

Uncertainty Analysis for Toxicity Assessment of Chemical Process Designs

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There is a growing awareness in the chemical industry that environmental aspects need to be incorporated more fully into the design and operation of chemical processes. There are several recently developed methodologies to perform environmental assessments of chemical process designs. However, the value of the environmental information is dependent upon the level of uncertainty in the predictions of these impacts. This paper presents an uncertainty analysis for toxicity assessment of chemical process designs. This uncertainty analysis generated representative normalized standard errors for several measured environmental properties (Henry's law constant, octanol–water partition coefficient, hydroxyl radical reaction rate constant, and lethal concentration for human inhalation toxicity) from a subset of the high production volume chemicals. Then, the propagation of these property uncertainties in the calculation of an inhalation toxicity index was conducted. This method of uncertainty analysis has been applied to the environmentally conscious design of a process for volatile organic compound recovery and recycle from a gaseous waste stream.

1. Introduction

There are several recently developed methodologies that can be used to perform environmental assessments of chemical processes. The method of minimizing environmental impact^{1–4} embeds principles from life cycle assessment within a chemical process optimization framework. The waste reduction algorithm,^{5–8} developed by the U.S. Environmental Protection Agency, characterizes the flow and generation of potential environmental impact through a chemical process. Nine potential impact indices ranging from the ozone depletion potential to human toxicity and ecotoxicity are used; however, the effects of energy consumption in the process are not considered in this method. Neither of these two methods accounts for the fate and transport of the emitted chemicals. The Environmental Fate and Risk Assessment Tool (EFRAT)⁹ integrates all of the key steps of impact assessment into a single methodology and software tool. These steps include (1) process release estimation, (2) pollutant fate and transport, (3) assessment of exposure potential, and (4) relative risk assessment. This assessment methodology and tool has been integrated with a commercial process simulator package, HYSYS.^{10,11} Although tremendous work has been done to include environmental concerns in process designs, the uncertainty of these assessments has not been adequately addressed.

For the environmental assessments to be of maximum value, the uncertainty of the predicted environmental impacts should be quantified and included in the analysis. The goal is to achieve the best design under uncertainty. As in any system, uncertainty is an inherent characteristic. There are several categories of uncertainty. One is "internal uncertainty"¹² caused by the

modeling procedure, which translates process phenomena into a set of mathematical formulations. Because of the complexity of the system and the limitation of human knowledge, the assumptions made in the modeling process introduce uncertainty. Another type of uncertainty is generated by the uncertainties in model parameters and is called "model-inherent uncertainty".¹³ This is a result of difficulties in obtaining data or data coming from different sources. This type of uncertainty can be characterized by a probability distribution function. The third type of uncertainty, "process-inherent uncertainty",¹³ is due to process parameter fluctuation, such as flow rate or temperature variations, and can also be described by a probability distribution function. In addition to those uncertainties discussed above, "external uncertainty" is driven by the factors external to the process, such as the predicted price of the product or custom orders.¹³ The uncertainty caused by the preference of the decision makers can also be categorized as external uncertainty. For example, in multicriteria decision analysis, the decision is sensitive to the weights assigned to the different criteria. The last category is "discrete uncertainty",¹³ which is due to the random discrete events such as catastrophe releases.

Several approaches have been developed for quantifying uncertainty. The error propagation method is the least complex, in which the errors of the input data accumulate through the calculation. Monte Carlo techniques can provide a probability function of calculated results using random values of raw data. Regression methods,¹⁴ such as Probit, Logit, and Weibull, are applicable for cases having limited data.

The uncertainty analysis of environmental impacts has received increasing attention recently with the development of assessment methodologies. Cano-Ruiz and McRae¹⁵ identified several research needs for environmentally conscious design, including "incorporating uncertainty information into databases of properties relevant to environmental characterization of processes and investigating the sensitivity of the design

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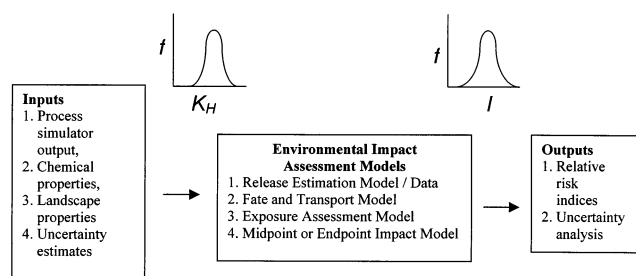


Figure 1. Propagation of model uncertainty through the EFRAT toxicity assessment method.

decisions due to those uncertainties". Although it has gained much interest, there are few publications in this area because it is hindered mainly by two factors, the difficulty of modeling and limited data. Several researchers have conducted studies on the uncertainty of toxicity assessment. Monte Carlo techniques have been applied for quantitative uncertainty analysis in public health risk assessment by Thompson et al.,¹⁶ Duncan et al.,¹⁷ and McKone and Bogen.¹⁸ The estimated distributions of the model parameters were used because the limited availability of data made it almost impossible to get the exact distribution. The analyses are applicable for determining the uncertainty of a specific chemical for which raw data are available, although limited. A limitation of these studies is that the uncertainty analyses were not carried through the stage of process design. It has not yet been investigated as to how the impact assessment uncertainties influenced the design of chemical processes and the selection of process operating configurations.

The purpose of conducting this study is to gain a better understanding of the uncertainties expected to be encountered when conducting environmental impact assessment of process designs. Because of the importance of toxicity in decision making, inhalation toxicity was chosen in this study as a representative environmental index. Also, because the high production volume (HPV) chemicals are so important to the economy and their potential environmental impacts so large, a subset of these chemicals formed the basis of the analysis. We will focus only on the characterization of *model-inherent* uncertainty for human inhalation toxicity assessment of chemical process design. The method presented can be extended to other types of environmental indices. Full assessment of all categories of environmental impacts requires a great deal of effort in collecting and analyzing data. Therefore, the uncertainty analysis of a single index is more manageable and is demonstrated here. Figure 1 shows the propagation of model inherent uncertainty (Henry's constant, K_H) through an environmental impact assessment method yielding uncertainty in an environmental index, I .

In the next section, the uncertainty of several environmental physical and toxicological properties will be characterized (Henry's law constant, octanol–water partition coefficient, oxidation reaction rate constant, and lethal concentration for human inhalation toxicity) from a subset of the HPV chemicals. The uncertainty in these properties will be propagated through the environmental impact assessment methodology (EFRAT).⁹ Finally, the uncertainty analysis will be applied to the assessment of inhalation toxicity of a solvent recovery process involving absorption and distillation.

