

## Use of interval optimization for finding limiting flows of batch extractive distillation

Erika R. Frits<sup>a,b,\*</sup>, Mihály Cs. Markót<sup>c</sup>, Tibor Csendes<sup>c</sup>, Zoltán Lelkes<sup>a</sup>, Zsolt Fonyó<sup>a,b</sup>,  
and Endre Rév<sup>a,b\*</sup>

<sup>a</sup>Budapest University of Technology and Economics, Dept. Chemical Engineering  
Budapest, H-1521, Hungary, e-mail: ufo@sunny.vemt.bme.hu

<sup>b</sup>Bud. Univ. of Techn. & Econ. – Hung. Acad. Sci. Res. Group of Techn. Chem.,  
Budapest, H-1521, Hungary, efrits@mail.bme.hu

<sup>c</sup>University of Szeged, Institute of Applied Informatics  
Pf. 652., Szeged, H-6701, Hungary, e-mail: csendes@inf.u-szeged.hu

### Abstract

The feasibility study on batch extractive distillation is based on analysing profile maps. Existence and loci of singular points and separatrices in these maps depend on the process parameters; and the limiting flows of the process belong to those parameter values at which the map changes shape. These data can be roughly estimated by graphical tools, but cannot be determined with certainty. One cannot be sure whether a singularity exists, if not found. Reliable computation of all the zeroes or all the minima of real functions, on the other hand, is provided by applying interval computation. Therefore, the problems of finding the singular points and the bifurcation points are reformulated as minimization problems and are solved by an interval arithmetic based branch and bound optimizer. All the singular points of the maps have been found in this way at specified process parameters. Limiting flows are determined with the same methodology by finding the bifurcation points and the corresponding parameter values.

**Keywords:** interval arithmetic, extractive distillation, feasibility, bifurcation, profile map

### 1. Introduction

Batch extractive distillation is a fed-batch process performed in a batch rectifier unit as is shown in *Figure 1*. The charge consisting of two components A and B, to be separated, is fed to the still. After heating up with total reflux, continuous feeding of entrainer component E to the column is started. Once the top composition reaches its specified value, producing distillate ( $D$ ) with a designed reflux ratio ( $R=L/D$ ) is started with maintaining continuous entrainer feeding with a designed ratio of its flow rate ( $F$ ) to the vapour flow rate ( $V$ ). Feasibility of the process is rather sensitive to  $R$  and  $F/V$ . The appropriate (feasible) range of  $R$  and  $F/V$ , as well as the feasible region of still

---

\* Author/s to whom correspondence should be addressed: E. R. Frits and E. Rev

compositions can be estimated by analysing the profile maps (Lelkes et al, 1998; Lelkes et al, 2002, Rev et al, 2003).

Such a map includes a curve (see Figure 3) approaching the rectifying profile started from a specified distillate composition  $x_D$  as initial value, and calculated by numerically solving the differential equation

$$\frac{dx}{dh} = \frac{V}{L} \left( y(x) - y^*(x) \right), \quad (1)$$

where  $h$  is dimensionless height,  $L$  is liquid flow rate,  $y^*(x)$  is equilibrium vapour composition, and  $y(x)$  is actual vapour composition according to the column's component balance (operating line) above the feed. The map also includes a series of curves (see Figure 2) approaching the extractive profiles started from potential still compositions  $x_S$  as initial values, and calculated by numerically solving the same differential equation (1) in the reverse direction, and with the actual vapour composition determined according to the balance (operating line) below the feed.  $x_S$  is feasible if the corresponding extractive profile meets the rectifying profile.

Singular points and separatrixes play a significant role in the feasibility of the process. For example, a particular map is shown in Figure 2 with singular points and 4 separatrixes two of which constitute borders against feasible still composition with the specified  $x_D$ .

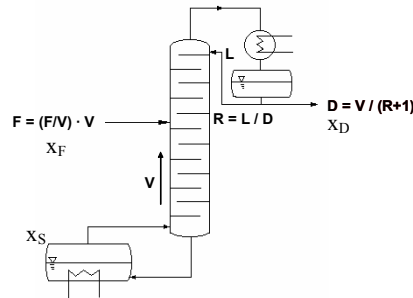


Figure 1. BED unit

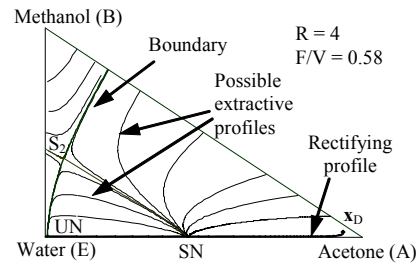


Figure 2. Profile map, separatrixes

Existence and loci of singular points and separatrixes in these maps depend on the process parameters; the limiting flows of the process belong to those parameter values at which the map changes shape. In order to find the characteristic stable, unstable, and saddle points of the map, one has to compute and visualise a dense bundle of profiles. This procedure is to be repeated several times with varied design/operational parameters, first of all  $R$  and  $F/V$ , for finding a feasible range of these parameters. Even in this way, the loci of saddle points cannot be precisely and certainly determined because of numerical reasons. That is why a new methodology has been developed utilizing a reliable, interval arithmetic based, optimization procedure.

