Computation of Reactive Azeotropes Using Interval Analysis

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Computing Reactive Azeotropes

• Why?
  – Identify limitations/benefits for reactive distillation operations
  – Evaluate thermodynamic models
  – Reduce time required for costly experimentation

• How?
  – Solve a system of nonlinear equations derived from equifugacity and chemical equilibrium conditions
  – This equation system has an unknown number of solutions
Reactive Azeotropy

- Equality of Transformed Mole Fractions (Ung and Doherty, 1995)

\[ Y_i = X_i, \ \forall i \in C_N \]

\[ Y_i = \left( \frac{y_i - \nu_i^T \mathbf{V}^{-1} y_{Ref}}{1 - \nu_{TOT}^T \mathbf{V}^{-1} y_{Ref}} \right) \]

\[ X_i = \left( \frac{x_i - \nu_i^T \mathbf{V}^{-1} x_{Ref}}{1 - \nu_{TOT}^T \mathbf{V}^{-1} x_{Ref}} \right) \]

- \( C_N \) is the set of non-reference components
- \( \mathbf{V} \) is the matrix of stoichiometric coefficients for the reference components
- \( \nu_i \) is the vector of stoichiometric coefficients for component \( i \)
- \( \nu_{TOT} \) is the vector of total mole generation for each non-reference component over all reactions
Reactive Azeotropy (Cont’d)

- Phase Equilibrium

\[ y_i P = x_i \gamma_i^L (T) P_i^{sat} (T), \quad \forall i \in C \]

- \( C \) is the set of all components

- Chemical Equilibrium

\[ K_r (T) = \prod_{i \in C} a_i^{\nu r_i}, \quad \forall r \in R \]

- \( R \) is the set of independent chemical reactions

- Summation Constraints

\[ \sum_{i \in C_N} X_i = \sum_{i \in C_N} Y_i = 1 \]

\[ \sum_{i \in C} x_i = \sum_{i \in C} y_i = 1 \]
Formulation

• Need to choose a set of independent variables and equations

• Solve phase equilibrium relations for $y_i$, and substitute into equations for $Y_i$

• Independent variables are the liquid phase mole fractions and temperature

• Formulation is

\[ X_i (x, T) = Y_i (x, T) , \forall i \in C_N \]

\[ K_r (T) = \prod_{i \in C} a_{ri}^{\nu} (x, T) , \forall r \in R \]

\[ \sum_{i \in C} x_i = 1 \]
Formulation (cont’d)

- All homogeneous reactive azeotropes are solutions

- Stability of solutions solved for separately, using the same solution technique

- Need solution method guaranteed to find all solutions, or to determine with certainty that there are none.
Some Current Solution Methods

• Various local methods — Fast, but initialization dependent and hard to find all roots

• Ung and Doherty (1995) derived transformed composition variables
  – Reduced the number of degrees of freedom
  – Convenient statement of reactive azeotropy
    \( X_i = Y_i \)

• Okasinski and Doherty (1997) used arc-length continuation with the equilibrium constant as the homotopy parameter
Interval Approach

- Interval Newton/Generalized Bisection (IN/GB)
  - Given a system of equations to solve, an initial interval (bounds on all variables), and a solution tolerance
  - IN/GB can find (enclose) with mathematical and computational certainty either all solutions or that no solutions exist. (e.g., Kearfott 1987, 1996; Neumaier 1990)

- A general purpose approach: requires no simplifying assumptions or problem reformulations

- Details of algorithm given by Schnepper and Stadtherr (1996)

- Implementation based on modifications of routines from INTBIS and INTLIB packages (Kearfott and coworkers)
Interval Approach (Cont’d)

Problem: Solve $f(x) = 0$ for all roots in interval $X^{(0)}$.

Basic iteration scheme: For a particular subinterval (box), $X^{(k)}$, perform root inclusion test:

- Compute the range of each function in the system.
- If 0 is not an element of each range, delete the box.
- If 0 is an element of each range, then compute the image, $N^{(k)}$, of the box by solving

$$F'(X^{(k)})(N^{(k)} - x^{(k)}) = -f(x^{(k)})$$

- $x^{(k)}$ is some point in the interior of $X^{(k)}$.
- $F'(X^{(k)})$ is an interval extension of the Jacobian of $f(x)$ over the box $X^{(k)}$. 
There was no solution in $X^{(k)}$
Unique solution in $X^{(k)}$
This solution is in $N^{(k)}$
Point Newton method will converge to it
Any solutions in $X^{(k)}$ are in the intersection of $X^{(k)}$ and $N^{(k)}$.