2. Methods

Toxicity Assessment Model. EFRAT⁹ was used to evaluate the effects of model-inherent uncertainty for human inhalation toxicity assessment. The human inhalation toxicity potential ($I_{\text{INH},i}^*$) is calculated using eq 1, where LC_{50} is lethal concentration for inhalation

$$I_{\text{INH},i}^* = \frac{\text{LC}_{50,B} \tau_A D_{A,i}}{\text{LC}_{50,i} \tau_{A,B} D_{A,B}} \quad (1)$$

toxicity (mg/m^3), τ_A is the reaction half-life in air at 25 °C (h; eq 2), D_A is the mole fraction of the emitted chemical partitioned to the atmosphere (eq 3), and the subscripts i and B represent the emitted chemical and the benchmark compound, respectively. The reaction half-life is calculated by eq 2, given the hydroxyl radical reaction rate constant k_{OH} (h^{-1}).

$$\tau_A = \frac{\ln 2}{k_{\text{OH}}} \quad (2)$$

D_A is calculated using a "level I" Mackay-like multimedia compartment model,¹⁹ as shown in eq 3, where

$$D_A = \theta_a(\theta_{aa}K_H + \theta_{aw} + \theta_{as}\rho_{as}K_{ds}) / \left[\theta_a(\theta_{aa}K_H + \theta_{aw} + \theta_{as}\rho_{as}K_{ds}) (\text{air}) + \theta_w(\theta_{ww} + \theta_{ws}\rho_{ws}K_{ds} + \theta_{ww}\rho_f \text{BCF}_f) (\text{water}) + \theta_s(\rho_{ss}K_{ds} + \theta_{sw} + \theta_{sa}K_H + A_s\rho_p \frac{K_{ps}}{F_{dps}}K_{ds}) (\text{soil}) + \theta_b(\theta_{bw} + \theta_{bs}\rho_{bs}K_{ds} + \rho_b \text{BCF}_b) (\text{sediment}) \right] \quad (3)$$

K_H is the Henry's law constant at 25 °C (m^3 of water/ m^3 of air), and BCF_f , BCF_b , K_{ds} , and K_{ps} are functions of K_{OW} . K_{OW} is the octanol–water partition coefficient at 25 °C (m^3 of water/ m^3 of octanol). Refer to the Nomenclature section for other elements.

The actual human inhalation toxicity is obtained by multiplying eq 1 by the emission rate of the chemical and summing over all chemicals emitted from the process, as shown in eq 4, where E_i is the emission rate

$$I_{\text{INH}} = \sum_{i=1}^{n'} (I_{\text{INH},i}^* E_i) \quad (4)$$

(kg/yr) of chemical i and n' is the number of chemicals emitted from the process. Thus, eq 4 represents the total impact of the process expressed in equivalent emission units of the benchmark compound, which for inhalation toxicity is chosen to be toluene.

The emission rate (E_i) to the air for each pollutant from a chemical process is given by

$$E_i = \sum_k m_i^k \text{EF}_i^k + \sum_l q_l \frac{\text{EF}_i^l}{\text{HV}_l \text{EFF}_l} + \sum_m E_i^m \quad (5)$$

where m_i^k is the mass flow rate of chemical i within unit operation k (kg/yr), EF_i^k is an emission factor of chemical i (kg of pollutant emitted/ kg of throughput) for unit operation k , q_l is the energy duty for unit l (kJ/yr), EF_i^l is an emission factor of chemical i for combustion-related emissions for criteria pollutants and toxic

releases (kg of pollutant/kg of fuel combusted) for unit l , HV_l is a heating value for the fuel (kJ/kg of fuel) in the unit l , EFF_l is a utility efficiency for unit l (approximately 0.85 for a reboiler), and E_i^m is a direct release of chemical i from the unit m as predicted by a process model (chemical process simulator for the absorber column, storage tank model, etc.).

Propagation of Uncertainty. The relevant properties for human inhalation toxicity assessment of these chemicals were Henry's law constant (K_H) at 25 °C (in eq 3), octanol–water partition coefficient (K_{OW}) at 25 °C (in eq 3), hydroxyl radical reaction rate constant (k_{OH}) at 25 °C (in eq 2), and lethal concentration (LC_{50}) for human inhalation toxicity (in eq 1). The root-mean-square error (e_{RMS}) for the human inhalation toxicity index is calculated by the error propagation method through eq 6.²⁰ Each term is the partial derivative of I_{INH} with respect to the variables in eqs 1 and 4 evaluated at the average value of these variables with all other variables held constant. Detailed derivations appear in the appendix.

$$e_{RMS, I_{INH}} = \left[\sum_{i=1}^n \left\{ \left(\frac{\overline{I_{INH,i}^*} \overline{E_i}}{\overline{LC_{50,B}}} e_{S, LC_{50,B}} \right)^2 + \left(\frac{\overline{I_{INH,i}^*} \overline{E_i}}{\overline{\tau_{A,i}}} e_{RMS, \tau_{A,i}} \right)^2 + \left(\frac{\overline{I_{INH,i}^*} \overline{E_i}}{\overline{D_{A,i}}} e_{RMS, D_{A,i}} \right)^2 + \left(\frac{\overline{I_{INH,i}^*} \overline{E_i}}{\overline{LC_{50,i}}} e_{S, LC_{50,i}} \right)^2 + \left(\frac{\overline{I_{INH,i}^*} \overline{E_i}}{\overline{\tau_{A,B}}} e_{RMS, \tau_{A,B}} \right)^2 + \left(\frac{\overline{I_{INH,i}^*} \overline{E_i}}{\overline{D_{A,B}}} e_{RMS, D_{A,B}} \right)^2 + \left(\frac{\overline{I_{INH,i}^*} \overline{E_i}}{\overline{E_i}} e_{RMS, E_i} \right)^2 \right\} \right]^{1/2} \quad (6)$$

where

$$e_{RMS, D_A} = \sqrt{\left(\frac{\partial D_A}{\partial K_H} e_{S, K_H} \right)^2 + \left(\frac{\partial D_A}{\partial K_{OW}} e_{S, K_{OW}} \right)^2} \quad (7)$$

and

$$e_{RMS, \tau_A} = \sqrt{\left(\frac{\overline{\tau_A}}{\overline{k_{OH}}} e_{S, k_{OH}} \right)^2} \quad (8)$$

and

$$e_{RMS, E_i} = \left[\sum_k \left[\left(\frac{\overline{E_i^k}}{\overline{m_i^k}} e_{S, m_i^k} \right)^2 + \left(\frac{\overline{E_i^k}}{\overline{EF_i^k}} e_{S, EF_i^k} \right)^2 \right] + \sum_l \left[\left(\frac{\overline{E_i^l}}{\overline{q_l}} e_{S, q_l} \right)^2 + \left(\frac{\overline{E_i^l}}{\overline{EF_i^l}} e_{S, EF_i^l} \right)^2 \right] + \sum_m \left(\frac{\overline{E_i^m}}{\overline{E_i^m}} e_{S, E_i^m} \right)^2 \right]^{1/2} \quad (9)$$

The overbars represent the mean values of the properties or the variables evaluated using average property values. The standard error for properties in

Table 1. Confidence Level Parameter for a Two-Sided t Test with the Average Number of Replicates of 7

confidence level (%)	t	confidence level (%)	t
99	3.71	80	1.44
95	2.45	50	0.72
90	1.94		

eqs 6–9 is represented by e_S , which measures the deviation of the mean value from the true value. In eq 9, E_i^k is the emission rate of chemical i from unit k ($m_i^k EF_i^k$) and E_i^l is the emission rate of chemical i from utility combustion unit l ($q_l EF_l / HV_l EFF_l$).

The root-mean-square error measures the deviation of the calculated value from the true value too. Unlike e_S , it is calculated by error propagation, not statistical analysis of data. It can be shown statistically that the true value of I_{INH} lies between

$$\overline{I_{INH}} - te_{RMS, I_{INH}} < I_{INH} < \overline{I_{INH}} + te_{RMS, I_{INH}} \quad (10)$$

where t is related to P (confidence level) as shown in Table 1.

