

# Locating All Heterogeneous And Reactive Azeotropes In Multicomponent Mixtures

Stephen T. Harding and Christodoulos A. Floudas <sup>1</sup>

*Department of Chemical Engineering,  
Princeton University,  
Princeton, New Jersey 08544*

**Submitted: July 14, 1999**

**Revised: September 24, 1999**

## Abstract

A novel approach for enclosing all heterogeneous and reactive azeotropes in multicomponent mixtures is presented. The thermodynamic conditions for azeotropy form a system of nonlinear equations. A deterministic global optimization approach is introduced in which the global optimization problem may contain multiple global minima and there is a one-to-one correspondence between each global minimum and a potential azeotrope. An algorithm is presented which provides a theoretical guarantee that all global minima can be enclosed. This method is general, and can be applied to multicomponent mixtures that are described by standard thermodynamic models. The problem formulations for finding all heterogeneous azeotropes and for finding all reactive azeotropes are presented. The effectiveness of the proposed approach is illustrated through several example problems using the Wilson, NRTL, UNIQUAC, and UNIFAC activity coefficient equations.

## 1 Introduction

An azeotrope is defined as a liquid mixture that boils at a constant temperature where the composition of the vapor phase is identical to the composition of the boiling liquid. When the boiling liquid contains a single phase, this phenomenon is called a homogeneous azeotrope. If the liquid consists of two or more phases it is classified as a heterogeneous azeotrope. Azeotropes may also occur in systems where one or more chemical reactions are occurring. These are denoted as reactive azeotropes, and may be classified as homogeneous reactive azeotropes or heterogeneous reactive azeotropes, depending upon the number of liquid phases.

---

<sup>1</sup>Author to whom all correspondence should be addressed. Ph: (609) 258-4595 Fax: (609) 258-2391  
Email: floudas@titan.princeton.edu

The phenomenon of azeotropy occurs in many industrial applications. Azeotropes restrict the amount of separation of a multicomponent mixture that can be achieved by distillation. Therefore, the ability to predict the occurrence of azeotropes in multicomponent mixtures is an essential tool in the design of separation processes. In addition, it is well known that systems can contain more than one azeotrope, so a method for locating azeotropes must be able to reliably predict *all* of the azeotropes in the system. A method for locating all azeotropes can also be used as a measure of the accuracy of a thermodynamic model based on how close the azeotropes that it predicts correspond to the experimentally determined azeotropes.

Several methods have been recently proposed to address the problem of locating all homogeneous azeotropes. Fidkowski et al.<sup>1</sup> presented a homotopy continuation approach which they applied to a number of systems containing up to five components. A deterministic global optimization approach was developed by Harding et al.<sup>2</sup>. This approach can provide a theoretical guarantee that all homogeneous azeotropes can be enclosed. Maier et al.<sup>3</sup> have applied an interval-Newton/generalized-bisection algorithm to compute all homogeneous azeotropes. A review on nonideal distillation, including a discussion on the computation of azeotropes was published by Widagdo and Seider<sup>4</sup>. As an extension of the problem of locating all azeotropes, Wasykiewicz and Castillo<sup>5</sup> have proposed a bifurcation and arc length continuation method for analyzing the sensitivity of homogeneous azeotropes with respect to changes in pressure.

There has been less attention given to the problem of finding all heterogeneous and reactive azeotropes. Chapman and Goodwin<sup>6</sup> presented a search method for finding homogeneous and heterogeneous azeotropes which uses a Levenberg-Marquardt algorithm to find homogeneous azeotropes and then checks the stability of each solution with the tangent plane criterion described by Michelsen<sup>7</sup>. A solution which is found to be unstable is then used as the starting point for a new search for an heterogeneous azeotrope. This method is limited by the fact that heterogeneous azeotropes do not necessarily correspond to an unstable homogeneous azeotrope solution and vice versa. Eckert and Kubicek<sup>8</sup> have extended the homotopy-continuation approach of Fidkowski et al.<sup>1</sup> for finding all homogeneous azeotropes to the problem of finding all heterogeneous azeotropes. They presented results using the NRTL equation for a four-component system.