## 2. Interval arithmetic based methodology

In order to solve the related root finding problems, we have implemented an interval arithmetic based optimization algorithm (Csendes, 2001; Csendes and Ratz, 1997).

Interval algebra provides us with a tool for determining real intervals that certainly include the range of the functions studied over a given domain. Utilizing this technique, all the roots of those functions, as well as all the minima of a real function, can be determined. Multivariate intervals are rectangular sets, called 'boxes'.

Criteria for singular points and bifurcation points can be described by algebraic equations. Instead of searching for zeroes of these equations, we formulated these problems as minimizing the sum of squares of the equation residues. The applied algorithm is the following:

Step 1: Let L be an empty list, the leading box  $A:=X$  (the total studied domain), and the iteration counter  $k:=1$ . Set the upper bound  $f^u$  of the global minimum 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  $f^u$  of the global minimum as the minimum of the old value and the upper bounds on the new subintervals. Step 3: Add the new subintervals to the list L. Step 4: Delete parts of the subintervals stored in L that cannot contain a global minimizer point. Step 5: Set A to be the subinterval from the list L that 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 is a branch-and-bound algorithm. Interval arithmetic and the interval extension of the used standard functions were realized by the PROFIL library (Knüppel, 1993). The algorithm itself is a customized version of the global optimization procedure published in Hammer et al, 1993, and improved in several steps. The computational environment was a Pentium IV PC (1 Gbyte RAM and 1.4 MHz) with Linux operation system.

### 3. Example problems

Acetone and methanol is to be separated with water as entrainer. Phase equilibrium is modelled with the Antoine equation for vapour tension, and NRTL equation for activity coefficient in the liquid phase. The vapour phase is considered ideal. The specifications are  $x_D = [0.94, 0.025, 0.035]$  (acetone, methanol, water), and pure water entrainer feed.

First the minimum reflux ratio  $R_{min}$  belonging to the process performed without entrainer feeding to the column (i.e. without extractive section) has been studied. This involves the problem of finding all the pinch points of an extended rectifying profile, as well as finding the bifurcation point. This is the ternary analogue to the case of binary distillation with inflecting equilibrium line.

Second, minimum feed ratio  $(F/V)_{min}$  belonging to several finite reflux ratios have been studied. Only the single case  $R=4$  is shown here. Again, the task was to determine all the singular points belonging to assumed  $F/V$  values, and the bifurcation point together with the actual value of  $F/V$ .

### 4. Determining $R_{min}$

The problem is illustrated in Figure 3. The profile ends at a pinch point, i.e. at a point where the right hand side of equation (1) is equal to zero. In case of  $R < R_{min}$ , this happens at three isolated points in the triangle, and the profile terminates at the first one in any way. There is exactly two such points if  $R = R_{min}$ , and only one if  $R > R_{min}$ . In principle,  $R_{min}$  can be determined by monitoring the presence and disappearance of the extra pinch

points.

Trials have earlier been performed (Lelkes et al, 2003) to find these points by solving the algebraic equation, e.g. with GAMS CONOPT (Brook et al., 1992); however, the conventional solvers always found only one type of these points.

As a contrary, the interval arithmetic tool was able to find all the three (or less) pinch points at any specified  $R$ . As a result, a bifurcation diagram can be plotted, as is shown in Figure 4. The stable points are arranged along curves of negative slope; the unstable points, could not be found with conventional solvers, form a curve of positive slope.