Environmental Property Data Analysis. This study analyzed variations in four measured environmental properties representing the top 100 HPV chemicals used in the industries.²¹ Literature sources were found, and replicate measurements of these properties^{19,22–26} were tabulated. For each property, between 9 and 16 chemicals were chosen from the list of the HPV chemicals. Table 2 lists the selected chemicals for each property. Statistical analyses on these physical properties were performed, such as calculating the mean (\bar{x}), standard deviation (σ), coefficient of variation ($COV = \sigma/\bar{x}$), and standard error ($e_S = \sigma/\sqrt{n}$, where n is the number of replicate measurements for each chemical) and creating probability plots. The COV represents the spread in the measured data normalized by the mean value. The probability plots help determine whether the data are described by a normal or a log-normal distribution. These analyses lead to the calculation of representative normalized standard errors (RNSE) for each property

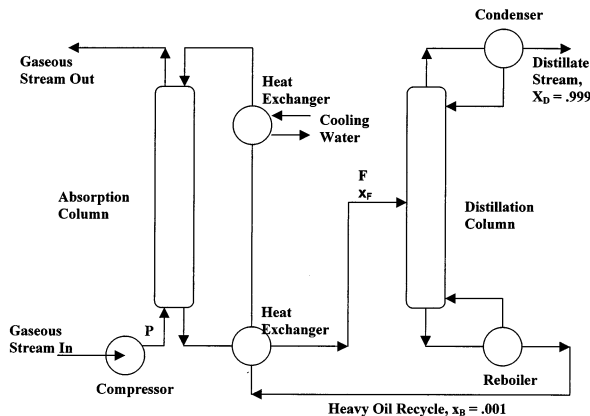
$$RNSE_i = \sum_{k=1}^{N_i} (e_{S,k} \sqrt{\bar{x}_k}) / N_i \quad (11)$$

where subscript i denotes the property, k denotes the selected chemical for statistical analysis for property i , and N_i is the number of chemicals from the HPV list for that property. The advantage of the RNSE for any property is that the standard error for any other HPV chemical can be estimated using the product of the chemical's mean property value and the RNSE ($e_S = \bar{x} RNSE$).

Test for Normality or Log-Normality. The COV test for normality is the simplest test available to determine whether the data can be characterized by a normal distribution. If COV exceeds 0.5 or 1.0, there is strong evidence that the data are not normally distributed. Probability plots are procedures routinely used for making quantitative and subjective statistical analyses of data sets by plotting the magnitude versus a cumulative distribution function. The abscissa scale of normal probability paper is an arithmetic scale and is defined by the sample values. The ordinate scale is calculated as a cumulative distribution function, such as Califor-

Table 2. Selected Chemicals from the HPV List for Statistical Analysis of Each Property

chemical name	chemical property			
	K_{OW}	K_H	k_{OH}	LC_{50}
toluene	toluene	toluene	toluene	toluene
nitrobenzene	chlorobenzene	chlorobenzene	<i>o</i> -xylene	styrene
benzenamine	trichloromethane	trichloromethane	<i>m</i> -xylene	acetic acid ethenyl ester
phenol	ethylbenzene	ethylbenzene	<i>p</i> -xylene	1,1,1-trichloroethane
	1,1-dichloroethane	1,1-dichloroethane	hexane	hydrocyanic acid
tetrachloroethene	1,1,1-trichloroethane	1,1,1-trichloroethane	octane	1,2-dichloroethane
ethylbenzene	dichloromethane	dichloromethane	butene	trichloromethane
trichloromethane	naphthalene	naphthalene	2-methyl-2-butene	dichloromethane
chlorobenzene	trichloroethylene	trichloroethylene	hexene	1,1,2-trichloroethane
bis(2-ethylhexyl)phthalate			2-methyl-1,3-butadiene	chlorine
			cyclopentene	trichloroethylene
			cyclohexene	acetaldehyde
			trichloroethylene	carbonic dichloride
			ethanol	(chloromethyl)oxirane
			formaldehyde	
			acetaldehyde	

**Figure 2.** Absorption/distillation process for recovery of toluene and ethyl acetate from a gaseous waste stream.

nia, Hazen, Beard, or Weibull. The Weibull plotting position formula was used in this work.

$$P_k = \frac{k}{n+1} \quad (12)$$

P_k is the Weibull plotting position, k is the rank of replicate values from low to high, and n is the total number of replicate values. If the data points appear as a straight line when plotted, they can be considered normally distributed. This procedure was then repeated using the logarithm of the data.

3. Application of the Uncertainty Analysis

This uncertainty analysis methodology was applied to a relatively simple separation process as shown in Figure 2. Both toluene and ethyl acetate flow at a rate of 193.5 kg/h each into the absorber in the inlet gas stream, with the remainder being dry nitrogen. A two-step separation process is used: absorption into a heavy oil (1-decanol), followed by distillation for separating the heavy oil from the volatile organic compounds (VOCs), which exit the column condenser at the top. x_B and x_D in this figure are the mole fractions of VOCs in the bottom and overhead products from the distillation column, respectively.

The following gaseous stream data were used in this analysis: 12 000 scfm, 1 atm of pressure, 150 °F, 193.5 kg of toluene/h, 193.5 kg of ethyl acetate/h. The objective of the analysis was to determine the effects of the absorber column pressure (1–5 atm) and percent re-

covery of VOCs (ethyl acetate-key component) (0–80%) on the inhalation toxicity index, venture profit, and uncertainty of the inhalation toxicity index.

Equipment Design. (a) Absorber. The flow rate of the absorption oil recycle rate (mol/s) into the absorber was set by

$$L_{in} = 1.5mG_{in}^{.27} \quad (13)$$

where G_{in} is the flow rate of the gaseous waste stream (mol/s) and m is the slope of the equilibrium line of ethyl acetate (key component) in the absorber, that is, the ratio of the partial pressure of ethyl acetate, P_{EA} (atm), to the total column pressure, P_{Total} (atm), assuming ideal liquid mixtures,

$$m = \frac{P_{EA}}{P_{Total}} \quad (14)$$

The mass balance for each component in the absorber column was completed, and the column was designed using Kremser's equation.²⁸ The minimum number of trays is

$$N_{min} = \frac{\ln\left[\left(1 - \frac{mG}{L}\right)(y_{in,EA} - mx_{in,EA}) + \frac{mG}{L}\right]}{\ln\left(\frac{L}{mG}\right)} \quad (15)$$

where G and L are gas and liquid flow rates in the column both having units of mol/s and $y_{in,EA}$ and $x_{in,EA}$ are the mole fractions of ethyl acetate in the gas entering the bottom and liquid phases at the top of the absorber, respectively.

The efficiency of absorption (η) is assumed to be 15%; therefore, the actual number of trays is $N_{actu} = N_{min}/\eta$.