If intersection is sufficiently small, repeat root inclusion test; otherwise bisect the result of the intersection and apply root inclusion test to each resulting subinterval.
Example Problems

• First 2 examples previously solved by Barbosa and Doherty (1988)

• Third example previously solved by Okasinski and Doherty (1997)

• Vapor phase modeled as ideal

• Full temperature dependence of $\gamma_i$ is included

• Times reported for Sun Ultra 30 workstation
Results - Problem 1

- $A + B \leftrightarrow C$

- 1 atm, 10-200 °C

- $\Delta G_f^o = -8314 J/mol$, ideal liquid phase

<table>
<thead>
<tr>
<th>Reactive Azeotrope</th>
<th>$x_i$</th>
<th>$y_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.07</td>
<td>0.17</td>
</tr>
<tr>
<td>B</td>
<td>0.50</td>
<td>0.55</td>
</tr>
<tr>
<td>C</td>
<td>0.43</td>
<td>0.28</td>
</tr>
<tr>
<td>$T = 121.7^\circ C$</td>
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<td></td>
</tr>
</tbody>
</table>

- $X_A = Y_A = 0.35$

- $X_B = Y_B = 0.65$

- CPU time = 2.1 sec
Results - Problem 2

- $A + B \leftrightarrow C + D$
- 1 atm, 10-200 °C
- $\Delta G_f^{\circ} = -831.4 J/mol$, ideal liquid phase

<table>
<thead>
<tr>
<th>Reactive Azeotrope</th>
<th>$x_i$</th>
<th>$y_i$</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>0.19</td>
<td>0.07</td>
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<tr>
<td>B</td>
<td>0.36</td>
<td>0.24</td>
</tr>
<tr>
<td>C</td>
<td>0.21</td>
<td>0.33</td>
</tr>
<tr>
<td>D</td>
<td>0.24</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>$T = 89.5^\circ C$</td>
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</tbody>
</table>

- $X_A = Y_A = 0.43$
- $X_B = Y_B = 0.60$
- $X_C = Y_C = -0.03$
- CPU time = 12.2 sec
Results - Problem 3

- Isobutene + Methanol $\leftrightarrow$ MTBE

- 8 atm, 10-200 °C

- $K_{eq} = 49.0$, Wilson Activity Coefficient Model

<table>
<thead>
<tr>
<th>Reactive Azeotropes</th>
<th>$x_i$</th>
<th>$y_i$</th>
<th>$x_i$</th>
<th>$y_i$</th>
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</thead>
<tbody>
<tr>
<td>$i - C4$</td>
<td>0.01</td>
<td>0.07</td>
<td>0.04</td>
<td>0.17</td>
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<tr>
<td>MeOH</td>
<td>0.40</td>
<td>0.44</td>
<td>0.12</td>
<td>0.24</td>
</tr>
<tr>
<td>MTBE</td>
<td>0.59</td>
<td>0.49</td>
<td>0.84</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>$T = 118.0°C$</td>
<td>$T = 119.1°C$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- $X_{I1} = Y_{I1} = 0.38$

- $X_{Me1} = Y_{Me1} = 0.62$

- $X_{I2} = Y_{I2} = 0.48$

- $X_{Me2} = Y_{Me2} = 0.52$

- CPU time (total) = 5.6 sec
Concluding Remarks

- Interval analysis provides a general-purpose approach for solving reactive azeotrope problems, providing a mathematical and computational guarantee of reliability.

- Can be used in conjunction with other activity coefficient models and EOS.

- Can also be used with multiple reactions and in the presence of inerts.

- Interval analysis is also a general-purpose approach for solving other types of azeotrope problems: nonreactive, homogeneous (Maier et al., 1998) or heterogeneous.

- Interval analysis provides powerful problem solving techniques with many other applications in the modeling of phase behavior and in other process modeling problems (e.g., Schnepper and Stadtherr, 1996; Hua et al., 1998)
• Acknowledgments
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