Optimizing safety-constrained solvent selection for process systems with economic uncertainties

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\textbf{A B S T R A C T}

Solvents are very commonly used in industrial facilities for a multitude of reasons. Traditionally, solvent selection has been based on minimizing the process operating cost while satisfying a set of operational requirements. Regrettably, safety considerations have typically been overlooked during the design phase. In this paper, a systematic approach is introduced to integrate safety issues into solvent selection and provides a computationally effective method for establishing tradeoffs between the economic and safety objectives. In order to quantify the risk associated with the solvent, we focus on the potential spillage of the solvent and introduce a risk index that is a function of the amount of solvent used and stored, as well as the Permissible Exposure Limit (PEL) dictated by regulatory directives. An optimization formulation is developed and the associated mathematical program solved to select optimal solvents and blends while incorporating economic, technical, and safety considerations. Tradeoff (Pareto) curves are developed to represent the multi-objective optimization results and tradeoffs. Furthermore, economic-data uncertainty and variability over expected ranges are included in the optimization formulation to conduct an insightful sensitivity analysis. Finally, an illustrative case study is considered via increasing levels of complexity in order to evaluate the proposed optimization method which considers both operating cost and safety risk implications in the presence of economic uncertainties.

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1. Introduction

Solvents are among the most important materials utilities used in the process industries. Numerous solvents and solvent blends are typically available for a specific application. Consequently, solvent selection is a challenging task. Systematic techniques have been proposed for screening solvent alternatives based on technical or techno-economic criteria (e.g., Achenie, Gani, & Venkatasubramanian, 2003; Gani, Jiménez-González, & Constable, 2005). Using the framework of property integration, Kazantzi, Qin, El-Halwagi, Eljack, and Eden (2007) and Eljack, Eden, Kazantzi, Qin, and El-Halwagi (2007) developed algorithmic procedures for the simultaneous tasks of solvent selection and process design based on techno-economic criteria. A multi-step solvent-selection procedure has been proposed for reaction systems by Folic, Gani, Jiménez-González, and Constable (2008) while including environmental issues. Elgue, Prat, Cabassud, and Cezerac (2006) examined solvents used in the pharmaceutical systems and proposed a replaced approach which includes economic and environmental criteria while staying within waste and safety constraints. An objective function is created to minimize cost, which is a function of time, replacement cost, amount of solvent, amount of waste, and cost of waste handling. This allows for less solvent waste, less solvent used, and less time wasted since solvent replacement in the pharmaceutical industries is often a batch process rather than a continuous one. Patel, Ng, and Mannan (2010) incorporated safety considerations in process design to create inherently safe processes by using computer-aided molecular design coupled with the requisite safety considerations. Pokoo-Aikins et al. (2010) addressed the economic and safety concerns when extracting oils from sludge, a potential candidate in the production of biofuels. They created a safety index that evaluates each solvent and assigns a number to each one based on its safety. Notwithstanding the usefulness of the existing procedures for solvent selection, there is
a need for a systematic approach which provides an efficient pro-
dure to screen and select solvents based on technical, economic, and
safety metrics.

The problem to be addressed in this paper can be described as
follows: Given an industrial application that requires the use of
solvent, it is desired to develop a systematic procedure for selecting
solvents and solvent blends that meet the process requirements
while considering and trading off economic and safety objectives. It
is also desired to include the economic uncertainties associated
with the cost of the candidate solvents.

The procedure to be developed should address the following
questions:

- How to generate candidate solvents?
- How to determine optimal blends of various solvents?
- How to assess the risk potential of the solvents and solvent
blends?
- How to account for the economic uncertainties associated with
the cost of the solvents?
- How to reconcile the economic and safety objectives while
meeting the technical objectives?

This paper describes a hierarchical approach to the selection of
solvents/solvent blends that achieve a set of technical requirements
at minimum cost subject to certain risk limits. A new risk index is
introduced and used in an optimization formulation that is used to
tradeoff cost versus risk. Potential uncertainty and variability in the
cost data are incorporated in the optimization formulation and the
generated optimization results are assessed via Pareto curves and
sensitivity analyses.