The column diameter (D_C ; m) was determined from the flooding velocity (U_f ; m/s) using eq 16, estimated from the flow conditions at the top stage of the column.²⁹

$$D_C = \left[\frac{4V}{0.9\pi\rho_v U_f} \right]^{1/2} \quad (16)$$

where ρ_v is the mass density of the gas stream (kg/m³) and V is the mass flow rate of the gas stream (kg/s). The calculation of U_f can be found in standard texts.²⁸

(b) Distillation Column. For the distillation column, toluene and ethyl acetate were combined into a single “pseudocomponent” having the properties of toluene (key component) and coupled with the absorption oil, a “binary” mixture resulted upon which to design the column. A constant relative volatility ($\alpha_{\text{Tol},1-\text{DOH}}$) was used in this design as defined by the following equation:

$$\alpha_{\text{Tol},1-\text{DOH}} = \frac{P_{\text{Tol}}}{P_{1-\text{DOH}}} \quad (17)$$

where P_{Tol} and $P_{1-\text{DOH}}$ are the partial pressures of toluene and 1-decanol in the distillation column evaluated at the average column temperature with the units of atm.

The oil from the absorber is fed into the distillation column; therefore, the feed information of the distillation column is obtained by the mass balance of the absorber. The flow rate of feed (F ; mol/s) is equal to the output flow rate of absorption oil from the absorber. The mole fraction of the pseudocomponent x_F is calculated by the following equation:

$$x_F = x_{\text{out,EA}} + x_{\text{out,Tol}} \quad (18)$$

where $x_{\text{out,EA}}$ and $x_{\text{out,Tol}}$ represent the mole fractions of ethyl acetate and toluene in the absorption oil from the absorber.

The minimum reflux ratio is obtained by assuming that the feed is at the bubble point

$$R_{D,\text{Min}} = \frac{F}{D} \frac{1}{(\alpha_{\text{Tol},1-\text{DOH}} - 1)} \quad (19)$$

where D is the flow rate of the overhead product (mol/s).

The optimum reflux ratio is approximately 1.2 times the minimum reflux ratio²⁷

$$R_D = 1.2 R_{D,\text{Min}} \quad (20)$$

The mole balance around the distillation column was calculated using standard equations.²⁸

The minimum number of trays is calculated by the Fenske–Underwood equation²⁷

$$N_{\text{min}} = \frac{\log\{[x/(1-x)]_{\text{ovhd}}/[x/(1-x)]_{\text{btms}}\}}{\log \alpha_{\text{Tol},1-\text{DOH}}} \quad (21)$$

where x is the mole fraction of the pseudocomponent in the liquid phase and subscripts ovhd and btms denote overhead and bottom products. The efficiency of the distillation column is assumed to be 75%, and therefore the actually number of trays is

$$N_{\text{actu}} = 2N_{\text{min}}/\eta \quad (22)$$

The distillation column diameter is obtained using eq 16 also.

Cost Analysis. The venture profit, VP (\$), is chosen as the economic indicator, and it includes the sales revenue of ethyl acetate and toluene, capital cost of the absorber and distillation column, utility costs, and taxes.

The purchase cost, C_{BM} (\$), equation for the absorber and distillation column is

$$C_{\text{BM}} = 1780L_C^{0.87}D_C^{1.2327} \quad (23)$$

where L_C is the column length (m), which is related to the actual number of trays.

The energy consumption in the process was calculated for the reboiler²⁸ and the compressor.³⁰ The reboiler duty (kJ/s) was calculated using the following equation:

$$Q_R = \bar{V}\lambda \quad (24)$$

where \bar{V} is the stripping section vapor flow rate (mol/s) and λ is the latent heat of vaporization of the absorption oil (1-decanol; 58.88 kJ/mol).

For the absorber compressor, the energy consumption (kJ/kg of the gas stream) was evaluated by

$$Q_C = \left(\frac{\gamma}{\gamma - 1} \right) \left(\frac{RT_{\text{in}}}{MW_{N_2}\eta_{\text{isentropic}}} \right) \left[\left(\frac{P_{\text{out}}}{P_{\text{in}}} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (25)$$

where γ is the heat capacity ratio (C_P/C_V), assumed to be 1.4, $\eta_{\text{isentropic}}$ is the isentropic coefficient (0.6), MW_{N_2} is the molecular weight of N_2 , P_{out} is the pressure out of the compressor (atm), and P_{in} is the gas pressure into the compressor, assumed to be 1 atm. The energy consumption was converted to the utility costs assuming steam was used in the reboiler and electricity in the compressor.

The venture profit was obtained by

$$VP = S - \text{COS} - \text{FIT} - rC_{\text{TCI}} \quad (26)$$

where S is the annual sales revenue of the ethyl acetate and toluene (\$), COS (cost of sales) is the annual utility cost including reboiler steam and compressor electricity (\$), FIT is the federal income tax (\$) and is given by $(t\%/100)(S - \text{COS})$ ($t\%$ is the tax rate, assumed to be 37%), C_{TCI} is the total capital investment cost (purchase cost of the absorber and distillation column) (\$), and r is the desired rate of return, assumed to be 0.20.

Toxicity Impact Assessment. The impact assessment presented here is “gate-to-gate” except for the releases caused by electricity generation remote from the facility. The major emission sources included in the study were direct emissions from the absorber vent and criteria pollutants from the energy consumption of the distillation column reboiler and absorber compressor. It was assumed that the emission of ethyl acetate and toluene dominated the direct emissions from the absorber and the emission of 1-decanol was insignificant. This assumption is valid based on the results of a prior study.³¹ The emission of ethyl acetate from the absorber was defined by the specified recovery, and the emission of toluene was calculated by the mass balance equations of the absorber. For the emissions from energy consumption, the major criteria pollutant of concern for inhalation toxicity is carbon monoxide (CO). Fuel oil no. 6 was assumed for the reboiler duty, and bituminous coal was the fuel source for the electricity used to power the gas compressor. The energy consumption was converted to emissions of criteria pollutants using emission factors³² and heating values of fuel oil and coal.²⁹ The emission factors of uncontrolled fuel oil combustion and bituminous coal are shown in Table 3.

4. Results and Discussion

Table 4 shows the results of the statistical analysis for a subset of chemicals representing the top 100 HPV chemicals for K_H , K_{OW} , k_{OH} , and LC_{50} . The correlation coefficients (r^2) for the probability plots of K_H (Figure

Table 3. Criteria Pollutant Emission Factors for Uncontrolled Fuel Oil No. 6 Combustion and Bituminous Coal Combustion³²

