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# Application of an interval optimization method for studying feasibility of batch extractive distillation

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**Abstract**

A global and reliable interval optimization tool, a Branch and Bound technique, developed at the Institute of Informatics, University of Szeged, and based on the C++ toolbox of R. Hammer et al., 1994, and the Profil/Bias routine library, is tried and successfully applied for solving a chemical engineering problem. For checking the feasibility (according to the method developed at Dept. Chem. Eng. BUTE) of batch extractive distillation, and determining the appropriate range of its operation parameters, reliable information is needed on the existence and location of singular points of a phase curve map belonging to a differential equation coupled with a complicated and nonlinear algebraic equation system. Conventional methodologies failed to provide reliable information. Here a subproblem of the feasibility methodology is introduced, the working cycle of the interval algebra based optimization tool is sketched, and its applicability on the targeted problem is demonstrated.

## Batch extractive distillation

Batch extractive distillation (Fig. 1) is a semibatch process applied to separate liquid mixtures of chemical compounds forming minimum boiling azeotrope [1, 2].

A binary liquid mixture of compounds A and B with composition $\mathbf{x}_S$ is charged to the still (S), the column is heated up with condensing the vapour ($V$), and all the condensate liquid is being fed back at the top as reflux stream. The condensed vapour is of azeotropic composition. After warming up, feeding (F) of a heavy boiling liquid compound, so-called entrainer (E) to the column is started. As a result, the condensate is enriched in A, and compound B remains in the still (run-up with total reflux). Product removal ($D$, distillate) is started when the required composition is reached in the top, and only $V$-$D$ is fed back as reflux. The separation is performed in this step, until compound A is removed from the still, and the required distillate composition cannot be maintained. The new mixture of B and E can then later be separated much easier.

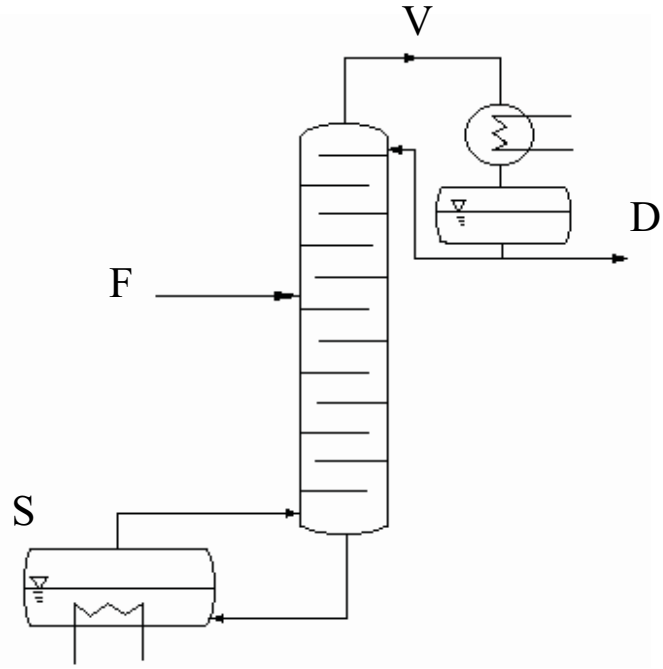


Figure 1: Batch extractive distillation process

The main parameters are the ratios $F/V$ (feed ratio) and $R = (V-D)/D$ (reflux ratio). The run-up step is characterized with $R = \infty$, infinite reflux ratio, i.e. total reflux. The process is feasible just in a narrow range of $F/V$ and $R$, and finding this range is difficult. Feasibility is conventionally checked graphically in a composition triangle $\{0 \leq x_A \leq 1,\ 0qleqx_B \leq 1\}$ of the mole fractions ($x_E = 1 - x_A - x_B$).

The composition curve along the column, projected to the composition space, without feeding F is called 'rectifying profile', and can be computed by solving the differential equation

$$\frac{dx_i}{dh} = \frac{V}{V-D}\left(y_i\left(x_i, x_{D,i}, R\right) - y_i^*\left(x_A, x_B\right)\right); \quad (i \in \{A, B\}) \tag{1a}$$

where $\mathbf{x}_D$ is the specified distillate composition, $h$ is column length, $y_i$ is a linear function of $x_i$, with parameter $R$, and $\mathbf{y}^*$ is a complicated implicit function of $\mathbf{x}$. For distillate composition near pure A, the profile runs along the A-E edge of the triangle, as on Fig. 2. The projected composition curve along the lower part of the column if entrainer E is fed to the column is called 'extractive profile'. It can be calculated from a given $\mathbf{x}_S$ still composition with the differential equation

