An approach for solvent selection in extractive distillation systems including safety considerations

Nancy Medina-Herrera,[1] Ignacio E. Grossmann,[2] M. Sam Mannan[3]

and Arturo Jiménez-Gutiérrez[1]*

[1]*Chemical Engineering Department, Instituto Tecnológico de Celaya, Celaya, GTO 38060 México*

[2]*Chemical Engineering Department, Carnegie Mellon University, Pittsburgh, PA 15213 U.S.A.*

[3]*Dept. of Chemical Engineering, Texas A&M University, College Station, TX 77843 and The Mary Kay O'Connor Process Safety Center, Texas A&M University, College Station, TX 77843 U.S.A.*

*Corresponding author. Tel. +52-461-611-7575 Ext. 5577. E-mail: arturo@iqcelaya.itc.mx

Abstract

The selection of solvents in the chemical industry is typically based on performance and economic considerations. Other relevant aspects, such as the safety implications that a given solvent generates for the process, are generally left for their consideration after the design of the process has been completed. In this work, an approach for solvent selection including safety considerations at the design stage of the process is presented. The safety component is included through a consequence analysis using an average distance for the risk of death as the major parameter. The approach is applied to the design of extractive distillation systems, for which a pre-selection step for the solvent is used, followed by the formulation of a multiobjective optimization problem in which both economic and safety aspects are taken into account. The approach is applied for the purification of bioethanol, for which solvents that offer the best cost-safety compromise are identified.

Keywords. Extractive distillation; Multiobjective optimization; Process safety; Solvents; Bioethanol

1. Introduction

Solvents are widely used in chemical and processing industries to aid in many separation processes. For instance, extractive distillation separates azeotropic mixtures into high purity products by the addition of a solvent, or entrainer. The search for candidate solvents for a given separation is a major task in process design, and can be performed following different criteria. For instance, Luyben and Chien[1] have proposed a screening procedure for solvents based on isovolatility, equivolatility and binary VLE diagrams. This method is fast and evaluates solvents ahead of equipment design. Another approach was proposed by Kossack et al.,[2] who developed a framework for entrainer selection based on solvent properties and a rectification body method, linked to the application of an optimization method for the process design. These works show examples of the efforts to provide methodologies for solvent selection. However, one relevant factor such as safety is typically not considered as part of the search for solvents, even when safety is a natural concept related to the use and selection of solvents. Regarding this point, pioneering work was reported by Patel et al.,[3] who used a screening methodology based on desired safety properties using computer aided molecular design (CAMD) to find safer entrainers for a liquid-liquid extraction system. One limitation of this work is that an optimization of the process was not carried out.

In this work, inherent safety is considered as part of the factors to design a separation process that involves solvents. Inherent safety is a concept that provides a valuable tool for process design, since it aims to avoid risk instead to relying on protection devices once the process has been installed. Potential *incidents*, or disruptions in the process that pose some type of risk, are anticipated and assessed. Several principles have been developed to account for inherent safety, the main ones being substitution, intensification or minimization, attenuation or moderation, limitation of effects, and simplicity.[4] Applications of inherent safety in process design are limited by the lack of a standardized measurement method. Some indeces have been proposed to account for inherent safety in complete plants.[5,6,7,8] However, their use for process design applications is limited because they are not sensitive to variations in the design variables. An alternative approach is that by Khan and Amyotte,[9] who proposed a quantification of inherent safety aided by the application of a consequence analysis methodology. The idea behind this application is that changes in the equipment design will also change consequences in case of an incident.

The objective of this paper is to develop a design method that includes safety for separation systems that require solvents. The method is applied to the design of extractive distillation processes. Economic terms are measured through total annual cost calculations, and safety is considered following inherently safe design principles. As a parameter to measure inherent safety, we use a consequence analysis to calculate a distance likely to cause death (DD), which provides a good metric for the initial design of the process, when a plant layout and information on the number of workers nearby are not yet available. This procedure gives rise to a multi-objective optimization problem, in which economic and safety metrics are conflicting factors to be minimized.

2. Design Methodology

The approach used in this work for the optimal design of extractive distillation systems including a solvent screening stage is shown in Figure 1. First, a pre-selection step gives a set of potential solvents that meets specified safety properties. Potential solvents are found using the ProCAMD tool available in the ICAS software version 15.0, which is based on computer aided molecular design (CAMD). A screening for potentially safer solvents is applied at this point. Next, optimal design and operating conditions are found taking into account economic and safety considerations as part of a multi-objective optimization method, which is carried out using genetic algorithms. The safety component is quantified through an analysis of the consequences that an incident may cause within the process, leading to the value of a distance likely to cause death (DD). The total annual cost (TAC) is used to measure the economic performance of the process. Within the optimization procedure, ASPEN simulation, and TAC and DD subroutines work as black boxes as part of the implementation. The principles of moderation and minimization are applied at this point of the methodology for an inherently safer design. The final assessment of the combination of solvents and equipment design yields an effective substitution application and an inherently safer design. The individual components of the methodology are described below.

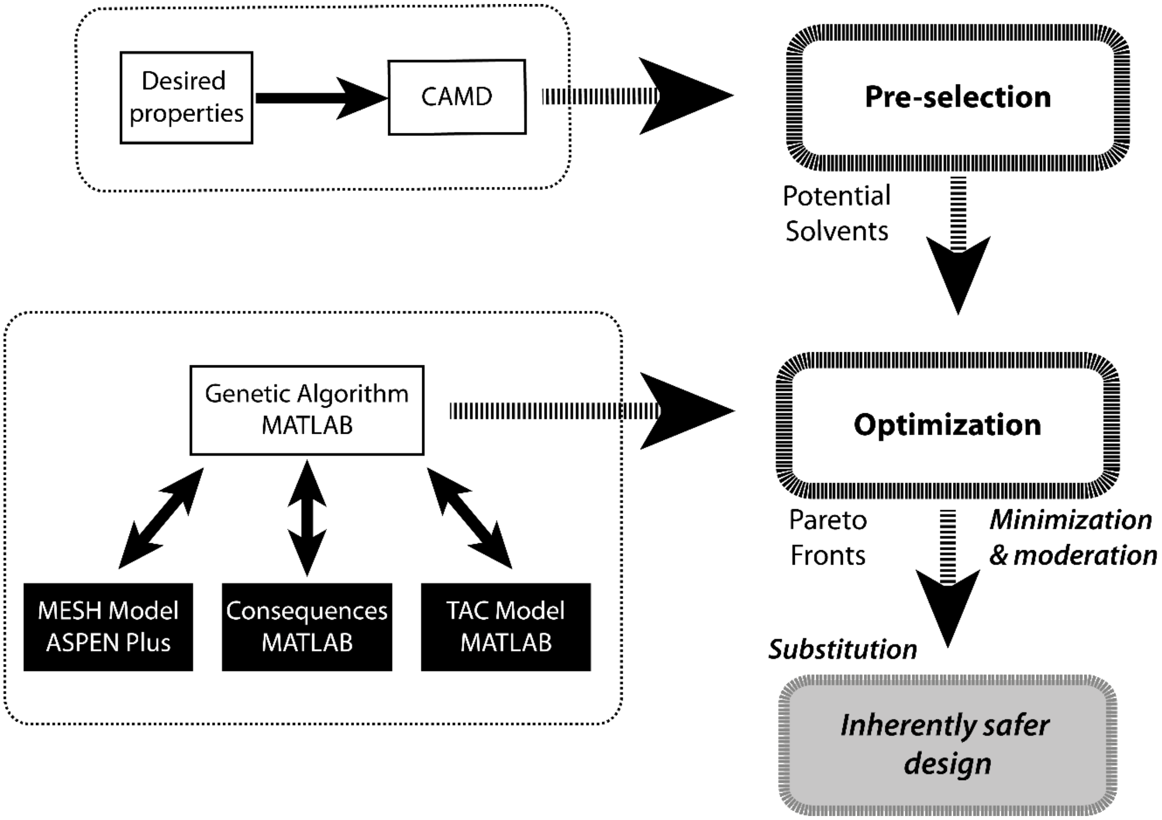

Figure 1. Approach used for the inherently safer design of extractive distillation systems.

