order to obtain WEC, Workplace Concentration (WC) should be corrected with the estimated exposure time, EET.

$$WEC_j = WC_i \times \frac{EET_j}{AWD} \tag{13}$$

## 5.0 ESTIMATION OF THE OCCUPATIONAL EXPOSURE LIMIT (OEL)

For materials with no Occupational Exposure Limit (OEL) or Threshold Limit Value (TLV) available due to lack of data, the values should be estimated. The collected OEL values for each compound are used to calculate the average OEL for the output stream from main reaction stage.

$$OEL_{avg} = {}_{\text{All i component}} OEL_i \times MF_i \tag{14}$$

## 6.0 CASE STUDIES

The index developed was tested on the MMA process. There are six main routes available to produce methyl methacrylate:

- Acetone Cyanohydrin Route (ACH)
- Ethylene via Propionaldehyde Route (C2/PA)
- Ethylene via Methyl Propionate Route (C2/MP)
- Propylene Route (C3)
- Isobutylene Route (i-C4)
- Tertiary Butyl Alcohol Route (TBA)

## 7.0 RESULTS AND DISCUSSION

A summary of PRHI for all process routes is presented in Table 4. In order to make the indeces more presentable and easier to compare to one another PRHI is scaled for each route. (*See* Table 5 and Figure 1)

$$PRHI_{scaled\ ProcessRoute} = \frac{PRHI_{unscaled\ ProcessRoute}}{PRHI_{max}} \tag{15}$$

**Table 4** Summary of results

| Process route | Act P | Cond P | ICPHI | HHI | MHI | WEC | OEL (kg/m$^3$) | PRHI |
|---|---|---|---|---|---|---|---|---|
| ACH | 25 | 43 | 68 | 289 | 39 | 1.33 | $1 \times 10^{-6}$ | 64 |
| C2/PA | 16 | 28 | 44 | 226 | 26 | 34.54 | $21 \times 10^{-6}$ | 4.81 |
| C2/MP | 8 | 17 | 25 | 181 | 16 | 35.84 | $293.2 \times 10^{-6}$ | 0.34 |
| C3 | 17 | 33 | 50 | 257 | 24 | 54.84 | $16.04 \times 10^{-6}$ | 0.34 |
| i-C4 | 12 | 20 | 32 | 213 | 15 | 0.72 | $14.51 \times 10^{-6}$ | 0.12 |
| TBA | 12 | 23 | 35 | 210 | 15 | 0.89 | $53 \times 10^{-6}$ | 0.04 |

Act P – Penalties for Activities, Cond P – Penalties for Conditions

**Table 5** Scaled process route healthiness index (PRHI)

| Process Route | Scaled PRHI | Ranking |
|---|---|---|
| ACH | 100 | 1 |
| C2/PA | 7.5 | 3 |
| C2/MP | 0.5 | 4 |
| C3 | 17 | 2 |
| i-C4 | 0.2 | 5 |
| TBA | 0.1 | 6 |

1 – Posses the worst case

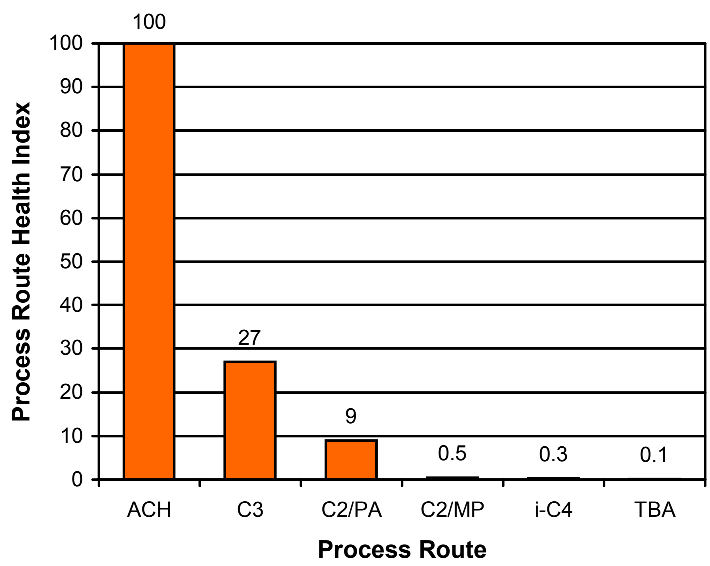


**Figure 1** Process route healthiness index for MMA process routes

The ACH process route gives the highest Process Route Healthiness Index among the six routes assessed. It has the highest penalty for activities and conditions, Health Hazard Index and Material Harmful Index and the lowest occupational exposure limits. This is due to the fact that ACH has the most reaction steps and hence, the most number of materials involved in the process.