$$\frac{dx_i}{dh} = \frac{V}{V-D}\left(y_i\left(x_i, x_{D,i}, R, F/V, x_{F,i}\right) - y_i^*\left(x_A, x_B\right)\right) \quad (i \in \{A, B\}), \tag{1b}$$

where $\mathbf{x}_F$ is the feed composition, $y_i$ is a linear function of $x_i$, with parameters $x_{F,i}$, $F/V$ and $R$, and is identical to $y_i$ used in (1a) when $F/V{=}0$. Any $\mathbf{x}_S$ still composition is called feasible if the extractive profile computed from it, as initial value, reaches a point of the rectifying profile, like in Fig. 2. Our task is to determine the range of $F/V$ and $R$ characterized by a reasonable domain of feasible still compositions. Those $F/V$ and $R$ values are also called feasible, other values are infeasible.

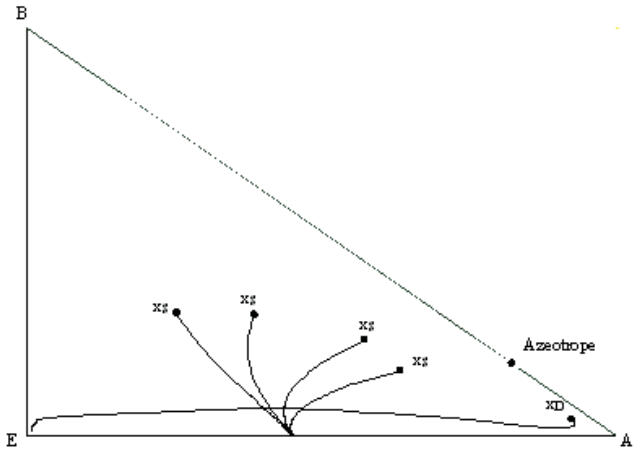


Figure 2: Rectifying profile and some extractive profiles. Feasible case.

Feasibility is controlled by the singular points and separatrices of the extractive profile map. If there is a stable node outside the triangle, below the A-E edge, then

a bunch of the extractive profiles is attracted to it, thus they cross the rectifying profile, and the process is feasible. Saddle points and the corresponding separatrices form the boundary of the feasible domain. The location of points and separatrices depends of the parameters; and there are sudden changes in the map's general shape at some values, i.e. there are bifurcations. Saddle points cannot be precisely found by graphical methods, and not all the singular points can reliably be found or their existence cannot be excluded with certainty using traditional stochastic methods. This is why we used an interval arithmetic based branch-and-bound technique.

## An interval arithmetic based branch-and-bound technique

To solve the related root finding problems we have implemented an interval arithmetic based optimization algorithm [3, 4]. Where it was necessary we have reformulated the original problem to the minimization of a nonlinear function in the n-dimensional real space. The applied algorithm was:

[Step 1] Let L be an empty list, the leading box A := X, and the iteration counter k := 1. Set the upper bound of the global minimum $f^u$ to be the upper bound of F(X).

[Step 2] Subdivide A into s subsets. Evaluate the inclusion function F(X) for all the new subintervals, and update the upper bound of the global minimum $f^u$ as the minimum of the old value and the minimum of the upper bounds on the new subintervals.

[Step 3] Add the new subintervals to the list L.

[Step 4] Use the accelerating devices: delete parts of the subintervals stored in L that cannot contain a global minimizer point.

[Step 5] Set A to be that subinterval from the list L which has the smallest lower bound on f, and remove the related item from the list.

[Step 6] While termination criteria do not hold let k := k+1 and go to Step 2.

This applied method was a branch-and-bound algorithm that utilized the inclusion function of the objective function that was built by the so called natural interval extension. Interval arithmetic and the interval extension of the used standard functions were realized by the PROFIL library [6]. The algorithm itself was an updated and customized version of the global optimization procedure published in [5], and improved in several steps as in [1] and [4]. The computational environment was a Pentium IV PC (1 Gbyte RAM and 1.4 MHz) with a Linux operation system. The implemented algorithm was successfully applied to constrained nonlinear optimization problems, both to test examples and to hard real life problems [7].