3. Pre-selection of solvents

Computer aided molecular design (CAMD) provides the capability to find components that meet desired properties.[10] ProCAMD, a CAMD application available in the ICAS (Integrated Computer Aided System) software, is used in this work as part of a pre-selection step to find entrainers with potential for the separation process in terms of performance and safety. The potential solvents must meet some safety properties to avoid dangerous materials. ProCAMD is based on the hydrid methodology for CAMD that predicts property values using experimental data, when available, and group contribution models. ProCAMD provides a set of predefined properties that the user can select within the search for solvents.

The safety properties available within ProCAMD toolbox are flash point and octanol/water partition coefficient, both of which are used in this analysis. Flash point is related to flammable hazard, and partition coefficient is indirectly related to toxicity through lethal concentration (LC_{50}).[11] The octanol/water partition coefficient is related to intoxication hazard, and it can be estimated using a group contribution model.[12] In order to consider a material as not hazardous, its flash point should be greater than 300-330 K, and its LC_{50} greater than 2 mg/l.[3,5] An inherently safer solvent should consider reactivity as well, but in this analysis we assume that there is no reaction in the distillation system. Restrictions for not forming new azeotropes and for the boiling point of the solvent are specified as a part of performance properties. As a result of this pre-selection step, a set of potential solvents is obtained. A limitation of CAMD is that, from the list of solvents, several new molecules could be detected that might not be yet synthesized or commercially available. The set of solvents subject to analysis, therefore, is limited to those included in the ICAS database. The selected solvents have different performance and consequently different optimal designs, which depend on the solvent-mixture interrelations. In terms of the inherent safety principles, an efficient application of the substitution concept must analyze solvent properties and solvent performance within the process. The reason is that sometimes the amount of solvent needed is more important in terms of risk than its properties.

4. Inherent Safety

As an inherent safety metric, the risk of death in terms of distance (DD) is used in this work. Thus, a safer process gives a lower value of the risk distance that might affect workers. Such value is calculated within a subroutine in MATLAB, based on the CCPS Guidelines for Chemical Process Quantitative Risk Analysis.[13] The consequence analysis assumes that a hazard identification analysis has been already developed, and a set of catastrophic incidents has been identified. The risk analysis for extractive distillation of this work is based on the treatment presented in the CCPS guidelines book for a conventional distillation system. Risk is a function of probability and consequences. The probabilities of the catastrophic incidents are taken from the CCPS source.[13] Those values were calculated through a frequency analysis procedure using fault and event trees for incident identification.

4.1 Consequence analysis

Figure 2 shows the calculation procedure for a consequence analysis of a process unit. First, the catastrophic event is selected; when there is more than one event, the procedure is repeated for all catastrophic events. The consequence analysis models a spill source, the dispersion of the spilled material, the characteristic variable of the catastrophic incident, and the effect of the characteristic variable of the incident. The models of each item in Figure 2 depend on the specific catastrophic incident. These items are described below. In this work, the consequence analysis is carried out for each of the three process units, the extractive column, the recovery column, and the storage tank (see Figure 3). Domino effects are not considered.

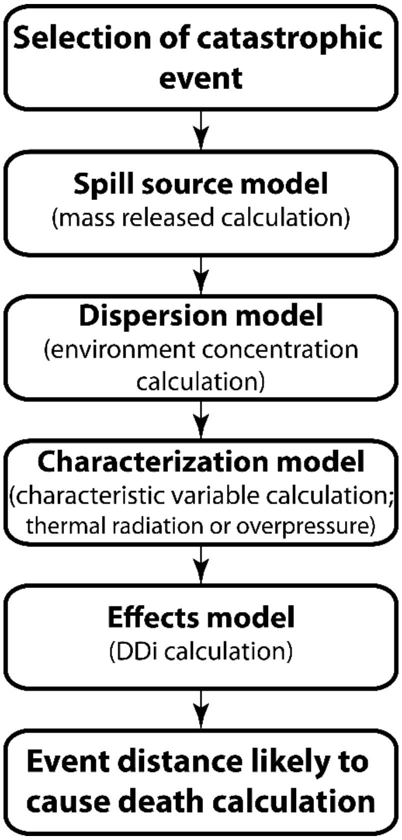

Figure 2. Major steps for a consequence analysis application.

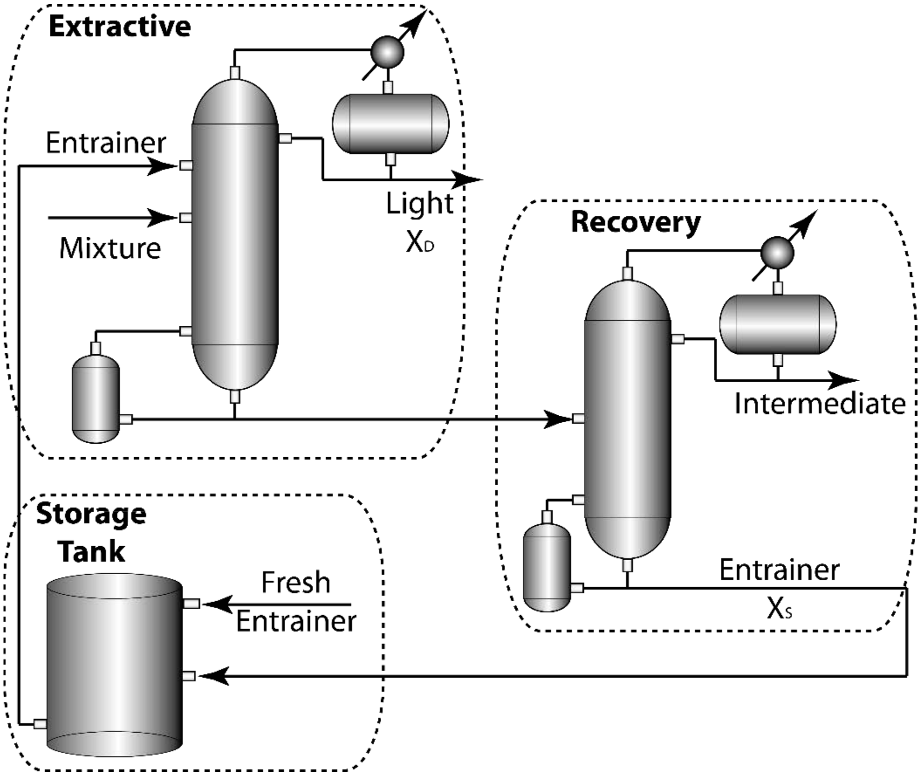

Figure 3. Process flowsheet for the extractive distillation system.

