Interval Analysis – An Application to Solvent Design

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This presentation discusses the use of an interval analysis based global optimization approach for the systematic design of cleaning solvent blends (commonly referred to as blanket washes) for lithographic printing. The simultaneous consideration of associated process constraints, property requirements, and environmental restrictions makes the blanket wash design a rather difficult problem. To address this, we present a framework for designing cleaning solvent blends that meet thermo-physical property requirements and environmental restrictions. The resulting mathematical program is a mixed-integer optimization problem involving (a) the selection of solvents from a set of pure component solvents (the discrete problem) and (b) finding the blend composition (the continuous problem).

The framework has been used to solve an industrially relevant problem of designing optimal blends for blanket wash applications in the printing industry taking into account solvent power, viscosity and surface tension.

1 Mixture Design Problem Formulation

The computer-aided mixture design is composed of three main steps:

(i) Selection of pure components from a database (for example, for designing a binary mixture from a set of 10 pure components can result in $\binom{10}{2}$ or 45 combinations),

(ii) Determining the mixture composition that satisfies the property targets and

(iii) Ranking the candidate mixtures by some criteria such as overall cost.

The first step is a combinatorial problem; the second step is a continuous problem, which can be non-convex depending on the nature of the property prediction techniques employed. We propose to use a mixed-integer nonlinear problem formulation that is general enough to handle several types of mixture estimation techniques. Obviously if the number of combinations (binary, ternary, etc) for pure components is small, one can enumerate them all and solve a series of continuous nonlinear programs.

In the proposed formulation, binary variables are used to denote the presence or absence of a pure-component solvent in the mixture, and a set of continuous variables are used to describe the mole fractions of the components in the mixture. Hence the formulation is mixed-integer in nature. First let us introduce the variables:

- y_i (binary variable) =1 if pure component i is present in the mixture, and =0 otherwise;
- x_i (continuous variable between 0 and 1) = mole fraction of pure component i in the mixture

Other parameters include:

- n number of pure component solvents (basis set)
- $n_{\max}$ maximum number of pure component solvents in the blend
- P_{ij} property j of pure component i.

Constraints are imposed for (a) limiting the number of pure component solvents in the blend; (b) ensuring that the mole fraction of an absent component is 0; and (c) all the mole fractions add to 1.0. These constraints are by no means exhaustive, and several different ones can be added to achieve a specific solvent mixture design objective.

$$P_{mix} : \min_{x,y} f(x,y)$$

$$\text{subject to :}$$

$$P^L \leq P(x,y) \leq P^U, \quad \sum_i y_i \leq n_{\min}, \quad \sum_i x_i = 1, \quad 0 \leq x_i \leq y_i$$

$$x = [x_1, \ldots, x_n]^T, \quad y = [y_1, \ldots, y_m]^T, \quad x_i \in [0,1] \text{ (real)}, \quad y_i \in \{0,1\} \text{ (binary)}$$

P^L and P^U are lower and upper limits on a vector of target properties P. These properties may be nonlinear and nonconvex with respect to the search variables x_i, y_i.

The last constraint in the above formulation ensures that if component i is not present in the mixture (i.e. $i = 0$), then the corresponding composition x_i is also 0. This however, can lead to cases where the composition of one component is infinitesimally small. To avoid this we replace it by: $u_i \cdot \varepsilon < x_i < u_i(1-\varepsilon)$, where ε is a small number (e.g. 0.01).

2 Interval Analysis Technique for Solving Mixture Problem

Since many property estimation techniques are generally non-convex, we have developed an interval analysis based optimization strategy that can design (globally) optimal mixtures. Interval analysis has emerged as a reliable mathematical tool that can automatically generate lower and upper bounds for a function [2]. It has been used for solving ordinary differential equations, linear systems, and verifying chaos. Interval arithmetic, which is at the heart of interval analysis, was developed by Moore [6].

