

Computation of Reactive Azeotropes Using Interval Analysis

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1 Introduction

In recent years, there has been an increasing interest in reactive distillation. Reasons for this interest include the need to separate close-boiling compounds, to save on equipment and operating costs, and to reduce environmental emissions (e.g., Barbosa and Doherty, 1988; Venimadhavan *et al.*, 1994). In some cases, compounds that are very expensive to separate using conventional techniques can be purified more cheaply, cleanly and efficiently using reactive distillation processes. An important question when considering the use of such techniques is whether or not any reactive azeotropes exist for the system. The presence of these reactive azeotropes may be either a deterrent, or in some cases may be an advantage for the proposed operation. Determining their existence from experiment alone can be both expensive and time consuming. Thus, it is desirable to have a reliable technique for computing reactive azeotropes from appropriate thermodynamic models.

There are two main difficulties in solving the problem. The first is the nonlinearity of the equilibrium conditions derived from most thermodynamic models, which may make finding any reactive azeotrope a nontrivial exercise. In addition, there is the question of whether or not all of the reactive azeotropes have been found, or of being certain that there are no reactive azeotropes if none have been found. Due to these difficulties, as well as the ramifications of the results on process design, there has been much recent interest in the reliable computation of reactive azeotropes. For problems involving vapor-liquid and chemical equilibrium, Ung and Doherty (1995b) provide a methodology for describing these systems in a transformed composition space, which has the effect of reducing the degrees of freedom for the problem by the number of independent equilibrium reactions present. The transformation also results in a convenient statement for the condition of reactive azeotropy, namely that the transformed compositions must be equal in the liquid and vapor phases, rather than the ordinary mole fractions of each component. Okasinski and Doherty (1997) used an arc-length continuation method to calculate reactive azeotropes for various systems. They used the equilibrium constant as a homotopy parameter, and tracked the value of the reactive azeotrope. They showed that there are ranges for the value of the equilibrium constant where reactive azeotropes may appear or disappear. Although continuation techniques have been used with success in many areas, they cannot provide theoretical or computational guarantees that the correct number of reactive azeotropes have been found.

2 Methodology

We describe here a new approach for reliably finding (enclosing) all homogeneous reactive azeotropes for systems in phase and chemical equilibrium. The technique is based on interval analysis, in particular the use of an interval-Newton/generalized bisection algorithm. The method can enclose *with mathematical and computational certainty* all reactive azeotropes for any system. The technique is general-purpose and can be applied in connection with any thermodynamic models. No model-specific convex underestimating functions need be

derived. The methodology used can also be applied to the computation of nonreactive azeotropes, homogeneous (Maier et al., 1998) or heterogeneous. In this presentation, we concentrate on the application of the technique to the reactive azeotrope problem, and describe the results obtained.

2.1 Problem Formulation

The conditions for homogeneous reactive azeotrope are phase equilibrium, chemical equilibrium, and the reactive azeotropy condition (Ung and Doherty, 1995a) itself, $Y_i = X_i$, where Y_i and X_i are the transformed mole fractions in the vapor and liquid phases, respectively, of component i . A complete description of the transformed mole fractions and the determination of reference components is given by Ung and Doherty (1995b). For the computations presented here, we use Antoine’s equation for the calculation of vapor pressures, the fully temperature dependent Wilson equation for activity coefficients and assume an ideal vapor phase. Note that these choices are arbitrary, there are no restrictions on the choice of the activity coefficient model or vapor pressure model, and the method can be easily extended to use equation of state models for both the liquid and vapor phases.

2.2 Interval Newton Generalized Bisection

The solution method used is the interval Newton/generalized bisection technique described by Kearfott (1987a,b), and implemented in INTBIS (Kearfott and Novoa, 1990). The algorithm is also summarized, in the context of chemical process modeling, by Schnepfer and Stadtherr (1996).

For a system of nonlinear equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ with $\mathbf{x} \in \mathbf{X}^{(0)}$, the basic iteration step in interval Newton methods is, given an interval $\mathbf{X}^{(k)}$, to solve the linear interval equation system

$$F'(\mathbf{X}^{(k)})(\mathbf{N}^{(k)} - \mathbf{x}^{(k)}) = -\mathbf{f}(\mathbf{x}^{(k)}) \tag{1}$$

for a new interval $\mathbf{N}^{(k)}$, where k is an iteration counter, $F'(\mathbf{X}^{(k)})$ is an interval extension of the real Jacobian $f'(\mathbf{x})$ of $f(\mathbf{x})$ over the current interval $\mathbf{X}^{(k)}$, and $\mathbf{x}^{(k)}$ is a point in the interior of $\mathbf{X}^{(k)}$, usually taken to be the midpoint. It can be shown (Moore, 1966) that any root $\mathbf{x}^* \in \mathbf{X}^{(k)}$ is also contained in the image $\mathbf{N}^{(k)}$, suggesting the iteration scheme $\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} \cap \mathbf{N}^{(k)}$. While this iteration scheme can be used to tightly enclose a solution, what is also of significance here is the power of equation (1) as an existence and uniqueness test. For several techniques for finding $\mathbf{N}^{(k)}$ from equation (1), it can be proven (e.g., Neumaier, 1990; Kearfott, 1996) that if $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then there is a *unique* zero of $\mathbf{f}(\mathbf{x})$ in $\mathbf{X}^{(k)}$, and that Newton’s method with real arithmetic can be used to find it, starting from any point in $\mathbf{X}^{(k)}$. This suggests a root inclusion test for $\mathbf{X}^{(k)}$:

1. (Range Test) Compute an interval extension $\mathbf{F}(\mathbf{X}^{(k)})$ containing the range of $\mathbf{f}(\mathbf{x})$ over $\mathbf{X}^{(k)}$ and test to see whether it contains zero. Clearly, if $0 \notin \mathbf{F}(\mathbf{X}^{(k)}) \supseteq \{\mathbf{f}(\mathbf{x}) \mid \mathbf{x} \in \mathbf{X}^{(k)}\}$ then there can be no solution of $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ in $\mathbf{X}^{(k)}$ and this interval need not be further tested.