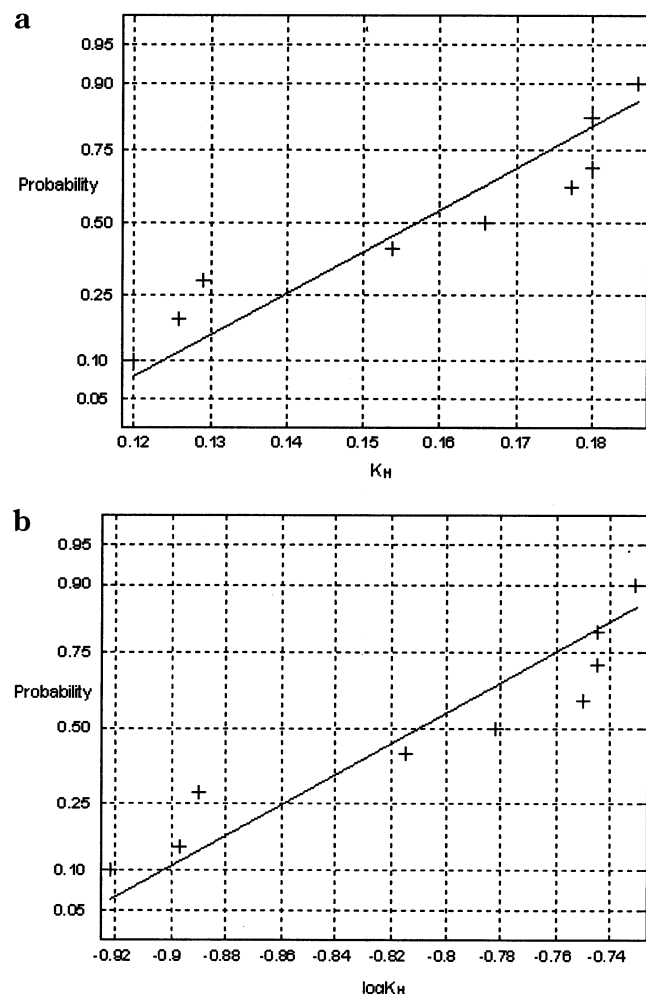
firing configuration	SO ₂ ^a (lb/1000 gal)	NO _x ^b (lb/1000 gal)	CO (lb/1000 gal)	CO ₂ ^c (kg/kJ)
no. 6 oil, normal firing	157 <i>S</i>	67	5	7.1 × 10 ⁻⁵
firing configuration	SO _x ^d (lb/ton)	NO _x ^b (lb/ton)	CO (lb/ton)	CO ₂ (lb/ton)
coal, spreader stoker	38 <i>S</i>	13.7	5	5510

^a *S* is the weight percent of sulfur in the oil. The emission factor for SO₂ is multiplied by *S*. ^b Expressed as NO₂. To express factors as NO, multiply the factor by 0.66. ^c Assuming *n*-decane combustion for fuel oil no. 6. ^d Expressed as SO₂, including SO₂, SO₃, and gaseous sulfates. In all cases, *S* is the weight percent of the sulfur content of coal as fired.

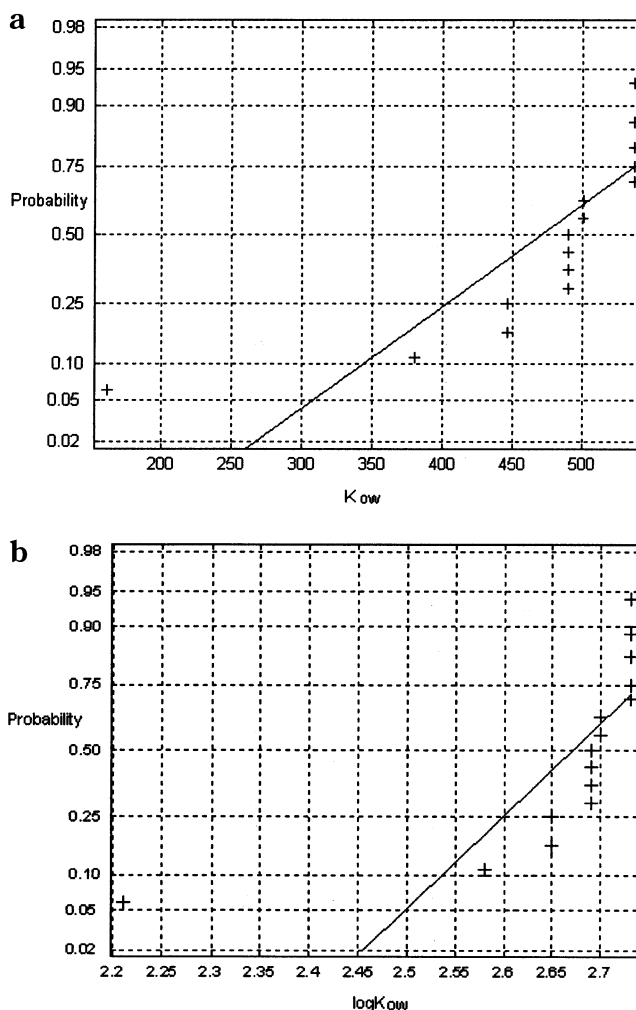
Table 4. Statistical Analysis of Measured Environmental Physical and Human Inhalation Toxicity Properties for Several of the Top 100 HPV Chemicals^a

chemical property	<i>N</i>	$\langle \sigma/\bar{x} \rangle$		$\langle n \rangle$	RNSE		$\langle r^2 \rangle$ normal		$\langle r^2 \rangle$ log-normal	
		avg	std		avg	std	avg	std	avg	std
<i>K</i> _H	9	0.29	0.17	10.1	0.093	0.06	0.83	0.10	0.79	0.12
<i>K</i> _{OW}	9	0.26	0.33	9.9	0.116	0.18	0.75	0.14	0.72	0.15
<i>k</i> _{OH}	16	0.12	0.08	3.8	0.061	0.04	NA		NA	
LC ₅₀	14	0.28	0.31	4.3	0.125	0.12	NA		NA	

^a *N* = number of chemicals from the HPV list used to generate the uncertainty statistics. $\langle n \rangle$ = average number of replicate measurements. NA = not enough replicate measurements. avg = average. std = standard deviation.

**Figure 3.** (a) Probability plot of K_H ($r^2 = 0.83$). (b) Probability plot of $\log K_H$ ($r^2 = 0.79$).

3a,b) and K_{OW} (Figure 4a,b) indicate a moderate preference for either a normal distribution or a log-normal distribution. The average value of the COV for each property is less than 0.30, indicating that the variance

**Figure 4.** (a) Probability plot of K_{OW} ($r^2 = 0.75$). (b) Probability plot of $\log K_{OW}$ ($r^2 = 0.72$).

of the data about the mean is not very large for each property. On the basis of these analyses, we assume that these properties are normally distributed in the remainder of the uncertainty analysis. The average number of replicates for K_H and K_{OW} is around 10, while for k_{OH} and LC₅₀, it is approximately four. We assume that these trends are representative for the other chemicals in the HPV list.

The relative normalized standard errors for the properties shown in Table 4 were propagated through the human inhalation toxicity index model using eq 6 for several column pressures and percent recoveries of ethyl acetate. In addition to the statistical parameters listed in Table 4, the uncertainty of air emissions was incorporated into the error propagation calculations using eq 9. We also included the errors of hot utility consumption and direct process emissions. This kind of information is provided by process calculation, which

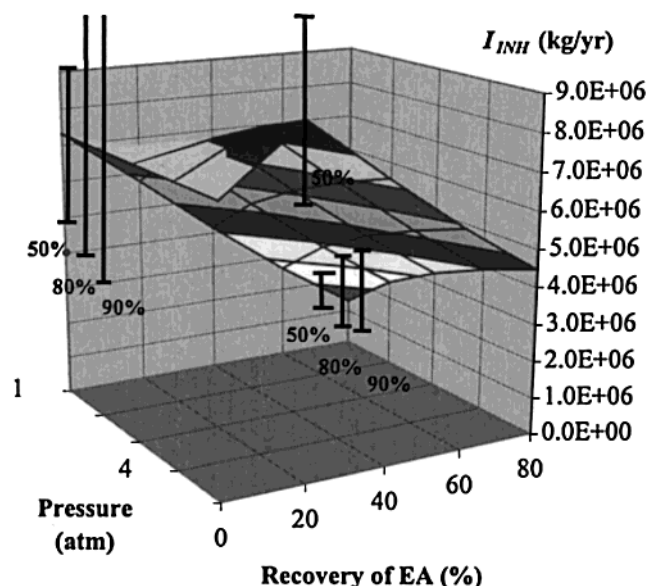


Figure 5. Variation of the human inhalation toxicity index with absorber pressure and percent recovery of ethyl acetate in the process shown in Figure 2.