4.2 Source Models

There are two ways in which a spill can be modeled. The first one considers a case when the material is released all at once or, in practice, a large amount of mass is released in a very short period of time. This incident is referred to as an *instantaneous spill*. In the second scenario, the material is released continuously and the model is non-time dependent, which is identified as a *continuous spill*.

4.2.1 Instantaneous spill

The source model for an instantaneous release for the three units considered here is given in Equation 1. The released material is taken as the total amount of mass within the column, reflux drum, and condenser and reboiler. The mass within the column, or recipient, $m_{recipient}$, is calculated by means of volume, $V_{recipient}$ (assuming a cylinder shape), vapor and liquid fraction, f_{vapor} and f_{liquid}, and their densities, ρ_{vapor} and ρ_{liquid}. Mass inside reflux drum and reboiler, m_{cond} and m_{reb}, are considered at maximum capacity. Reflux drum and reboiler capacities are based on 12 and 6 minutes of feed respectively. The total mass released from a column unit due to an instantaneous release, Q^*_{column}, is the sum of the mass inside the column, the reflux drum and the reboiler. For the storage tank, the amount of released material, Q^*_{tank}, is calculated from the tank volume and the liquid density.

$$\left.\begin{aligned}
H_{recipient} &= 0.61\left(\frac{S}{\eta}\right) + 4.27 \\
V_{recipient} &= H_{recipient} * \pi\left(\frac{D_{recipient}}{2}\right)^2 \\
m_{recipient} &= \left(\rho_{liquid} * f_{liquid} + \rho_{vapor} * f_{vapor}\right)V_{column} \\
m_{cond} &= F * 720 \\
m_{reb} &= F * 360 \\
Q^*_{column} &= m_{recipient} + m_{cond} + m_{reb} \\
V_{tank} &= H_{tank} * \pi\left(\frac{D_{tank}}{2}\right)^2 \\
Q^*_{tank} &= V_{tank} * \rho_{liquid}
\end{aligned}\right\} \quad (1)$$

4.2.2 Continuous spill

The model for a continuous release for the three units is shown in Equation 2. The flow of released mass, $\dot{m}$, initiates from a pipe or recipient leaking gas or liquid. The mass released as a leak is considered as a mixture of vapor and liquid. The model follows the guidelines of CCPS[13] and assumes vapor sonic flow.

$$\left.\begin{aligned}
\dot{m}_{liquid} &= \rho A C_D \sqrt{2\left(\frac{g_c P_g}{\rho} + g h_L\right)} \\
\dot{m}_{vapor} &= \dot{m}_{choked} = C_D A P_1 \sqrt{\frac{k g_c M}{R_g T_1}\left(\frac{2}{k+1}\right)^{(k+1)/(k-1)}} \\
\dot{m} &= \frac{\dot{m}_{liquid} + \dot{m}_{choked}}{2}
\end{aligned}\right\} \quad (2)$$

4.3 Dispersion Models for Spills

The two types of releases have different dispersion models.[13,14,15] The dispersion model by Pasquill-Gifford[16] is used in this work. This model is simple and represents passive dispersion. The following dispersion conditions are assumed: rural field, class F stability (very stable) and slow wind velocity conditions, which provide conservative results. Equations 3 and 4 provide models for ground level release due to instantaneous and continuous dispersions. The instantaneous dispersion coefficients are modeled for unstable conditions, to provide conservative results. The instantaneous release is time-dependent.

The average downwind concentration for both models, $< \mathrm{C} >$, is a function of location, $(\mathrm{x}, 0{,}0)$, wind velocity, u, and dispersion coefficients in Cartesian directions (σ_x, σ_y and σ_z).

$$\left.\begin{array}{c} < C_i > (x,0,0,t) = \dfrac{Q^*}{\sqrt{2}(\pi)^{1.5}\sigma_x\sigma_y\sigma_z} exp\left\{-\dfrac{1}{2}\left[\left(\dfrac{x-ut}{\sigma_x}\right)^2 + \dfrac{y^2}{{\sigma_y}^2} + \dfrac{z^2}{{\sigma_z}^2}\right]\right\} \\ \sigma_x = 0.14x^{0.92} \\ \sigma_y = 0.14x^{0.92} \\ \sigma_z = 0.53x^{0.73} \end{array}\right\} \quad (3)$$

$$\left.\begin{array}{c} < C_c > (x,0,0) = \dfrac{\dot{m}}{\pi\sigma_y\sigma_z u} exp\left\{-\dfrac{1}{2}\left[\dfrac{y^2}{{\sigma_y}^2} + \dfrac{z^2}{{\sigma_z}^2}\right]\right\} \\ \sigma_y = \dfrac{0.04x}{\sqrt{1+0.0001x}} \\ \sigma_z = \dfrac{0.016x}{1+0.0003x} \end{array}\right\} \quad (4)$$

4.4 Characterization of catastrophic incidents

We assume that an extractive column and a tank have the same failure frequencies as a conventional distillation column. The following types of catastrophic incidents are considered: boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud explosion (UVCE), flash fire due to an instantaneous release (FFI) and due to a continuous release (FFC), and jet fire (JF). The models to describe the catastrophic incidents are discussed below.

4.4.1 BLEVE

A BLEVE occurs when there is an instantaneous release, followed by immediate ignition. The two main hazards in a BLEVE incident are the release of projectiles and thermal radiation. We consider here only thermal radiation as the characterization variable. Equation 5 shows the BLEVE characterization model, which involves empirical and radiation equations. Emissive radiation hazard, $\mathrm{E_r}$, is a function of the instantaneously released material, Q^*, diameter of the fireball, $\mathrm{D_{max}}$, duration of the BLEVE, $\mathrm{t_{BLEVE}}$, and thermal emissive power, E. Mudan and Croce[17] have proposed an expression for partial pressure, $\mathrm{P_w}$, as a function of relative humidity, RH, and air temperature, $\mathrm{T_{air}}$. In this analysis, the combustion heat radiation fraction, R, was taken as 0.4 in order to obtain conservative results.[18]

$$\left.\begin{array}{ll}
\begin{array}{c}
D_{max} = 5.8Q^{*^{1/3}} \\
t_{BLEVE} = 0.45Q^{*^{1/3}}\ for\ Q^* < 30000\ Kg \\
t_{BLEVE} = 2.6Q^{*^{1/6}}\ for\ Q^* > 30000\ Kg \\
H_{BLEVE} = 0.75D_{max}
\end{array}
&
\begin{array}{c}
X_s = \sqrt{{DD_{BLEVE}}^2 + H_{BLEVE}^2} - \frac{D_{max}}{2} \\
P_w = 1013.25(RH)exp\left(14.4114 - \frac{5328}{T_a}\right) \\
\tau_a = 2.02(P_w X_s)^{-0.09} \\
For\ DD_{BLEVE} > \frac{D_{max}}{2} \left\{ F_{21} = \frac{DD_{BLEVE}\left({}^{D_{max}}/_{2}\right)^2}{\left({DD_{BLEVE}}^2 + H_{BLEVE}^2\right)^{1.5}} \right. \\
For\ DD_{BLEVE} < \frac{D_{max}}{2} \left\{ F_{21} = \frac{H_{BLEVE}\left({}^{D_{max}}/_{2}\right)^2}{\left({DD_{BLEVE}}^2 + H_{BLEVE}^2\right)^{1.5}} \right. \\
E = \frac{RQ^*H_{comb}}{\pi D_{max}^2 t_{BLEVE}} \\
E_r = \tau_a E F_{21}
\end{array}
\end{array}\right\} \quad (5)$$