Ung and Doherty<sup>9</sup> derived a necessary and sufficient condition for the existence of reactive azeotropes. Okasinski and Doherty<sup>10</sup> presented a homotopy-continuation approach for the determination of reactive azeotropes. In addition, they studied the effect of different reaction equilibrium constants on the existence and composition of reactive azeotropes.

The purpose of this study is to extend the method of Harding et al.<sup>2</sup> for enclosing all homogeneous azeotropes to the problems of enclosing all heterogeneous and reactive

azeotropes. In this paper, the vapor phase is modeled as an ideal gas at low pressure, and activity coefficient models are used for the liquid phases. However, the approach is general and can be applied to equation of state models as well. The activity coefficient models examined are: the Wilson equation, the NRTL equation, the UNIQUAC equation, and the UNIFAC equation. The problem is formulated as a global optimization problem in which each global minimum solution corresponds to a heterogeneous or a reactive azeotrope. Computational studies demonstrating the performance of the proposed method are presented for both formulations.

It is interesting to note that many chemical engineering problems can be formulated as a system of nonlinear equations. Typically, local solutions are located using iterative methods or even graphical methods. The framework of the global optimization method for enclosing all solutions that is presented in this paper could be extended to address such problems as design and simulation of distillation columns, or determining the multiple steady states of reactors or distillation columns. The convex lower bounding functions developed in this paper could be directly applied to the thermodynamic functions that occur in these problems.

## 2 Problem Description and Formulation

### 2.1 Heterogeneous Azeotropes

Heterogeneous azeotropes occur in a boiling mixture of two or more liquid phases when the composition of the vapor phase is the same as the overall composition of the liquid.

#### 2.1.1 Thermodynamic Conditions for Heterogeneous Azeotropy

There are three thermodynamic conditions which a system must meet in order for a heterogeneous azeotrope to exist. These conditions are: 1) equilibrium between all phases, 2) the composition of vapor phase must be identical to the overall composition of the liquid, and 3) the mole fractions of the components in each phase must sum to unity and must be non-negative.

*The equilibrium condition* requires that the chemical potential of each component must be the same in all phases. This condition can be satisfied by requiring that, for every liquid phase ( $L_j$ ), the chemical potential of each component in the liquid phase be identical to the chemical potential of the corresponding component in the vapor phase:

$$\mu_i^V = \mu_i^{L_j} \quad \forall i \in N \quad \forall j \in P^L \quad (1)$$

where  $\mu_i^V$  and  $\mu_i^{L_j}$  represent the chemical potential of component  $i$  in the vapor and in liquid phase  $j$ , and  $P^L$  denotes the set of liquid phases. The chemical potential for component  $i$

can be written,

$$\mu_i = G_i^o + RT \ln \frac{\hat{f}_i}{f_i^o} \quad (2)$$

where  $\hat{f}_i$  represents the fugacity of component  $i$  in the mixture. By selecting the same standard state for all phases, equation (1) can be rewritten as,

$$\hat{f}_i^V = \hat{f}_i^{Lj} \quad \forall i \in N \quad \forall j \in P^L \quad (3)$$

In this work, we treat the vapor phase as ideal and the liquid phases as nonideal. For the ideal vapor phase, the fugacity is  $\hat{f}_i^V = y_i P$ . For the nonideal liquid phase, the fugacity is  $\hat{f}_i^{Lj} = x_i^{Lj} \gamma_i^{Lj} P_i^{sat}$ . Substituting these definitions into equation (3) gives,

$$y_i P = x_i^{Lj} \gamma_i^{Lj} P_i^{sat} \quad \forall i \in N \quad \forall j \in P^L \quad (4)$$

Because  $P_i^{sat}$  and  $\gamma_i$  are usually given as  $\ln P_i^{sat}$  and  $\ln \gamma_i$ , it is convenient to take the natural log of the simplified equilibrium constraint, resulting in:

$$\ln P + \ln y_i - \ln P_i^{sat} - \ln \gamma_i^{Lj} - \ln x_i^{Lj} = 0 \quad \forall i \in N \quad \forall j \in P^L \quad (5)$$