is typically undertaken by a process simulator. According to Whiting,³³ the normalized standard errors of hot utility consumption ($e_{S,q_i}/\bar{q}_i$) and direct process emissions ($e_{S,E_i^m}/\bar{E}_i^m$) as calculated by a commercial process simulator are approximately 0.10 for each. We will use these values to represent the expected uncertainty for any process calculations (even though a process simulator was not used in this study). The emission factors for combustion processes are among the more accurate available from the U.S. EPA and will be represented by a relative normalized standard error of 0.10 ($e_{S,EF}/\bar{EF}$). After the propagation of error analysis is conducted, the normalized root-mean-square error for I_{INH} ($e_{RMS,I_{INH}}/\bar{I}_{INH}$) varies from 0.229 and 0.314 over the range of pressures and percent recoveries in this study.

Figure 5 shows the variation of I_{INH} with the column pressure and percent recovery of ethyl acetate in the absorber. The index is near maximum at 0% recovery when all of the VOCs are emitted and no energy is consumed in the process (note that there is no effect of pressure in this case because there is no process). The maximum in I_{INH} occurs for 5 atm of pressure and 20% recovery. The minimum in I_{INH} occurs at 1 atm of pressure and 80% VOC recovery (the highest percent recovery used in this study). There is a strong dependence of I_{INH} on the column pressure at constant percent recovery of VOC because of the effects of CO emissions from utility consumption, with I_{INH} increasing quickly with increasing column pressure. Figure 6 shows the variation of the venture profit with absorber pressure and percent recovery of ethyl acetate in the absorber. VP reaches a minimum at 5 atm of pressure and 20% recovery. There is no profit at 0% recovery because there is no process. The process makes maximum profit at 80% recovery and 1 atm of pressure.

The normalized root-mean-square error for I_{INH} ($e_{RMS,I_{INH}}/\bar{I}_{INH}$) indicates that the influence of model-inherent uncertainty for the properties K_H , K_{OW} , k_{OH} , and LC_{50} is small relative to the calculated value of I_{INH} . Decisions regarding process configurations and tech-

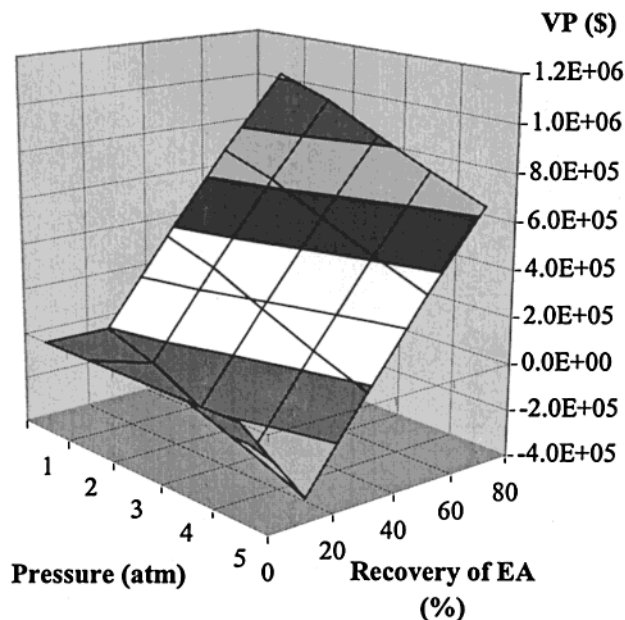


Figure 6. Variation of the venture profit with absorber pressure and percent recovery of ethyl acetate in the process shown in Figure 2.

nologies can be made with levels of confidence using an equation for the confidence intervals of I_{INH} as shown in eq 10 and Table 1.

The effects of various levels of confidence on the predicted value of I_{INH} are seen in Figure 5. From these error bars, it is clear that, even at the 90% confidence level, there is a significant difference between the inhalation toxicity index for widely different values of column pressure (1 versus 5 atm) and percent recovery (0 versus 80%). However, even at the 50% level, the error bars start to overlap for adjacent values (e.g., 20 versus 40% recovery or 1 versus 2 atm).

Another outcome from this study is the identification of the major sources of uncertainty within this propagation of error approach. Over the entire parameter space in this VOC recovery process, on average 26.5% of the uncertainty in I_{INH} ($e_{RMS,I_{INH}}$) is due to emissions properties and models (last term in eq 6) and 73.5% is due to environmental fate properties and models (K_H , K_{OW} , k_{OH} , and LC_{50}).

In this case study, we propagated the representative errors of HPV chemicals instead of specific chemicals involved in the process through the impact assessment model. Although using the specific chemicals leads to more accurate results, we obtain more generally applicable information on the behavior of HPV chemicals by using representative errors.

Although these properties are the major chemical-specific model properties for this human health impact assessment, this study omitted several other sources of uncertainty from the analysis. First, error distributions for the parameters are not in strong agreement with the normal distribution. Thus, the use of an error propagation method based on a normal distribution of property uncertainty will cause additional uncertainty in our analysis. Second, the uncertainty analysis in this study was constrained by the type of environmental fate and transport model employed. A more complex model, such as a "level III" multimedia compartment model, would propagate model-inherent property uncertainty

differently than the more simplistic "level I" model employed. Third, there is uncertainty in the ability of the impact assessment models to correctly predict the actual damage to the environment and to human health. For example, multimedia compartment models are considered to achieve only order-of-magnitude accuracy in predicting actual environmental distributions of chemicals, though relatively little field data are available to validate these models. Recent studies³⁴ comparing multimedia model predictions with field data in the Great Lakes Basin suggest that the errors can be smaller or larger than the order of magnitude, depending upon the environmental compartment being considered (air, water, soil, sediment, or groundwater). This aspect of "internal uncertainty", or the ability of the environmental model to accurately represent the fate and transport processes under consideration, is very important and should be studied further.

5. Conclusions

A propagation of error methodology for toxicity assessment of chemical process designs has been developed. Statistical analyses of several environmental properties yielded RNSE for HPV chemicals, though the number of chemicals included in the study is relatively small compared to the HPV list. These RNSEs should aid in uncertainty analysis when other HPV chemicals are involved in chemical process designs.

Although the uncertainty analysis presented in this study is limited to model-inherent uncertainty, it demonstrates that the level of uncertainty for predicting human inhalation toxicity using the EFRAT methodology is relatively small compared to the predicted impact index values ($e_{\text{RMS}, I_{\text{INH}}}/\overline{I_{\text{INH}}}$ varies from 0.229 and 0.314 over the parameter space). Combining process simulation models with impact assessment models into a more complete uncertainty analysis will address the broader issues of both model-inherent uncertainty and internal uncertainty in the prediction of environmental impacts for pollution prevention and an environmentally conscious design of chemical processes.