4.4.2 UVCE

UVCE is the result of an instantaneous release that finds an ignition source when the atmospheric conditions allow the formation of a vapor cloud. The UVCE main hazard is overpressure, p^o. A TNT model is used, which is based on the association of TNT explosion with the solvent combustion heat H_{comb} and the released mass, Q^*, considering an explosion efficiency, η_e. The distance of interest for this incident is DD_{UVCE}. Mathematical expressions to characterize UVCE are given in Equation 6.[13]

$$\left.\begin{array}{c}
W = \frac{\eta_e Q^* H_{comb}}{H_{TNT}} \\
Z = \frac{DD_{UVCE}}{W^{1/3}} \\
log_{10}(p^o) = \sum_{i=0}^{12} c_i(a + blog_{10}Z)^i \\
a = -0.2144 \\
b = 1.3503 \\
c_i\ = [2.7808, -1.6959, -0.1542, 0.5141, 0.0989, -0.2939, \\
0.0268, 0.1091, 0.0016, -0.0215, 0.0001, 0.0017]
\end{array}\right\} \quad (6)$$

4.4.3 Flash Fire

A flash fire is produced by any type of release that finds ignition after a flashing cloud of material is formed. Flash fire does not have a well-accepted characterization model due to the complexity of the physical phenomena. An alternative for the characterization of this incident is to consider DD as the distance where the concentration is equal to the lower flammability limit (LFL).[19] The distances at LFL are calculated using equations 3 and 4 for instantaneous and continuous releases. The variable $\mathrm{DD}_{\mathrm{incident}}$ is related to the distance x in such equations.

4.4.4 Jet fire

A jet fire is produced by the combustion of a continuous pressurized leak that finds immediate ignition. In general, jet fire has lower consequences than the other incidents, but it has a higher probability of occurrence. The main hazard of a jet fire is thermal radiation, E_{r}, which depends on the discharge rate, $\dot{\mathrm{m}}_{\mathrm{r}}$, flame size, $\mathrm{L}_{\mathrm{flame}}$, heat of combustion, $\mathrm{H}_{\mathrm{comb}}$, and point view factor, F_{P}. The jet fire model is given in Equation 7.[13]

$$\left.\begin{aligned}
\frac{L_{flame}}{d_j} &= \frac{15}{C_T}\sqrt{\frac{M_a}{M_f}} \\
X_s &= \sqrt{{DD_{JF}}^2 + L_{flame}^2} \\
P_w &= 1013.25(RH)exp\left(14.4114 - \frac{5328}{T_a}\right) \\
\tau_a &= 2.02(P_w X_s)^{-0.09} \\
F_P &= \frac{1}{4\pi {DD_{JF}}^2} \\
E_r &= \tau_a \eta_j \dot{m}\, H_{comb} F_P
\end{aligned}\right\} \quad (7)$$

4.5 Model for prediction of effects

A Probit model is used to quantify the effects of the characteristic variable or main hazard of incidents. Probit models are generalized time-dependent functions, which can be used for toxic, thermal radiation and blast effects. This method relates the damage as a fraction, P, with a probit variable, Y. Then, this probit variable is related to the characteristic variable, V, and fixed constants, k_1 and k_2. The Probit model is given in Equation 8,[13] with values for constants and causative variables reported in Table 1.

$$\left.\begin{aligned}
Y &= k_1 + k_2 lnV \\
P &= 50\left[1 + \frac{Y-5}{|Y-5|} erf\left(\frac{|Y-5|}{\sqrt{2}}\right)\right]
\end{aligned}\right\} \quad (8)$$

Table 1 Parameters for the Probit model

Event type	k_1	k_2	V
Thermal Radiation (BLEVE, JET FIRE)	-14.9	2.56	$\left(\frac{t_e * I^{4/3}}{10^4}\right)$
Overpressure (UVCE)	-77.1	6.91	p^o

4.6 Calculation of distance likely to cause death

In general, risk is defined as a function of frequency and consequences. In this work, consequences are taken as the distance at which there is a 50% probability of death. Given a set of catastrophic incidents CI, the average distance, DD_{aver}, is defined by the sum of all incident distances, DD_i, times their probability of occurrence, P_i. Equation 9 shows the calculation of DD, where CI refers to all catastrophic incidents for all units.

$$DD_{aver} = \sum_{i}^{CI} P_i DD_i \quad (9)$$

5. Implementation of the Methodology

Three components are needed for the implementation of the safety-cost optimization methodology (see Figure 1). Such items are described in this section.

5.1 Safety Calculation Subroutine

A subroutine calculates the average value of DD using a consequence analysis. From Equation 9 the incident distances are calculated for every design. In order to calculate individual distances (DD_i) the model of the incident must be applied. Since DDs are distances where the percentage of death is 50%, the damage is fixed to 50% ($P = 0.50$) in Equation 8, which provides the value of the characteristic variable (V), which can be thermal radiation or overpressure (see Table 1). Then, this value is substituted into the corresponding characterization model of the incident (Equation 5, 6, or 7) and solved simultaneously with the corresponding source model (Equation 1 or 2). In the case of flash fire, equations 1 and 3 give the effects due to an instantaneous release and equations 2 and 4 to a continuous release. Once individual distances have been calculated, DD_{aver} is obtained from Equation 9.

5.2 ASPEN Plus Simulation Subroutine

Figure 3 shows the flowsheet for an extractive distillation system. In ASPEN Plus, the recycled stream has a purity specification design to ensure that purity and flowrate of the entrainer stream are the same as the recycle stream. In addition there is a purity specification for the top product of the extractive column. In both specifications, the reflux ratio is the design variable. The input information needed by the subroutine are values for the eight optimization variables. Then the values are assigned within ASPEN Plus, and the results are sent to a subroutine in MATLAB, which reports the equipment design and energy requirement to the optimization algorithm.

5.3 TAC Subroutine

The total annual cost includes the capital cost of equipment (columns, reboilers, condenser and storage tank), assuming 2 ft spacing between trays for the columns plus an additional 20% for the top and bottom sections.[20] The heat transfer coefficients are 0.852 and 0.568 kW/K-m^2 for the reboilers and condenser respectively. The capital cost payback period is assumed at 3 years.[20] The steam cost is \$4.7/KJ. Table 2 summarizes the TAC components.