2. (Interval Newton Test) Compute the image $\mathbf{N}^{(k)}$ by solving equation (1).
 - (a) If $\mathbf{X}^{(k)} \cap \mathbf{N}^{(k)} = \emptyset$, then there is no root in $\mathbf{X}^{(k)}$.
 - (b) If $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then there is exactly one root in $\mathbf{X}^{(k)}$.
 - (c) If neither of the above is true, then no further conclusion can be drawn.

In the last case, one could then repeat the root inclusion test on the next interval Newton iterate $\mathbf{X}^{(k+1)}$, assuming it is sufficiently smaller than $\mathbf{X}^{(k)}$, or one could bisect $\mathbf{X}^{(k+1)}$ and repeat the root inclusion test on the resulting intervals. This is the basic idea of interval Newton/generalized bisection methods. If $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ has a finite number of real solutions in the specified initial box, a properly implemented interval Newton/generalized bisection method can enclose *with mathematical and computational certainty* any and all solutions to a specified tolerance, or can determine *with mathematical certainty* that there are no solutions in the given box (Kearfott and Novoa, 1990; Kearfott, 1990).

3 Results and Discussion

We discuss the results from one of our test problems below. This system contains 3 components (isobutene, methanol, and MTBE), and one reaction (isobutene + methanol \leftrightarrow MTBE). This problem has also been considered by Okasinski and Doherty (1997). This system is of particular interest as it has been shown to have two reactive azeotropes for some values of the equilibrium constant. For this particular case, we use 49.0 as the equilibrium constant value. The other parameters used were the same as those provided by Okasinski and Doherty (1997).

Table 1 - Computational results for the system isobutene, methanol, and MTBE at 8.0 atm. The equilibrium constant is 49.0. The temperature range for search was 10-200 °C.

x_1	x_2	x_3	y_1	y_2	y_3	$T(^{\circ}\text{C})$	CPU time (sec)
0.014	0.404	0.582	0.076	0.440	0.484	118.0	
0.045	0.120	0.835	0.174	0.238	0.588	119.1	
Total							5.81

The CPU time is for a Sun Ultra 30 workstation.

The results obtained are in good agreement with the solutions given by Okasinski and Doherty (1997). We have additional results for many other examples, including those using the NRTL activity coefficient model.

4 References

- Barbosa, D. and M. F. Doherty, The influence of equilibrium chemical reactions on vapor-liquid phase diagrams. *Chem. Eng. Sci.*, 43, 529–540 (1988).
- Kearfott, R. B., Abstract generalized bisection and a cost bound. *Math. Comput.*, 49, 187–202 (1987a).
- Kearfott, R. B., Some tests of generalized bisection. *ACM Trans. Math. Softw.*, 13, 197–220 (1987b).
- Kearfott, R. B., Interval arithmetic techniques in the computational solution of nonlinear systems of equations: Introduction, examples, and comparisons. *Lectures in Applied Mathematics*, 26, 337–357 (1990).
- Kearfott, R. B., *Rigorous Global Search: Continuous Problems*. Kluwer Academic Publishers, Dordrecht, The Netherlands (1996).
- Kearfott, R. B., and Manuel Novoa III. Algorithm 681: INTBIS, a portable interval-Newton / bisection package. *ACM Trans. Math. Softw.*, 16, 152–157 (1990).
- Maier, R. W., J. F. Brennecke and M. A. Stadtherr, Reliable computation of homogeneous azeotropes, *AIChE J.*, 44, 1745–1755 (1998).
- Moore, R. E., *Interval Analysis*. Prentice-Hall, Englewood Cliffs (1966).
- Neumaier, A., *Interval Methods for Systems of Equations*. Cambridge University Press, Cambridge, England (1990).
- Okasinski, M. J., and M. F. Doherty, Thermodynamic behavior of reactive azeotropes. *AIChE J.*, 43, 2227–2238 (1997).
- Ung, S., and M. F. Doherty, Necessary and sufficient conditions for reactive azeotropes in multireaction mixtures. *AIChE J.*, 41, 2383–2392 (1995a).
- Ung, S., and M. F. Doherty, Vapor-liquid phase equilibrium in systems with multiple chemical reactions. *Chem. Eng. Sci.*, 50, 23–48 (1995b).
- Schnepper, C. A. and M. A. Stadtherr, Robust process simulation using interval methods. *Comput. Chem. Eng.*, 20, 187–199 (1996).
- Venimadhavan, G., G. Buzad, M. F. Doherty and M. F. Malone, Effect of kinetics on residue curve maps for reactive distillation. *AIChE J.*, 40, 1814–1824 (1994).