## Solution of a particular problem

We are looking for the stationary solutions of the differential equation (1), i.e.

$$y_i - y_i^* = 0; \quad (i \in \{A, B\}) \tag{2}$$

together with the following additional equations:

$$Py_i^* = \gamma_i x_i p_i^\circ; \quad (i \in \{A, B, E\}), \tag{3}$$

$$\sum_{i \in \{A,B,E\}} x_i = 1, \tag{4}$$

$$\sum_{i \in \{A,B,E\}} y_i^* = 1, \tag{5}$$

$$\lg p_i^\circ = A_i - \frac{B_i}{T - 273.14 + C_i}; \quad (i \in \{A, B, E\}), \tag{6}$$

$$\begin{aligned} \ln \gamma_i \quad = \quad & \frac{\sum\limits_{j \in \{A,B,E\}} \tau_{ji} G_{ji} x_j}{\sum\limits_{l \in \{A,B,E\}} G_{li} x_l} + \\ & \sum_{j \in \{A,B,E\}} \frac{x_j G_{ij}}{\sum\limits_{l \in \{A,B,E\}} G_{lj} x_j} \left( \tau_{ij} - \frac{\sum\limits_{n \in \{A,B,E\}} x_n \tau_{nj} G_{nj}}{\sum\limits_{l \in \{A,B,E\}} G_{lj} x_j} \right); \\ & (i \in \{A, B, E\}), \end{aligned} \tag{7}$$

$$\tau_{ij} = \frac{U_{ij}}{R_G T}; \quad (i, j \in \{A, B, E\}), \tag{8}$$

$$G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right); \quad (i, j \in \{A, B, E\}), \tag{9}$$

$$y_i = \left( \frac{R}{R+1} + \frac{F}{V} \right) x_i + \frac{1}{R+1} x_{D,i} - \frac{F}{V} x_{F,i}; \quad (i \in \{A, B\}), \tag{10}$$

where $A_i, B_i, C_i, U_{ij}$, and $\alpha_{ij}$ are material model parameters, $R_G$ is a general physical constant, $P, x_{D,i}$, and $x_{F,i}$ are problem specifications. The unknown variables of the problem itself are $x_A, x_B, x_E$, and $T$; whereas $p_i^\circ, \gamma_i, y_i, y_i^*, \tau_{ij}$, and $G_{ij}$ are unknown variables whose values are not interesting.

The particular problem to be solved is assigned by the model form (equations 3 and 6 to 9), the model parameters, and problem specifications. Long computations are usually performed with a set of possible $R$ and $F/V$ values. Below we demonstrate how one particular computation case of a problem is solved with our procedure.

Table 1. Material model parameters $A_i, B_i$, and $C_i$

| $i$ | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| A | 7.11714 | 1210.595 | 229.664 |
| B | 8.08097 | 1582.271 | 239.726 |
| E | 8.07131 | 1730.63 | 233.426 |

Table 2. Material model parameters $U_{ij}$, and $\alpha_{ij}$

| $i$ | $j$ | $U_{ij}$ | $U_{ji}$ | $\alpha_{ij} = \alpha_{ji}$ |
|---|---|---|---|---|
| A | B | 399.395 | -16.784 | 0.292 |
| A | E | -47.613 | 1919.523 | 0.291 |
| B | E | -347.817 | -347.817 | 0.302 |

In the particular case considered here $R_G = 1.98721$, $A_i, B_i$, and $C_i$ are given in Table 1, $U_ij$, and $\alpha_{ij}$ are given in Table 2. The specifications are $\mathbf{x}_D = [0.94, 0.025, 0.035]$, $\mathbf{x}_F = [0, 0, 1]$. The parameter values are $R = 4$, and $F/V = 0.2$.

There are four stationary points in the triangle with these values (one stable node, one unstable node, and two saddle points, and all of them are found. The stable node is located at $\mathbf{x}_{SN} \in [[0.572164 to 0.572274], [0.09436 to 0.094491], [0.33344 to 0.33368]]$.

Figure 3 shows how the composition triangle was originally decomposed in order to ease the search. The stable node is found in the middle lower subdomain. How the subdomain was successively subdivided into smaller subdomains in course is (partially) shown in Figures 4a-4c.