2. Approach

We propose an optimization approach which integrates safety
issues into solvent selection and provides a computationally effective
method for establishing tradeoffs between the economic and safety
objectives. To quantify the risk associated with the solvent, we focus
on the potential spillage of the solvent. Currently, OSHA has restric-
tions on the Permissible Exposure Limits (PELs) of various solvents
often used in industrial plants. The lower the PEL of a solvent, the
more hazardous the solvent is. Under OSHA’s Regulations Section 29
CFR 1910.1000, the guidelines on how to compute the cumulative
exposure for an 8-h work shift are discussed. The PEL only accounts
for the permissible exposure limits for various substances but does not
take into account the amount of solvent used and stored. Typically,
a certain amount of the solvent is stored to provide security of
supply (e.g., storage of 60-days worth of consumption). Therefore, we
propose the definition of a risk index as:

\[
\text{Risk Index of Solvent } s = \frac{\text{Amount of Stored Solvent } s}{\text{PEL of Solvent } s} \quad (1a)
\]

When the storage time is the same for all solvents, the definition of
the risk index may be revised to be based on the flowrate of the
solvent, i.e.,

\[
\sum_{s} \frac{F_s}{\text{PEL}_s} = \text{Risk}_{\text{Index}} \quad (1b)
\]

where \( F_s \) is the flowrate of the \( s \)th solvent. Based on process analysis,
the performance of the various solvents and blends can be
identified and expressed in functional form that relates the needed
flowrates of the different solvents that are required to meet the
technical objectives, i.e.,

\[
\Omega(F_1, F_2, ..., F_s, ..., F_{\text{Solvents}}) = 0 \quad (2)
\]

A hierarchical solvent-selection procedure is proposed. First,
process characteristics are considered. An appropriate process
model is developed accounting for all the required solvent flow-
rates. In addition, safety considerations are explicitly integrated
within the model, in particular through a risk index which depends
directly on the aforementioned solvent flowrates. Then, a base case
scenario is realized through an appropriately formulated optimi-
zation problem for optimal solvent selection, in which solvent cost
is at first considered as a fully known input (fixed current solvent
market prices) and risk constraints are explicitly incorporated. The
ensuing paragraphs encompass the optimization formulation as
well as the solution approach to the problem under consideration.

In particular, the following optimization formulation is developed
for minimizing the solvent cost for various limits on the Risk
Index:

\[
\text{Minimize } \sum_s \text{Cost}_s \cdot F_s \quad (3)
\]

where \( s \) is an index for solvents, \( \text{Cost}_s \) is cost of the \( s \)th solvent per
unit mass and \( F_s \) is the flowrate of the \( s \)th solvent. This objective
function is subject to the following constraints:

- **Solvent-Performance Model:**
  \[ \Omega(F_1, F_2, ..., F_s, ..., F_{\text{Solvents}}) = 0 \]

- **Risk-Index Calculation:**
  \[ \sum_s \frac{F_s}{\text{PEL}_s} = \text{Risk}_{\text{Index}} \]

where PEL\(_s\) is the Permissible Exposure Limit of the \( s \)th solvent, and:

\[
\text{Risk}_{\text{Index}} \leq \text{Risk}_{\text{Index}}^{\text{Limit}} \quad (4)
\]

It should be pointed out that in addition to the performance
model and the risk-index calculations, there may be other
property-based models and constraints to be considered. Examples
include density, viscosity, vapor pressure, sulfur content, etc. In
such cases, property-mixing models and constraints (e.g.,
Kazantzis & El-Halwagi, 2005; Shelley & El-Halwagi, 2000) should be used as
follows:

- **Property-mixing rules:**
  \[ F_s \psi(p) = \sum_s F_s \psi(p_s) \quad (5) \]

where \( \psi(p_s) \) is the property-mixing operator and \( F \) is the total
flowrate of the mixture which is given by:

\[
F = \sum_s F_s \quad (6)
\]

Property constraints: each user has specifications on the
acceptable ranges of solvent properties, i.e.,

\[
p^{\text{min}} \leq p \leq p^{\text{max}} \quad (7)
\]

where \( p^{\text{min}} \) and \( p^{\text{max}} \) are the specified lower and upper bounds on
admissible property of the solvent blend.

The optimization formulation and the associated solution
method aim at minimizing the cost for a base case with a selected
value of the risk index. Next, the optimization problem is repeat-
eadly solved over different constraints on the risk index. The result is
a cost-risk Pareto curve for the above nominal situation (base-case
scenario). Next, the fact that solvent market prices can be reason-
ably viewed as uncertain inputs to the above model determined by
continuously changing aggregate demand and supply conditions in the pertinent solvent markets is accounted for. Therefore, the economic uncertainty and variability are used in the optimization formulation. The above findings are amenable to comprehensive sensitivity analyses and yield insightful Pareto tradeoffs between cost and risk over the range of economic uncertainty. The profiles of solvent cost versus risk help decision makers evaluate the uncertainty implications on the system in a more realistic setting and select the most appropriate solvent/solvent blends on the basis of trading-off cost and safety considerations. It should be pointed out that for the selected scenarios, process simulation and quantitative risk analysis (QRA) should be conducted to verify that the selected scenarios meet the required specifications. Un-met specifications are added as constraints to the optimization formulation. The methodology procedure described above is illustrated in Fig. 1.