Table 2. Values for total annual cost calculations

Vessel (diameter and length in meters)
Capital cost = 17,640 $(D)^{1.066}$ $(L)^{0.802}$
Condensers (area in m^2)
Capital cost = 7296 $(\text{area})^{0.65}$
Reboilers (area in m^2):
Capital cost = 7296$(\text{area})^{0.65}$
$\boldsymbol{TAC} = \frac{capital\ cost}{payback\ period} + energy\ cost$

6. Optimization Algorithm

The model is a multi-objective optimization problem that establishes trade-offs as pareto-optimal solutions to optimize both safety and economic constraints. The optimization variables include the pressure, the number of stages and the feed stages for each column, and the entrainer flowrate and entrainer feed stage for the extractive column. The rigorous model that describes the physical phenomena is highly nonlinear, and in this case it is solved through the use of the ASPEN Process simulator. Derivative free optimization (DFO) techniques provide a suitable choice for the optimization of these types of problems.[21] DFO methods have been applied for the optimal design of complex distillation systems, as in Garcia-Herreros et al.[22] who used a simulated annealing algorithm for the optimization of extractive distillation, and Gutiérrez-Antonio and Briones-Ramírez[23] who used a multi-objective genetic algorithm for the design of thermally coupled distillation columns. In this work, the search for an optimal solution is carried out via the DFO method of genetic algorithms.

The multi-objective optimization problem can be formulated as,

$$\begin{gathered} \min(TAC, DD_{aver}) \\ s.t. \\ Fs_e - NT_e \leq -1 \\ SS_e - Fs_e \leq -1 \\ Fs_r - NT_r \leq -1 \\ MESH\ model\colon f(\boldsymbol{x}) = 0 \\ DD_{aver}\ model\colon g(\boldsymbol{x}) = 0 \\ TAC\ model\colon h(\boldsymbol{x}) = 0 \\ \boldsymbol{x^L} \leq \boldsymbol{x} \leq \boldsymbol{x^U} \end{gathered} \qquad (10)$$

Where $\boldsymbol{x}$ is the set of design variables, Fs_e, NT_e, and SS_e, are the feed stage for the azeotropic mixture, the total number of trays, and the solvent feed stage for the extractive column; Fs_r, and NT_r are the feed stage and total number of trays of the recovery column. The MESH model is provided by the ASPEN Plus simulation subroutine, $DD_{aver}\ model$ is the DD subroutine and $TAC\ model$ is the TAC subroutine.

We use the ε-epsilon method for the solution of the multi-objective optimization problem. A set of Pareto curves that reflect the compromise between economics and safety is thus generated. The procedure starts with two minimization problems. In the first one, minimization of the TAC objective without DD constraints is obtained. In the second one, the DD minimization is carried out without constraints on TAC to produce another solution. This procedure identifies the range in which one of the variables, in this case the distance likely to cause dead, can be used as a constraint as part of a series of problems minimizing the other objective, in this case the total annual cost. The first solution then identified the maximum value for DD_{aver}, or ε^{max}, while the second solution provided the minimum value, or ε^{min}. Therefore, the range of distance for death for the analysis is identified ($\varepsilon^{min} \le DD_{aver} \le \varepsilon^{max}$), and a set of optimizations is carried out with a problem of the form,

$$\text{Min TAC}$$

$$\text{s.t.}$$

$$DD_{aver} \le \varepsilon$$

Plus other constraints in Equation (10)

Where ε is varied between their minimum and maximum values.

7. Case study

The selected case study consists in the design of a purification process of bio-ethanol. For the sake of this analysis, we assume that the feed mixture to the extractive distillation system has been pre-concentrated after the fermentation step to an ethanol content of 80 mole percent. A flowrate of 100 Kmol/h is assumed, and the desired molar purity for ethanol is 0.96847. We used the methodology described above to find alternative entrainers for this process.

The ProCAMD tool included in ICAS software was first used to find potential solvents that met a set of desired properties. The solvent boiling temperature had to be greater than the water boiling point (T_b>100°C). Flash point constraint was fixed as greater than 353K (T_{FP}>353 K) and the LC_{50} value as lower than 2 mg/lt, which is related to the octanol/water partition coefficient ($\log K_{ow}$ <3). A specification to prevent the formation of new azeotropes with ethanol or water was set.

A total of 282 solvents that meet the specified safety properties were identified by ProCAMD toolbox within ICAS. Figure 4 gives a representation of the position of such solvents in a flash point versus octanol/water partition coefficient diagram. The safer solvents are the ones with lower partition coefficients and higher flash points (i.e. solvents close to the upper left hand corner of Figure 4).

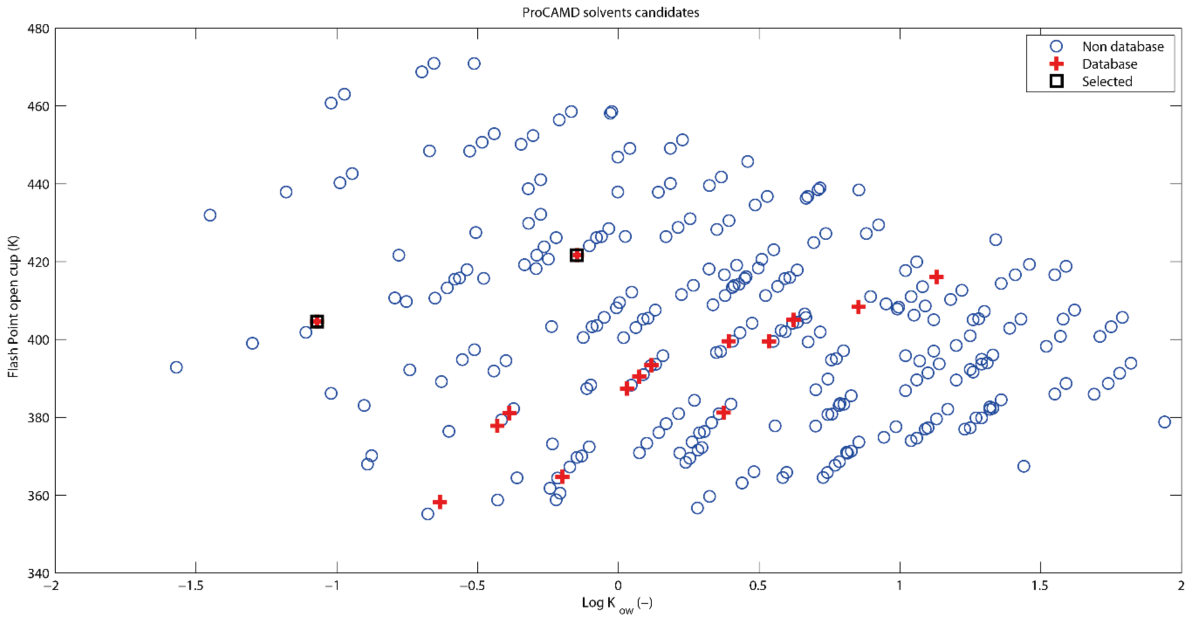

Figure 4. Position of different molecules for safe solvents obtained from ICAS.

ProCAMD found 282 compounds with the desired properties. Out of those, 15 compounds are included in the database of ICAS; the remaining solvents are therefore new molecules that could potentially be developed with appropriate safety properties. The list of solvents identified as candidates for entrainers along with their relevant properties are available in Table S1 of the Supporting Information. From the set of 15 candidates given by ICAS, the two top solvents with respect to their safety properties (dipropylene glycol and diethylene glycol) were selected for further analysis. Dipropylene glycol was selected because it was the safest solvent with respect to flammable hazard ($T_{FP} = 421.65K$), and diethylene glycol because it was the safest from toxicity considerations (logK_{ow} =-1.07). Additionally, two solvents commonly used as entrainers for this separation (ethylene glycol and dimethyl formamide) were also considered.