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Appendix: Detailed Derivations of the Root-Mean-Square Error of D_A

1. Root-Mean-Square Error of D_A . D_A is calculated by eq 3, that is,

$$D_A = \theta_a(\theta_{aa}K_H + \theta_{aw} + \theta_{as}\rho_{as}K_{ds})/ \\ \theta_a(\theta_{aa}K_H + \theta_{aw} + \theta_{as}\rho_{as}K_{ds}) (\text{air}) + \\ \theta_w(\theta_{ww} + \theta_{ws}\rho_{ws}K_{ds} + \theta_{ww}\rho_f\text{BCF}_f) (\text{water}) + \\ \theta_s\left(\rho_{ss}K_{ds} + \theta_{sw} + \theta_{sa}K_H + A_s\rho_p\frac{K_{ps}}{F_{dps}}K_{ds}\right) (\text{soil}) + \\ \theta_b(\theta_{bw} + \theta_{bs}\rho_{bs}K_{ds} + \rho_b\text{BCF}_b) (\text{sediment}) \quad (\text{A.1})$$

The Nomenclature section gives the definitions of the symbols in the above equation. Assume A , W , S , and BS are the four items in the denominator of the above equation representing air, water, soil, and sediment compartments, respectively.

$$A = \theta_a(\theta_{aa}K_H + \theta_{aw} + \theta_{as}\rho_{as}K_{ds}) \quad (\text{A.2})$$

$$W = \theta_w(\theta_{ww} + \theta_{ws}\rho_{ws}K_{ds} + \theta_{ww}\rho_f\text{BCF}_f) \quad (\text{A.3})$$

$$S = \theta_s\left(\rho_{ss}K_{ds} + \theta_{sw} + \theta_{sa}K_H + A_s\rho_p\frac{K_{ps}}{F_{dps}}K_{ds}\right) \quad (\text{A.4})$$

$$BS = \theta_b(\theta_{bw} + \theta_{bs}\rho_{bs}K_{ds} + \rho_b\text{BCF}_b) \quad (\text{A.5})$$

where BCF_f , BCF_b , K_{ps} , K_{ds} , K_{oc} , and F_{dps} are calculated by the following equations:

$$\text{BCF}_f, \text{BCF}_b = 0.05K_{OW} \quad (\text{A.6})$$

$$K_{ps} = 7.7K_{OW}^{-0.578} \quad (\text{A.7})$$

$$K_{ds} = K_{oc}f_{oc}(S) \quad (\text{A.8})$$

$$K_{oc} = 0.41K_{OW} \quad (\text{A.9})$$

$$F_{dps} = 0.2 \quad (\text{A.10})$$

where $f_{oc}(S)$ is the organic fraction in the soil compartment.

The root-mean-square error of D_A is obtained by the following equation, where the partial derivatives of D_A with respect to K_H and K_{OW} evaluated at the mean property values are shown in eqs A.12 and A.13.

$$e_{\text{RMS}, D_A} = \sqrt{\left(\frac{\partial D_A}{\partial K_H}e_{S, K_H}\right)^2 + \left(\frac{\partial D_A}{\partial K_{OW}}e_{S, K_{OW}}\right)^2} \quad (\text{A.11})$$

$$\frac{\partial D_A}{\partial K_H} = \overline{D_A} \frac{1}{A} \frac{\partial A}{\partial K_H} - (\overline{D_A})^2 \frac{1}{A} \left(\frac{\partial A}{\partial K_H} + \frac{\partial S}{\partial K_H} \right) \quad (\text{A.12})$$

$$\frac{\partial D_A}{\partial K_{OW}} = \overline{D_A} \frac{1}{A} \frac{\partial A}{\partial K_{OW}} - \\ (\overline{D_A})^2 \frac{1}{A} \left(\frac{\partial A}{\partial K_{OW}} + \frac{\partial W}{\partial K_{OW}} + \frac{\partial S}{\partial K_{OW}} + \frac{\partial BS}{\partial K_{OW}} \right) \quad (\text{A.13})$$

where the partial derivatives of A , W , S , and BS with respect to K_H and K_{OW} evaluated at the mean property values are listed in eqs A.14–A.19.

$$\frac{\partial A}{\partial K_H} = \theta_a \theta_{aa} \quad (\text{A.14})$$

$$\frac{\partial S}{\partial K_H} = \theta_s \theta_{sa} \quad (\text{A.15})$$

$$\frac{\partial A}{\partial K_{OW}} = \theta_a \theta_{as} \rho_{as} \frac{\partial K_{ds}}{\partial K_{OW}} = 0.41 \theta_a \theta_{as} \rho_{as} f_{oc}(S) \quad (\text{A.16})$$

$$\frac{\partial W}{\partial K_{OW}} = \theta_w \theta_{ws} \rho_{ws} \frac{\partial K_{ds}}{\partial K_{OW}} + \theta_w \theta_{ww} \rho_f \frac{\partial BCF_f}{\partial K_{OW}} = 0.41 \theta_w \theta_{ws} \rho_{ws} f_{oc}(S) + 0.05 \theta_w \theta_{ww} \rho_f \quad (\text{A.17})$$

$$\frac{\partial S}{\partial K_{OW}} = \theta_s \rho_{ss} \frac{\partial K_{ds}}{\partial K_{OW}} + \theta_s A_s \rho_p \frac{\left(K_{ps} \frac{\partial K_{ds}}{\partial K_{OW}} + K_{ds} \frac{\partial K_{ps}}{\partial K_{OW}} \right)}{F_{dps}} = 0.41 \theta_s \rho_{ss} f_{oc}(S) + \frac{\theta_s A_s \rho_p}{F_{dps}} [0.41 f_{oc}(S) \times 7.7 K_{OW}^{-0.578} + 0.41 f_{oc}(S) K_{OW} \times 7.7 (0.578) K_{OW}^{-1.578}] = 0.41 \theta_s \rho_{ss} f_{oc}(S) + 0.41 \times 7.7 \times 0.422 f_{oc}(S) \frac{\theta_s A_s \rho_p}{F_{dps}} K_{OW}^{-0.578} \quad (\text{A.18})$$

$$\frac{\partial BS}{\partial K_{OW}} = \theta_b \theta_{bs} \rho_{bs} \frac{\partial K_{ds}}{\partial K_{OW}} + \theta_b \rho_b \frac{\partial BCF_b}{\partial K_{OW}} = 0.41 \theta_b \theta_{bs} \rho_{bs} f_{oc}(S) + 0.05 \theta_b \rho_b \quad (\text{A.19})$$

2. Root-Mean-Square Error of τ_A . τ_A is calculated by eq 2, that is,

$$\tau_A = \frac{\ln 2}{k_{OH}} \quad (\text{A.20})$$

The root-mean-square error of τ_A , provided that the partial derivative of τ_A with respect to k_{OH} is evaluated at the mean property value, is

$$e_{\text{RMS}, \tau_A} = \sqrt{\left(\frac{\partial \tau_A}{\partial k_{OH}} e_{S, k_{OH}} \right)^2} = \sqrt{\left(\frac{\overline{\tau_A}}{\overline{k_{OH}}} e_{S, k_{OH}} \right)^2} = \left| \frac{\overline{\tau_A}}{\overline{k_{OH}}} \right| e_{S, k_{OH}} \quad (\text{A.21})$$