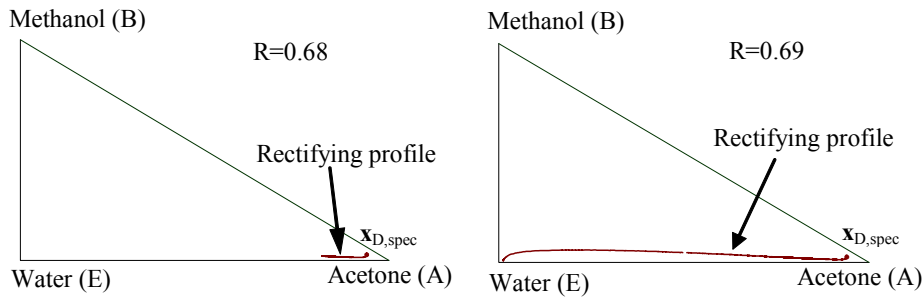


Figure 3. Rectifying profiles with reflux ratios around  $R_{min}$

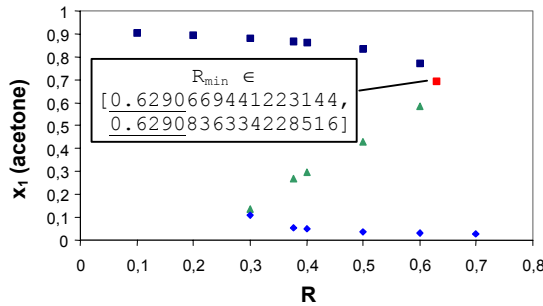


Figure 4. Plot of  $x_{Acetone}$  component of the found pinch points in function of  $R$

However, we were not able to well approximate the exact locus of the bifurcation even in this way because it is a meeting point of two solution curves.

Therefore,  $R_{min}$  was more precisely determined by formulating the bifurcation as an algebraic equation, and by including this equation as a new constraint in the problem. Our software then successfully found the right locus in the interval  $R=0.6290[66,84]$ .

## 5. Determining $(F/V)_{min}$

Four singular points of the extractive map are located in the arbitrary small neighbourhoods of the three vertices, and the arbitrary small neighbourhood of the azeotrope, if total reflux is applied and  $F/V$  approaches zero. How these points are shifted with increasing  $F/V$  is shown in Figure 5. These points are determined by the interval arithmetic optimization tool with stepwise incremented  $F/V$  parameters. The stable node originated from the azeotrope moves along the isovolatility curve (as is shown by Safrit et al, 1995, and proven by Lelkes et al, 1998), and meets an other point,

originated from the acetone vertex, just at the acetone/water edge. The  $F/V$  value at which this meeting happens is  $(F/V)_{\min}$ . At higher values, a stable point moves on the same edge toward the water vertex. As a result, all the extractive profiles (in case of total reflux) arrive to this point, and cross the rectifying profile, with the consequence of feasibility.