The four selected solvents were subjected to the optimization procedure that included safety and economic considerations. The parameters for the GA algorithm were taken from the work by Gutérrez-Antonio et al.,[24] in which those values were used with good results for the design of other complex distillation systems. For the consequence analysis, we took the catastrophic incidents and their probability of occurrence as reported in CCPS.[13] From this step, the Pareto curves reported in Figure 5 were obtained. The design details for each of the points in the Pareto curves (i.e. for each value of ε used for the multi-objective problem) is available in Table S2 of the Supporting Information. From those results, it can be observed that the process using ethylene glycol needs a smaller extractive column, and the process using dipropylene glycol, the safest solvent from flammability hazard considerations, requires the largest single equipment, which is the first column of the separation sequence. Also, the solvent flowrates for diethylene glycol and dipropylene glycol, the safest solvents, are higher, with a molar solvent/feed ratio of 1.2 to 1.6, which is equivalent to 4 to 7 times the amount of solvent needed with respect to the ethylene glycol and dimethyl formamide, the commonly used entrainers. Thus, the safest solvents from the pre-selection step drive designs with higher inventory within the separation system, which affects another one of the principles for process safety. In addition, the use of diethylene glycol and dipropylene glycol require a higher pressure for the separation. All these factors affect the analysis of consequences and are translated into a higher DD_{aver}. These safe solvents are not as effective for carrying out the separation, which affects the amount and operating conditions required for the extractive distillation process. Hence, the individual safety properties of the solvents must be complemented with a risk analysis for the process in order to provide a more complete safety assessment. The resulting Pareto fronts reflect such observations. One can observe in Figure 5 that in terms of the consequence analysis the safest solvent for the extractive distillation process is dimethylformamide. However, it is important to point out that the intoxication incident for this solvent was not considered due to the lack of constants for a probit model. This is relevant for this case since dimethylformamide has been related with cancer in workers who have been exposed to the solvent.[25] Therefore, the safety for the process using this solvent would need to be revised with the inclusion of a toxicity probit model that needs to be developed for this molecule. On the economic side, diethylene glycol provides the design with the lowest TAC. It can be observed that the safer solvents from the pre-selection step yield slightly lower safety results for the process, based on the consequence analysis, although they provide an economic incentive for its consideration. It is interesting to observe that there is a flat region of the Pareto curve for dipropylene glycol, indicating that different designs provide the same economic output but with different inherently safety properties. The same is observed for designs with diethylene glycol as entrainer, although the TCA for similar safety metrics reach higher values.

From the Pareto fronts, one could also identify areas where the replacement of a commonly-used entrainer by an inherently safer solvent provides favorable cost-benefit incentives. For example, in the highlighted square in Figure 5, referred to as opportunity area, in economic terms the use of dipropylene glycol instead of ethylene glycol provides an incentive with savings of 200,000 $/yr for similar values of the distance likely to cause death.

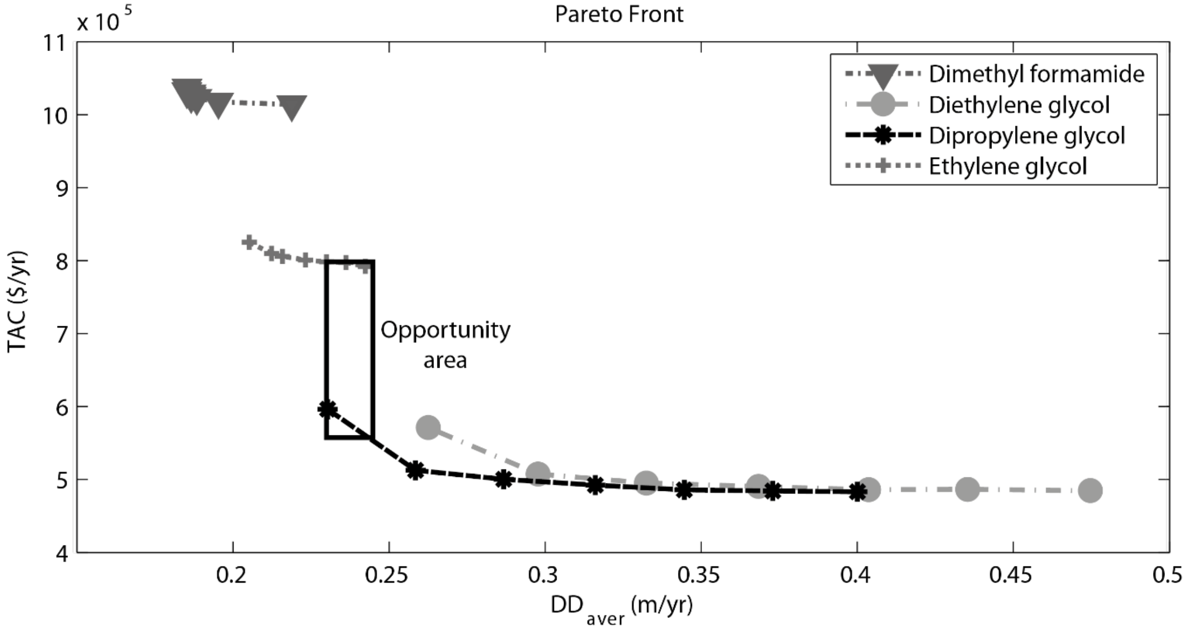

Figure 5. Pareto fronts obtained for the candidate solvents.

Some additional detail on the individual results for the economic and safety parameters is given in Figure 6. The results for the individual optimization of TAC and DD_{aver}, which correspond to the extreme points of the Pareto curve, are first shown. When TAC was minimized, diethylene glycol and dipropylene glycol gave the most economical designs, with dimethyl-formamide giving the most costly option. When DD_{aver} was optimized, dimethyl formamide and ethylene glycol provided the safest designs (although, as discussed above, dimethyl formamide should be analyzed further due to evidence of cancer risk), while diethylene glycol gave the design with the largest distance of affectation. The solvent properties, valid for any point in the Pareto curve, are also shown. Dipropylene glycol provides the lowest partition coefficient, with diethylene glycol being the most toxic option, although it gives the highest flash temperature.