Nomenclature

A_S = surface area of soil for plants per volume of soil (m^{-1}) = 10
 BCF_f = bioconcentration factor for fish ([mol/kg of fish]/[mol/ m^3 of water])
 BCF_b = bioconcentration factor for biota ([mol/kg of biota]/[mol/ m^3 of water])
 C_{BM} = purchase cost for the absorber and distillation column (\$)
 COS = cost of sales (\$)
 COV = coefficient of variation
 C_{TCI} = total capital investment cost (\$)

e_{RMS} = root-mean-square error

e_S = standard error

D = overhead product flow rate of the distillation column (mol/s)

D_A = mole fraction of the emitted chemical partitioned to the atmosphere

D_C = column diameter (m)

E_i = emission rate of chemical i (kg/yr)

E_i^k = emission rate of chemical i from unit k (kg/yr)

E_i^l = emission rate of chemical i from utility combustion unit l (kg/yr)

E_i^m = direct emission of chemical i from unit m (kg/yr)

EF_i^k = emission factor of chemical i for unit k

EF_i^l = emission factor of chemical i for combustion-related emissions for unit l (kg of pollutant/kg of fuel combusted)

EFF_l = utility efficiency for unit l

F = feed flow rate of the distillation column (mol/s)

F_{dps} = dry plant solid ratio (kg of dry plant solids/kg of fresh plant vegetation) = 0.2

FIT = federal income tax (\$)

$f_{oc}(S)$ = organic fraction in the soil compartment = 0.02

G = gas flow rate in the absorber (mol/s)

G_{in} = flow rate of gaseous waste stream (mol/s)

HV_l = heating value for fuel combustion in unit l (kJ/kg of fuel)

I_{INH}^* = relative human inhalation toxicity index

I_{INH} = human inhalation toxicity index (kg/yr)

k = rank of replicate values from low to high

K_{ds} = partition coefficient for sorption to solids (m^3 of water/kg of dry solid)

K_H = Henry's law constant at 25 °C (m^3 of water/ m^3 of air)

k_{OH} = hydroxyl radical reaction rate constant (h^{-1})

K_{OW} = octanol–water partition coefficient (m^3 of water/ m^3 of octanol)

K_{ps} = plant/soil partition coefficient ([mol/kg of fresh plant vegetation]/[mol/kg of dry soil])

L = liquid flow rate in the absorber (mol/s)

L_C = column length (m)

LC_{50} = lethal concentration for inhalation toxicity (mg/ m^3)

L_{in} = flow rate of the recycle oil rate into the absorber (mol/s)

m = slope of the equilibrium line of ethyl acetate in the absorber

m_i^k = mass flow rate of chemical i within unit k (kg/yr)

MW_{N_2} = molecular weight of N_2

n = total number of replicate values

n' = number of chemicals emitted from the process

N_{actu} = actual number of trays in columns

N_i = number of chemicals selected from the HPV list for property i

N_{min} = minimum number of trays in columns

P = confidence level

P_{1-DOH}^o = partial pressure of 1-decanol in the distillation column (atm)

P_{EA}^o = partial pressure of ethyl acetate in the absorber (atm)

P_k = Weibull plotting position

P_{in} = gas pressure into the compressor = 1 atm

P_{out} = gas pressure out of the compressor (atm)

P_{Tol}^o = partial pressure of toluene in the distillation column (atm)

P_{Total} = total absorber pressure (atm)

Q_C = energy consumption of the compressor (kJ/kg of gas stream)

q_l = energy duty for unit l (kJ/yr)

Q_R = energy consumption of the reboiler (kJ/s)

r = rate of return = 0.20

R = ideal gas constant

R_D = optimum reflux ratio of the distillation column
 $R_{D,Min}$ = minimum reflux ratio of the distillation column
 RNSE = root-mean-square error
 S = annual sales revenue of ethyl acetate and toluene (\$)
 $t\%$ = tax rate = 37%
 T_{in} = gas temperature into the compressor (K)
 U_f = flooding velocity (m/s)
 V = mass flow rate of the gas stream in the columns (kg/s)
 \bar{V} = stripping section vapor flow rate (mol/s)
 VP = venture profit (\$)
 \bar{x} = average of sample values
 x_B = mole fraction of VOCs in the bottom product of the distillation column
 x_D = mole fraction of VOCs in the overhead product of the distillation column
 x_F = mole fraction of the pseudocomponent in the feed of the distillation column
 $x_{in,EA}$ = mole fraction of ethyl acetate in the liquid phase at the top of the absorber
 $x_{out,EA}$ = mole fraction of ethyl acetate in the feed of the distillation column
 $x_{out,Tol}$ = mole fraction of toluene in the feed of the distillation column
 $y_{in,EA}$ = mole fraction of ethyl acetate in the gas phase at the bottom of the absorber
 $\alpha_{Tol,1-DOH}$ = relative volatility of toluene with 1-decanol
 λ = latent heat of vaporization of absorption oil = 58.88 kJ/s
 η = efficiency of the columns
 $\eta_{isentropic}$ = isentropic coefficient = 0.6
 γ = heat capacity ratio = 1.4
 σ = standard deviation of sample values
 τ_A = reaction half-life in air at 25 °C (h)
 ρ_V = mass density of the gas stream (kg/m³)
 θ_a = volume fraction of the air compartment in the system = $1 - \theta_w - \theta_b - \theta_s$
 θ_{aa} = volume fraction of air in the air compartment (m³ of gas/m³ of air) = 1
 θ_{as} = volume fraction of soil/dust in the air compartment (m³ of solid/m³ of air) = 2×10^{-11}
 θ_{aw} = volume fraction of water in the air compartment (m³ of water/m³ of air) = 10^{-4}
 θ_b = volume fraction of bottom sediment in the system = 10^{-6}
 θ_{bw} = volume fraction of water in the bottom sediment (m³ of water/m³ of bottom sediment) = 0.5
 θ_{bs} = volume fraction of solids of the bottom sediment (m³ of solids/m³ of bottom sediment) = 0.5
 θ_s = volume fraction of soil in the system = 9×10^{-5}
 θ_{sa} = volume fraction of air in the soil compartment = 0.2
 θ_{sw} = volume fraction of water in the soil compartment = 0.3
 θ_w = volume fraction of water in the system = 0.002
 θ_{ws} = volume fraction of sediment in the water compartment (m³ of solids/m³ of water) = 5×10^{-6}
 θ_{ww} = volume fraction of water in the water compartment (m³ of water/m³ of water body) = 1
 ρ_{as} = air solids mass density (kg of dry solids/m³ of dry solids) = 2400
 ρ_b = mass density of biota (kg of biota/m³ of bottom sediment) = 1
 ρ_{bs} = mass density of the bottom sediment (kg of dry solids/m³ of sediment solids) = 1500
 ρ_f = mass density of fish (kg of fish/m³ of water) = 10^{-3}
 ρ_p = area density of plants (kg of dry plants/m² of area) = 1

ρ_{ss} = mass density of solids in soil (in water) (kg of dry solids/m³ of dry solids) = 2400
 ρ_{ws} = mass density of solids in water (kg of dry solids/m³ of dry solids) = 1500

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