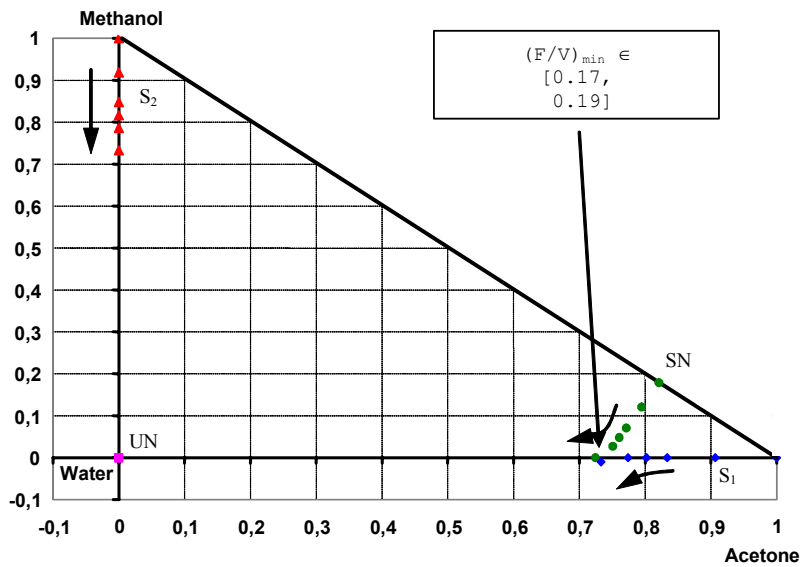


Figure 5. Singular point paths with evolving  $F/V$  with  $R=\infty$

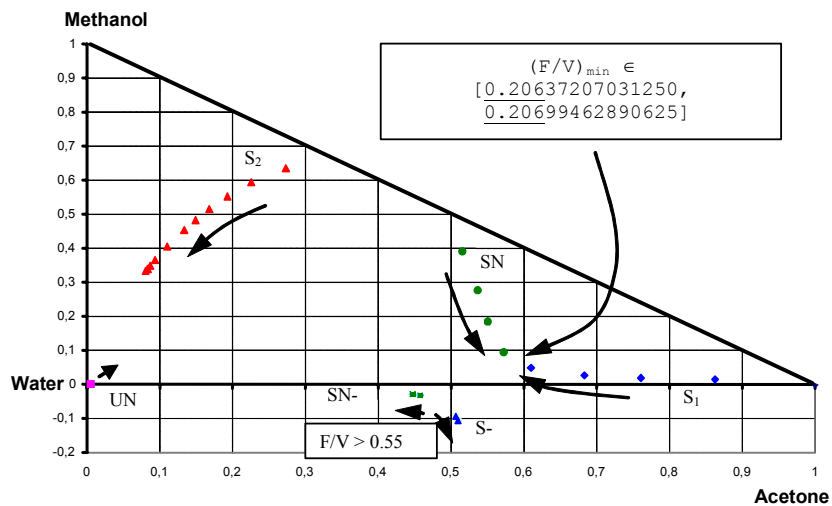


Figure 6. Singular point paths with evolving  $F/V$  with  $R=4$

All the singular points move into the interior of the triangle at decreasing  $R$ . A singular point path map is shown in Figure 6 with  $R=4$ . The most striking result, a novelty, is that the stable node originated from the azeotrope does not reach the acetone/water edge. There is a bifurcation at  $F/V=0.207$ , approximately; this is  $(F/V)_{\min}$ . Above this value the

extractive profiles are directed toward a point somewhere outside the triangle. A second bifurcation happens at about  $F/V=0.55$ . A new stable point SN- appears outside the composition triangle, and moves toward the water vertex. All these points were determined by the interval arithmetic optimization tool with stepwise incremented  $F/V$  parameters. The loci of points approaching the bifurcation had been again uncertain, but were then more precisely determined by inserting the bifurcation criterion as a constraint. Here we met the difficulty that the equation contains temperature as an implicit variable, and this is the boiling point assigned by a system of equations including activity coefficients as functions depending on both temperature and composition. This difficulty was overcome by applying the implicit function theorem.

## 6. Conclusions and recommendations

The interval arithmetic based branch and bound optimization tool can be applied to reliably determine all the singular points of the rectifying profile and of the extractive profile map related to the feasibility study of batch extractive distillation. The same methodology can be applied to reliably determine the bifurcation points of these maps. Minimum reflux ratio and minimum feed ratio can be determined using this methodology.

The stable node of the extractive map, originated from the azeotrope, does not reach the binary mixture's edge of the light component and the entrainer in case of applying finite reflux ratio, when the feed ratio is increased from zero. Instead, it meets the saddle point originated from the light component vertex, and they both disappear at minimum feed ratio, bifurcating to outside of the composition triangle.

As a consequence, the minimum feed ratio cannot be determined at finite reflux ratio according to the idea of tracing the stable node's path until it reaches the base edge. Instead, either the extractive curves have to be traced, or the bifurcation point has to be determined by algebraic tools. The implicit function theorem is to be applied for formulating the algebraic constraint of the bifurcation.

## References

- Brook, A., D. Kendrick, and A. Meeraus, 1992, GAMS. A User's Guide., boyd & fraser, USA.
- Csendes, T. and D. Ratz, 1997, SIAM J. Num. Anal. 34, 922.
- Csendes, T.: Interval Analysis: Subdivision Directions in Interval B&B Methods, 2001, in In: Floudas, C.A. and Pardalos, P.M. (eds.): Encyclopedia of Optimization, Kluwer, Dordrecht
- Hammer, R., M. Hocks, U. Kulisch and D. Ratz 1993, Numerical Toolbox for Verified Computing I., Springer-Verlag, Berlin
- Knüppel, O., 1993, PROFIL - Programmer's Runtime Optimized Fast Interval Library. Bericht 93.4, Technische Universität Hamburg-Harburg
- Lelkes, Z., P Lang, B. Benadda and P. Moszkowicz, 1998, AIChE Journal, 44, 810.
- Lelkes, Z., E. Rév, C. Stéger and Z. Fonyó, 2002, AIChE Journal, 48, 2524.
- Lelkes, Z., Z. Szitkai, T. Farkas, E. Rév and Fonyó, Z., 2003, Proc. ESCAPE-13, p. 203.
- Rév, E., Z. Lelkes, V. Varga, C. Stéger and Z. Fonyó, 2003, I&EC Res., 42, 162.
- Safrit, B.T., A.W. Westerberg, U. Diwekar and O.M. Wahnschafft, 1995, I&EC Res., 34, 3257.

## Acknowledgements

This research was partially supported by OTKA F046282, OTKA T034350, OTKA 032118 and OTKA T037191.