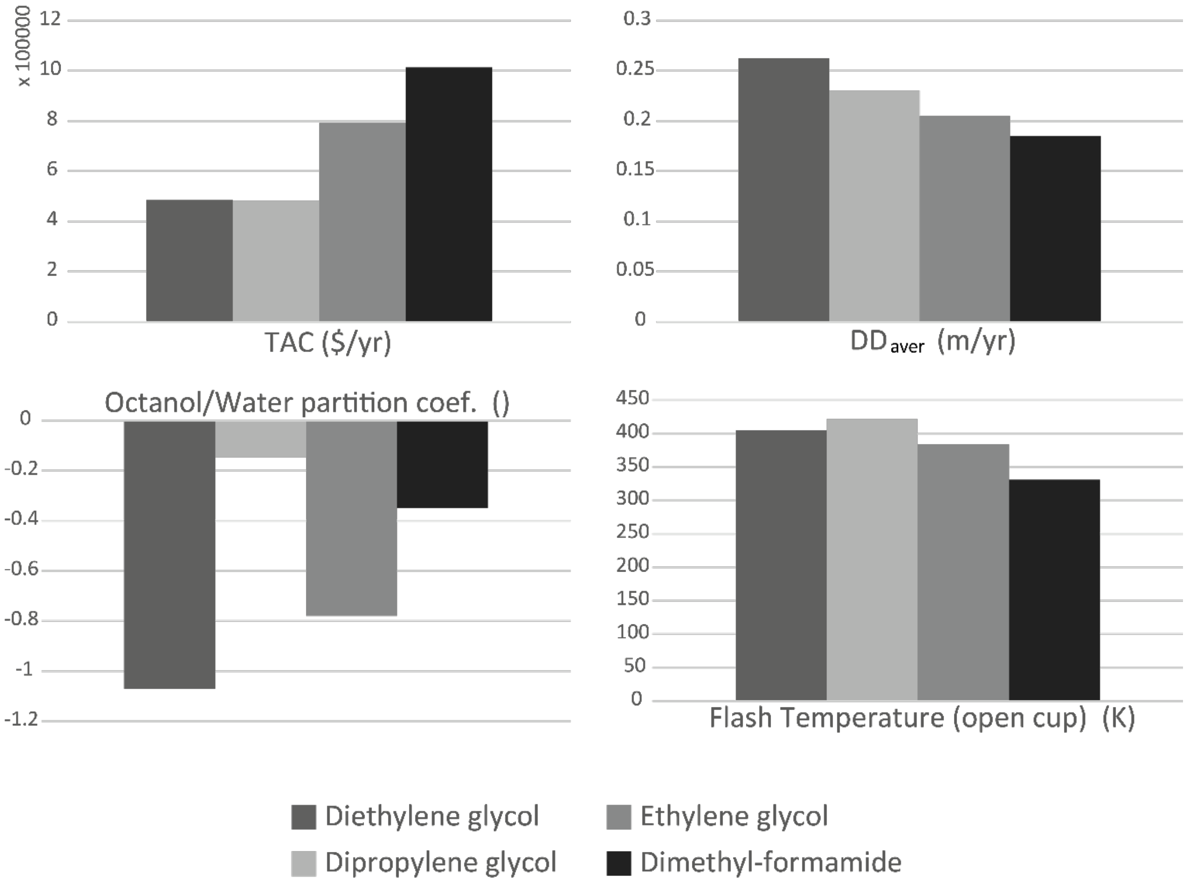

Figure 6. Total annual cost and values of safety parameters for the four solvents.

The results from this application show that the pre-selection step of inherently safer solvents must be complemented with the design of the process that includes a consequence analysis in order to assess the overall safety performance. In this way, properties such as relative volatilities provided by the solvents, which were not considered during the pre-selection process, are taken into account since they affect reflux ratios and equipment dimensions, and such effect is included as part of the design and economics of the resulting distillation sequence.

The safety/economic analysis that was used in the search for entrainers for the bioethanol purification process via extractive distillation identified the use of dipropylene glycol as a solvent worth of consideration, since it could provide a design with favorable economics and a good compromise with its safety characteristics.

8. Conclusions

An approach for the screening for solvents based on safety properties and a consequence analysis as part of the design of the process has been presented. The safety principles here considered are aimed at developing an inherently safer design of the process. The proposed approach has been applied to the design of extractive distillation systems. A pre-selection step, aided by the CAMD module of the ICAS software, was used in order to identify components with desired safety properties. A set of potential solvents that accomplished safety heuristics was then selected and embedded into the formulation of a multi-objective optimization problem, whose solutions provided the best compromise between safety and economics, measured through distance likely to cause death and total annual cost. The results showed that, for the case study here considered, the safer solvents from the pre-selection step were less effective to carry out the separation than two solvents of common use, such that higher amounts were required, which affects safety principles based on minimum inventory. However, the Pareto curves indicated that dipropylene glycol, a component identified as an inherently safer solvent from the pre-selection step, can be an entrainer worth of consideration for the purification of bioethanol. The design based on dipropylene glycol can provide favorable economics with similar process safety metrics with respect to ethylene glycol, a commonly-used entrainer for this process. The approach presented here represents an effort to include safety as part of the design of industrial processes, and in particular can be extended to other separation systems that are based on the use of solvents.

Acknowledgments

The authors would like to thank Prof. Rafiqul Gani, from the Technical University of Denmark, for making available the ICAS software for the development of this project. Also, funding from the Mary Kay O’Connor Process Safety Center and financial support from CONACyT, Mexico, through project CB-84493 and for the support of N. Medina for a 7-month stay at Carnegie Mellon University, are gratefully acknowledged.

Supporting Information Available

Supporting Information with the details on solvent properties and on the design of the extractive distillation systems with the use of the four solvents considered in this work has been prepared. This information is available free of charge via the Internet at http://pubs.acs.org.

Nomenclature

A	Hole cross-sectional area (m^2)
a, b, c_i	UVCE constants for overpressure peak calculations
$< C_c >$	Average concentration due to a continuous spill (Kg/m^3)

$< C_i >$	Average concentration due to an instantaneous spill (Kg/m^3)
C_D	Discharge coefficient
C_T	Fuel mole fraction in a stoichiometric fuel-air mixture
D_{max}	Maximum diameter of fireball (m)
$D_{recipient}$	Diameter of recipient (m)
D_{tank}	Diameter of storage tank (m)
DD_{aver}	Average distance likely to cause death (m/yr)
DD_i	Distance likely to cause death of the catastrophic incident i (m)
d_j	Diameter of the jet, physical diameter of the nozzle (m)
E	Radiative emissive flux (KJ/m^{2}s)
E_r	Radiative emissive flux received by a worker (KJ/m^{2}s)
F	Feed flowrate (kg/s)
F_{21}	View factor
F_P	Point source view factor (m^{-2})
Fs_e	Feed stage in the extractive column
Fs_r	Feed stage in the recovery column
f_{liquid}	Liquid fraction inside recipient
f_{vapor}	Vapor fraction inside recipient
g_c	Gravitational constant
H_{BLEVE}	Height of the fireball (m)
H_{TNT}	Heat of combustion of TNT (KJ/Kg)
H_{comb}	Energy of combustion of the fuel (KJ/kg)
$H_{recipient}$	Height of recipient (m)
H_{tank}	Height of storage tank (m)
h_L	Liquid head (m)

k	Specific heats relation
k_1, k_2	Probit constants
L_{flame}	Length of the visible turbulent flame measured from break point (m)
M	molecular weight (Kg/Kmol)
$\dot{m}$	Mass released due to continuous release (Kg/s)
$\dot{m}_{choked}$	Gas discharge rate, choked flow (Kg/s)
$\dot{m}_{liquid}$	Liquid mass discharge (Kg/s)
$\dot{m}_{vapor}$	Vapor released discharge (kg/s)
m_{cond}	Mass released from condenser (Kg)
m_{reb}	Mass released from reboiler (Kg)
$m_{recipient}$	Mass released from recipient (Kg)
NT_e	Total number of trays of extractive column (-)
NT_r	Total number of trays of recovery column (-)
P	Probability (%)
P_1	Upstream absolute pressure (bar)
P_g	Upstream gauge pressure (KPa)
P_i	Probability of catastrophic incident i (yr^{-1})
P_w	Water partial pressure (N/m^2)
p^o	Peak side-on overpressure (Pa)
$\mathrm{Q}^*{}_{column}$	Released mass from distillation column (Kg)
$\mathrm{Q}^*{}_{tank}$	Released mass from storage tank (kg)
R	Radiative fraction of the heat of combustion
RH	Relative humidity (%)
R_g	Ideal gas constant (J/Kmol/°K)