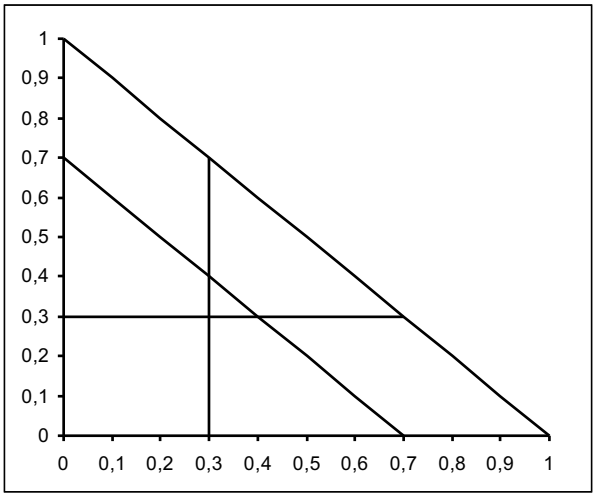


Figure 3: The original subdivision of the composition space

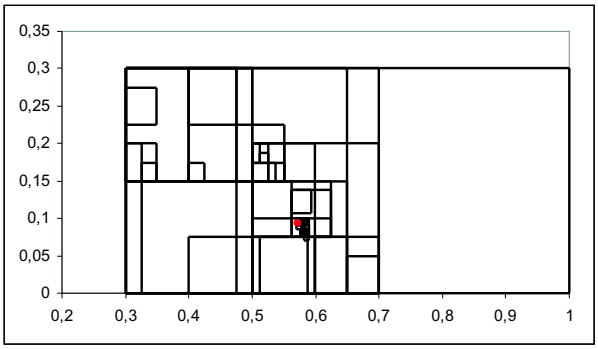


Figure 4.a: A subdivision in course

A set of boxes is shown in Figure 4a, with box borders along constant $x_A$ and constant $x_B$, but without indicating the box borders constituted by inequality constraints applied on $x_E$. That is, wider boxes are shown in the figure, for the sake of lucidity, than really used. The box containing a bold point is found as a candidate for containing a solution. All the other boxes were examined and then discarded because the method excluded the existence of a solution there. The box where solutions cannot be excluded were further subdivided.

A later subdivision is shown on Figure 4b; and an even later is on Figure 4c. The box containing a bold point contains a solution, and the existence of a solution in that box is proven by the method.

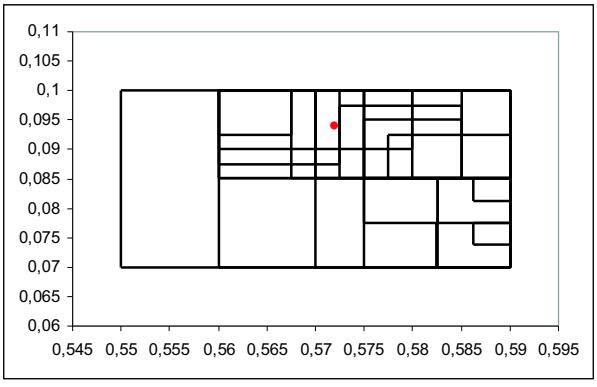


Figure 4.b: A later subdivision

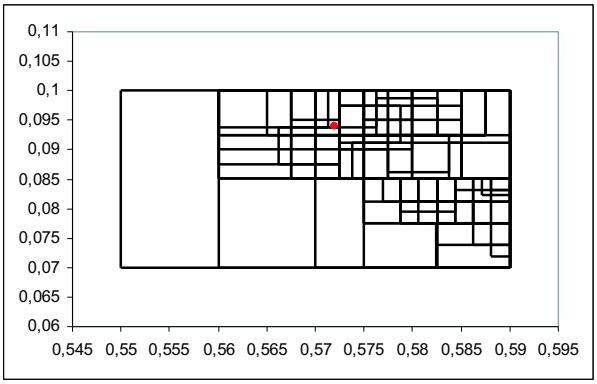


Figure 4.c: A later subdivision

## Summary

A methodology, recently developed at the Dept. Chem. Eng. BUTE, for checking feasibility of batch extractive distillation, an important chemical unit operation, applies graphical criteria for deciding whether a given set of design and operating parameters is applicable, and for finding the appropriate range of parameters. The use of graphical criteria is based on numerical solution of initial value problems. Feasibility of the process on phase curve maps, more precisely on the existence or absence of some singular points and separatrices in the phase space. Saddle points cannot be precisely located by graphical methodology. Conventional root finding procedures have also been used to find singular points, but their results are uncertain considering which zeros are found and which are not.

Looking for a more reliable methodology, a global and reliable interval optimization tool, a Branch and Bound technique, developed at the University of Szeged, and based on the C++ toolbox of R. Hammer et al., 1994, and the Profil/Bias routine library, is tried and successfully applied. The new methodology verified some known singular point paths and bifurcations, and also discovered new paths and bifurcations hitherto hidden.

Here we have introduced a subproblem of the feasibility methodology, sketched the working cycle of the interval algebra based optimization tool, and demonstrated its applicability on the targeted problem.

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