For the C3 process route, the boiling point for all materials in reaction step 1 is less than 0°C, thereby resulting in a very high quantity of airborne generated from the liquid flashed. The PRHI for the C3 is high due to this factor.

A high operating pressure of 350 atm and a large number of reaction steps involved in the C2/PA route are the two main causes of high PRHI calculated. However, PRHI for the C2/MP route is very low as compared to the PRHI for the other three processes. This is because of the small number of reaction steps involved in the C2/MP route.

The i-C4 process route is more or less the same with the TBA route in terms of the process conditions and the materials involved. The only difference is the usage of tert-butyl alcohol as the raw material in TBA process route and isobutylene in i-C4 process route. The latter poses higher health effects to human than the tert-butyl alcohol.

## 8.0 COMPARING PRHI WITH ISI, EHI AND COP

Edwards and Lawrence had assessed the routes to MMA in term of their inherent safety and cost of production (COP)[1]. Index Safety Index (ISI) had been developed to rank MMA process routes in terms of inherent safety. The cost of production index, COP ranked the economics of the six process routes of MMA on the basis of producing one tonne with a return on investment of 20%. Sion Cave had developed another index called Environmental Hazard Index (EHI)[10]. EHI is a dimensionless number, which indicates the potential environmental hazards for a given route. Like PRHI; the higher the EHI, the higher the hazards. A comparison of the routes based on PRHI, COP, ISI and EHI is shown in Table 6.

**Table 6** Comparison of safety, health, environmental and cost indexes

| Order Scaled | PRHI | COP | ISI | EHI |
|---|---|---|---|---|
| Worst process | ACH | ACH | ACH | ACH |
| ↑ | C3 | C2/PA | C2/PA | C2/PA |
| | C2PA | i-C4 | C3 | C3 |
| Best process | C2/MP | C3 | C2/MP | C2/MP |
| | i-C4 | TBA | i-C4 | TBA |
| | TBA | C2/MP | TBA | i-C4 |

Based on the comparison, the ACH is the least safe, healthy and environmentally friendly process with the highest cost of production. The ranking order for the ISI is very similar to that for the PRHI. The only difference is in the order of the C3 and C2/PA. Routes ranking in the PRHI are different from that of the ISI and the EHI since the two latter indices are fundamentally based on the inventory of the routes whereas PRHI does not consider inventory in the assessment. The similarity of the calculation methods in ISI and EHI resulted in the similarity in terms of the ISI and the EHI ranking (*See* Figure 2).