S	Total number of stages
SS_e	Solvent feed stage in the extractive column
TAC	Total annual cost ($/yr)
T_a	Air temperature (K)
t	Time of interest in instantaneous release (s)
t_{BLEVE}	Duration of fireball (s)
t_{BLEVE}	Duration of fireball (s)
u	Wind velocity (m/s)
V	Causative variable (thermal radiation, overpressure)
$V_{recipient}$	Volume of the recipient (m^3)
V_{tank}	Volume of the tank (m^3)
W	Equivalent mass of TNT (Kg)
X_s	Path length distance (m)
x	Downwind distance (m)
$\boldsymbol{x}$	Vector of optimization variables
Y	Probit variable
y	Cross-wind direction (m)
Z	Scaled range TNT equivalency model ($m/Kg^{1/3}$)
z	Distance above the ground (m)

Greek symbols

η	Thermodynamic efficiency of the stage
η_e	Empirical explosion efficiency
ρ_{liquid}	Liquid density (kg/m^3)
ρ_{vapor}	Vapor density (kg/m^3)

σ_x	Dispersion coefficient in x direction (m)
σ_y	Dispersion coefficient in y direction (m)
σ_z	Dispersion coefficient in z direction (m)
τ_a	Atmospheric transmissivity fraction

References

(1) Luyben, W. L.; Chien, I. L. *Design and Control of Distillation Systems for Separating Azeotropes*. Wiley: 2011.

(2) Kossack, S.; Kraemer, K.; Gani, R.; Marquardt, W. A Systematic Synthesis Framework for Extractive Distillation Processes. *Chem. Eng. Res. Des.* **2008,** *86*, 781.

(3) Patel, S. J.; Ng, D.; Mannan, M. S. Inherently Safer Design of Solvent Processes at the Conceptual Stage: Practical Application for Substitution. *J. Loss Prev. Process Ind.* **2010,** *23*, 483.

(4) Kletz, T. Chapter 21 - Inherently Safer Design. In *What Went Wrong? (Fourth Edition)*, Gulf Professional Publishing: Houston, 1999; pp 367-379.

(5) Heikkilä, A.-M.; Hurme, M.; Järveläinen, M. Safety Considerations in Process Synthesis. *Comput. Chem. Eng.* **1996,** *20* (Supplement 1), S115.

(6) Gentile, M.; Rogers, W. J.; Mannan, M. S. Development of a Fuzzy Logic-Based Inherent Safety Index. *Process Saf. Environ. Prot.* **2003,** *81*, 444.

(7) Suardin, J.; Sam Mannan, M.; El-Halwagi, M. The Integration of Dow's Fire and Explosion Index (F&EI) into Process Design and Optimization to Achieve Inherently Safer Design. *J. Loss Prev. Process Ind.* **2007,** 20, 79.

(8) Leong, C. T.; Shariff, A. M. Inherent Safety Index Module (ISIM) to Assess Inherent Safety Level During Preliminary Design Stage. *Process Safety and Environmental Protection* **2008,** *86*, 113.

(9) Khan, F. I.; Amyotte, P. R. Integrated Inherent Safety Index (I2SI): A Tool for Inherent Safety Evaluation. *Process Saf. Prog.* **2004,** *23*, 136.

(10) Gani, R.; Achenie, L. E. K.; Venkatasubramanian, V. Chapter 1: Introduction to CAMD. In *Comput. Aid. Chem. Eng.* Luke E.K. Achenie, R. G.; Venkat, V., Eds. Elsevier: 2002; Vol. 12, pp 3-21.

(11) Veith, G. D.; Call, D. J.; Brooke, L. T. Estimating the Acute Toxicity of Narcotic Industrial Chemicals to Fathead Minnows. In *Aquatic Toxicology and Hazard Assessment: Sixth Symposium*, Philadelphia, PA, USA, 1983; pp 90-97.

(12) Marrero, J.; Gani, R. Group-Contribution-Based Estimation of Octanol/Water Partition Coefficient and Aqueous Solubility. *Ind. Eng. Chem. Res.* **2002,** *41*, 6623.

(13) AIChE *Guidelines for Chemical Process Quantitative Risk Analysis*. 2 ed.; AIChE: New York, New York, 2000.

(14) Crowl, D. A.; Louvar, J. F. *Chemical Process Safety Fundamentals with Applications*. Second ed.; Prentice Hall International Series: 2002.

(15) Mannan, S. Lees' Loss Prevention in the Process Industries: Hazard Identification, Assessment, and Control. In 3rd ed.; Elsevier Butterworth-Heinemann: Amsterdam; Boston, 2005.

(16) Gifford, F. A. Horizontal diffusion in the atmosphere: A Lagrangian-dynamical theory. *Atmos. Environ. (1967)* **1982,** *16*, 505.

(17) Mudan, K. S., Croce, P.A. *Fire Hazard Calculations for Large Open Hydrocarbon Fires*. Nation Fire Protection Association: 1988.

(18) Hymes, I. The Physiological and Pathological Effects of Thermal Radiation, SRD R275 . In Office, H. S., Ed. London, 1983.

(19) Rew, P. J.; Deaves, D. M.; Hockey, S. M.; Lines, I. G. *Review of Flash Fire Modelling*. HSE Books: 1996.

(20) Luyben, W. L. Comparison of Extractive Distillation and Pressure-Swing Distillation for Acetone/Chloroform Separation. *Comput. Chem. Eng.* **2013,** *50*, 1.

(21) Rios, L.; Sahinidis, N., Derivative-free Optimization: A Review of Algorithms and Comparison of Software Implementations. *J. Glob. Optim.* **2013,** *56*, 1247.

(22) García-Herreros, P.; Gómez, J. M.; Gil, I. D.; Rodríguez, G. Optimization of the Design and Operation of an Extractive Distillation System for the Production of Fuel Grade Ethanol Using Glycerol as Entrainer. *Ind. Eng. Chem. Res.* **2011,** *50*, 3977.

(23) Gutiérrez-Antonio, C.; Briones-Ramírez, A. Pareto Front of Ideal Petlyuk Sequences Using a Multiobjective Genetic Algorithm with Constraints. *Comput. Chem. Eng.* **2009,** *33*, 454.

(24) Gutérrez-Antonio, C.; Briones-Ramírez, A.; Jiménez-Gutiérrez, A., Optimization of Petlyuk Sequences Using a Multiobjective Genetic Algorithm with Constraints. *Comput. Chem. Eng.* **2011,** *35*, 236.

(25) Chen, J. L.; Fayerweather, W. E.; Pell, S., Cancer Incidence of Workers Exposed to Dimethylformamide and/or Acrylonitrile. *J. Occup. Environ. Med.* **1988,** *30*, 813.

CAPTIONS FOR FIGURES

Figure 1. Approach used for the inherently safer design of extractive distillation systems.

Figure 2. Major steps for a consequence analysis application.

Figure 3. Process flowsheet for the extractive distillation system.

Figure 4. Position of different molecules for safe solvents obtained from ICAS.

Figure 5. Pareto fronts obtained for the candidate solvents.