In essence, interval analysis based optimization continually deletes portions of the search space with the goal of maintaining a final box of desired width that contains the global solution. A number of interval-based optimization procedures have been developed (e.g. [2, 3, 5, 7, 10]). Most of these procedures are tailored to unconstrained optimization problems. In addition, these techniques can only handle continuous variables. In other words they do not handle discrete variables. Notwithstanding the attractive features of interval-based global optimization, they are in general computationally intensive. To address some of these issues, we have developed new acceleration strategies, and extended the capabilities of the algorithm to solve mixed integer problems.

Almost all interval analysis based global optimization algorithms employ a successive domain reduction approach by eliminating portions of search regions, which do not contain the global solution. Consider the continuous optimization model

$$
\begin{gathered}
\text{globally } \min_{x} f(x) \\
\text{subject to :} \\
g(x) \leq 0; \quad h(x) = 0 \qquad (2) \\
x = [x_1, \ldots, x_n]^T \text{ (real)}; \quad x \in \mathbf{X}_0
\end{gathered}
$$

Almost all domain reduction algorithms invariably use the following tests to systematically remove portions of the domain that cannot contain the global minimum: (a) Upper Bound Test, (b) Infeasibility Test, (c) Monotonicity Test, (d) Non-convexity Test, and (e) Distrust Region Test [10]. An interval-based global optimization algorithm can be constructed based on the above tests. However, in our experience it is computationally slow especially for problems with a large number of constraints. We propose additional domain reduction tests. These are (a) Upper Bound via SQP local optimization and (b) Local Feasibility Test. In (b) the idea is to relax the optimization model and only consider the convex constraints and determine if this relaxed search space contains a feasible solution. This requires the prior specification of which constraints are convex and which are not. This is not always straightforward. However, linear equality and linear inequality constraints are simple convex constraints. Based on this reduced set of constraints the feasibility of a sub-region $\mathbf{X}_k$ is checked by solving a feasibility problem.

Mixture design problems have relatively small dimension. For a design with a basis set of m pure components the interval dimension is $2m$. Current interval based global optimization algorithms can only solve continuous optimization problems. An extension of the algorithm is made for solving mixed integer nonlinear programs (MINLP) such as the mixture design problem.

3 Case Study: Design of Environmentally Acceptable Blanket Wash Blends

The Printing Industry of America (PIA) and the USEPA started a major initiative in the early 1990's to search for alternative water-based blanket wash solvents [9]. This case study explores the systematic development of aqueous blends for use as blanket wash solvents.

The EPA report on blanket wash risk assessment [1] lists 40 different formulations (or solvent blends) used as blanket washes by different printing facilities throughout the United States. However, due to propriety reasons their compositions are not reported. Out of these, 21 formulations contain petroleum distillates (hydrocarbons and/or aromatic hydrocarbons), which pose considerable environmental health and safety risks. Two common aromatic hydrocarbons used in blanket washes are 1-2-4 trimethyl benzene (C_9H_{12}) and isomers of xylene (C_8H_{10}). Trimethyl benzene has a flash point of 54.4∘C and $\log K_{OW}$ of 3.78. Isomers of xylene have flash point as low as 17∘C and $\log K_{OW}$ of 3.15. Thus both are flammable and have high bioaccumulation and toxicity.

The pure component solvents employed in this case study are non-halogenated and non-aromatic water-soluble compounds. Also only those solvents, which have relatively small environmental and health impact are selected. The desired attributes for optimal blanket wash formulation target the solvent power, its flow characteristics, surface contacting and environmental impact.

An MINLP model of the blanket wash mixture design problem was formulated and solved two ways. In Case 1, the model was solved by fixing the binary variables resulting in an NLP model. Specifically each binary mixture was constructed by fixing the binary variables for water and one of the other pure component solvents to 1; the remaining binary variables were set at 0. In Case 2 the MINLP model was solved rigorously, i.e. without fixing the binary variables. This is a relatively more difficult problem with 17 variables and 8 binary variables. Also in this case we only considered 2-component blends (i.e. binary blend, not to be confused with binary variable). Thus the solution approach not only picks the best combination of 2-component solvents (discrete problem) but also finds the optimal composition (continuous problem).

The two models were solved to obtain 7 different binary mixtures. Among all solutions, the lowest objective value was achieved by a γ-butyrolactone and water blend.

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