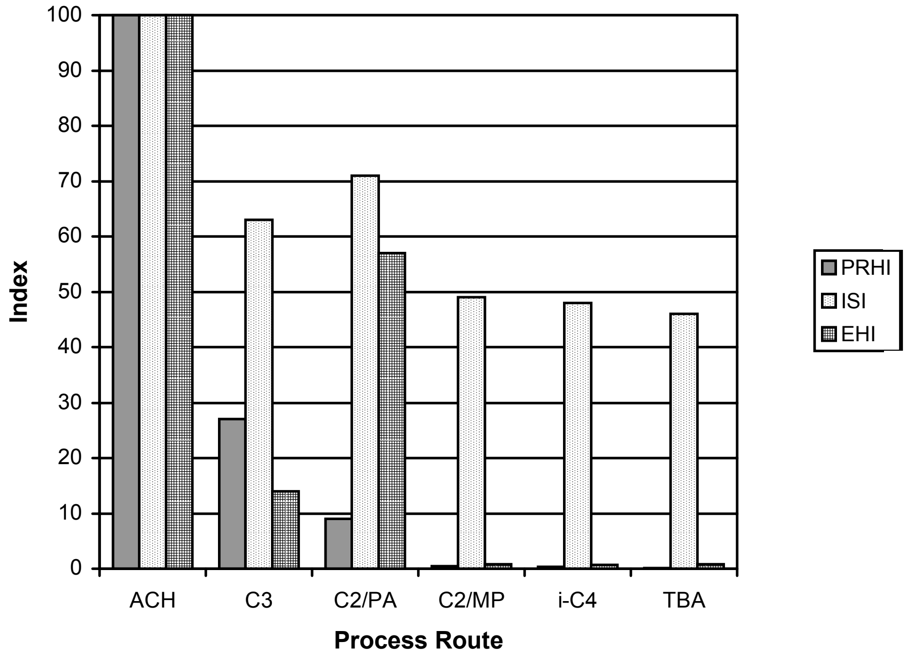


**Figure 2** Comparison of index for the MMA process routes

## 9.0 CONCLUSIONS

As a conclusion, it has been noted that the level of health hazard can be influenced by several operating conditions. The conditions include the operating pressure, temperature, and boiling point that can directly affect the value of PRHI. Besides, high level of health hazards can be attributed to the number of reaction steps and materials involved.

The PRHI is only an estimation for a proposed plant at the preliminary design stage. It is not intended to be absolutely accurate because much data is still lacking during the early stages of a plant design. Instead, this index is only developed to give a brief idea in selecting the best chemical process route to produce the desired product.

## NOTATION

| | | |
|---|---|---|
| PRHI | = | Process Route Healthiness Index |
| ICPHI | = | Inherent Chemical and Process Hazard Index |
| HHI | = | Health Hazard Index |
| MHI | = | Material Harmful Index |
| $WEC_{max}$ | = | Worker exposure concentration for $j^{th}$ group of worker, with $i^{th}$ ventilation rate ($kg/m^3$) |
| $OEL_{min}$ | = | Average Occupational Exposure Limit ($kg/m^3$) |

| | | |
|---|---|---|
| AQ | = | Airborne quantity |
| $P_a$ | = | Absolute pressure = ($P_g$ + 101.35) |
| $P_g$ | = | Gauge pressure (kPa gauge) |
| MW | = | Molecular weight of the material |
| T | = | Operating temperature (°C) |
| D | = | Diameter of the hole (mm) |
| L | = | Liquid Leak Rate (kg/sec) |
| $\rho_l$ | = | Liquid density (kg/m$^3$) |
| $P_g$ | = | Gauge pressure (kPa gauge) |
| $F_v$ | = | Mass rate of vapor due to flashing (kg/sec) |
| $C_p$ | = | Specific heat at constant pressure (J/kg/°C) |
| $H_v$ | = | Heat of vaporization of the liquid (J/kg) |
| $T_s$ | = | Storage or operating liquid temperature (°C) |
| $T_b$ | = | Normal liquid boiling point (°C) |
| $W_p$ | = | Total mass entering the pool (kg) |
| $A_p$ | = | Pool area (m$^2$) |
| $P_v$ | = | Vapor pressure of the liquid (kPa) |
| T | = | Operating temperature (°C) |
| $E_{TOC}$ | = | Emission rate of TOC from all equipment in the stream of a given equipment type (kg/hr) |
| $F_A$ | = | Emission Factor (kg/hr/source) |
| N | = | Number of pieces of equipment of applicable equipment type in the stream |
| $WF_{TOC}$ | = | Average weight fraction of TOC in the stream |
| WC | = | Workplace concentration (kg/m$^3$) |
| SM | = | Flowrate due to Small Leaks (kg/hr) |
| FE | = | Flowrate due to Fugitive Emissions (kg/hr) |
| Q | = | Ventilation Rate (m$^3$/hr) |
| $OEL_i$ | = | Occupational Exposure Limit for $i^{th}$ component |
| $MF_i$ | = | Mass Fraction for $i^{th}$ component |
| $EET_j$ | = | Estimated Exposure Time (hr) for $j^{th}$ group of worker |
| AWD | = | Average Work Day (8 hours) |

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