The following figure outlines the necessary steps to solvent-selection.

3. Case study

An industrial facility uses solvent absorption to reduce the content of certain pollutants in the off-gas emission leaving the plant. Table 1 provides the data for seven candidate solvents. The required flowrate for each solvent is the amount needed to reach the environmental target by using that solvent. Solvent blends may be used. The fractional removal task of each solvent is given by its actual flowrate divided by the required flowrate, i.e.

$$\sum_{s} \frac{F_s}{\text{Required}_s} = 1$$  \hspace{1cm} (8)

where Required$_s$ is the required flowrate of the $s$th solvent. For blends, a linear mixing rule is assumed to account for the fractional removal task of the blend. When the fraction is equal to one, the environmental removal task is fulfilled. Table 1 also gives the values for the PEL and the cost of the solvents.

The optimization problem is formulated for the case study and coded using the software LINGO (Schrage, 2006). Solvent storage of 60 days was used for all solvents. Therefore, the definition of the Risk Index given by Eq. (1a) was used. After running LINGO multiple times with different Risk Indices, the following curve balancing cost and Risk Index was obtained. Fig. 2 shows the Pareto curve for the obtained solutions establishing the tradeoff between cost and risk. These are all feasible solutions that meet the desired design specifications. Therefore, there is no need to add more constraints for performance. What is now needed is to study the tradeoff between cost and risk. As shown by Fig. 2, the cost increases as the risk index decreases. Thus, industries have to find a specific balance between safety and cost to optimize solvent use.

Next, a sensitivity analysis was carried out by altering the price of methanol in the range $0.45–0.59$/kg. The Pareto curves

![Fig. 1. Flowchart of the hierarchical solvent-selection approach.](image1)

![Fig. 2. The Pareto solution for the case study. The total solvent cost decreases as the risk index increases.](image2)
resulting from the sensitivity analysis are shown by Fig. 3. Such results constitute an insightful basis for the decision makers. It is worth noting that as the unit cost of methanol increases, other solvents will partially or completely substitute the use of methanol. This may necessitate the incorporation of flexibility considerations early enough in the design stage to enable the substitution of methanol with other solvents depending on the changes in prices and/or safety regulations. The problem is further compounded when solvent blends are selected as part of the solution with environmental regulations set for the whole system (e.g., Dunn, Dobson, & El-Halwagi, 1997). The design of the system and the solvent-blend regeneration system should include flexibility analysis to allow proper usage and regeneration of solvent blends as the fractional contribution of each solvent may change due to time-based variations in the solvent economics and/or safety objectives while complying with the overall environmental regulations for the solvent system. Fig. 4 illustrates the changes in the flowrates of the different solvents at the optimum solutions versus cost variability of methanol.

4. Conclusions

This work has introduced a hierarchical approach to selecting solvents and blends while considering technical, economic, and safety metrics. A new risk index is introduced to assess the inherent safety of the solvent. An optimization formulation is developed to determine the optimal flowrate of the solvent or solvent blend at minimum cost while satisfying technical and risk requirements. Cost-risk tradeoffs are established by solving the optimization program for various levels of risk. Potential variations in the economic data are incorporated as inputs to the optimization formulation to generate a sensitivity analysis while characterizing the cost-risk tradeoffs under economic uncertainty. A case study has been solved to illustrate the applicability of the devised approach and the sensitivity of the obtained solutions to risk constraints and economic variability.

Nomenclature

- \( C_s \): Cost of the sth solvent
- \( F_s \): Flowrate of the sth solvent
- \( F \): Flowrate of the solvent blend
- \( N_{solvents} \): Number of candidate solvents
- \( p_s \): Property of the sth solvent
- \( \mathcal{P} \): Property of the solvent blend
- \( \text{PEL}_s \): Permissible exposure limit for the sth solvent
- \( \text{Risk\_Index} \): Risk index (defined by Eq. (1))
- \( s \): Index for the solvents
- \( \Omega \): Function describing performance
- \( \psi \): Property-mixing operator

References