*The heterogeneous azeotropy condition* requires that the composition of the vapor phase is identical to the overall composition of the liquid. If we let  $m^{Lj}$  represent the fraction of material in the overall liquid that is contained in liquid phase  $j$ , then the composition of the vapor is written as:

$$y_i = \sum_{j \in P^L} m^{Lj} x_i^{Lj} \quad \forall i \in N \quad (6)$$

*The third condition* requires that the mole fractions in each phase sum to unity and have values between 0 and 1.

$$\begin{aligned} \sum_{i \in N} y_i &= 1 \\ \sum_{i \in N} x_i^{Lj} &= 1 \quad \forall j \in P^L \\ \sum_{j \in P^L} m^{Lj} &= 1 \\ 0 \leq y_i, x_i^{Lj}, m^{Lj} &\leq 1 \quad \forall i \in N \quad \forall j \in P^L \end{aligned} \quad (7)$$

### 2.1.2 Heterogeneous Azeotrope Mathematical Formulation

In order to find all heterogeneous azeotropes, one must find all solutions to the system of nonlinear equations (4), (6), and (7) listed in the previous section. This paper uses the approach outlined in Maranas and Floudas<sup>11</sup>, which reformulates the problem of enclosing all solutions of nonlinear systems of constrained equations into a global optimization problem in which the task is to enclose all global solutions. In this approach, every nonlinear equality is replaced by two inequalities and a single slack variable is introduced. For the location of all heterogeneous azeotropes, this corresponds to employing equations (5), (6), and (7) and reformulating them as the following global optimization problem:

$$\begin{aligned}
& \min_{\mathbf{x}, \mathbf{y}, T, s} && s \\
\text{subject to} &&& \ln P + \ln y_i - \ln P_i^{sat} - \ln \gamma_i^{L_j} - \ln x_i^{L_j} - s \leq 0 \quad \forall i \in N \quad \forall j \in P^L \\
&&& -\ln P - \ln y_i + \ln P_i^{sat} + \ln \gamma_i^{L_j} + \ln x_i^{L_j} - s \leq 0 \quad \forall i \in N \quad \forall j \in P^L \\
&&& y_i - \sum_{j \in P^L} m^{L_j} x_i^{L_j} - s \leq 0 \quad \forall i \in N \\
&&& -y_i + \sum_{j \in P^L} m^{L_j} x_i^{L_j} - s \leq 0 \quad \forall i \in N \\
&&& \sum_{i \in N} y_i = 1 \\
&&& \sum_{i \in N} x_i^{L_j} = 1 \quad \forall j \in P^L \\
&&& \sum_{j \in P^L} m^{L_j} = 1 \\
&&& s \geq 0 \\
&&& 0 \leq y_i \leq 1 \quad \forall i \in N \\
&&& 0 \leq x_i^{L_j} \leq 1 \quad \forall i \in N \quad \forall j \in P^L \\
&&& 0 \leq m^{L_j} \leq 1 \quad \forall j \in P^L \\
&&& T^L \leq T \leq T^U
\end{aligned} \tag{8}$$

Due to the nonconvex constraints that arise from the phase equilibrium condition and the heterogeneous azeotrope condition, problem (8) may have multiple global minima. Each global minimum of Problem (8) (where the solution  $s^* = 0$ ) corresponds to an heterogeneous azeotrope since when  $s = 0$  the constraints (5), (6), and (7) are satisfied. Note that the first two sets of constraints of (8) correspond to the nonlinear equations (5) of the equilibrium constraint written as two inequalities. In addition, note that the nonlinear terms  $\ln P_i^{sat}$ ,  $\ln \gamma_i^{L_j}$ , and  $\ln x_i^{L_j}$  appear as both positive and negative terms. The terms  $m^{L_j} x_i^{L_j}$  and  $-m^{L_j} x_i^{L_j}$  in the heterogeneous azeotrope conditions are bilinear and therefore also nonconvex. If a local

optimization approach is used to solve Problem (8), some or all of the global solutions may be missed.

## 2.2 Reactive Azeotropes

We consider that a reactive azeotrope occurs when a liquid mixture that is undergoing one or more chemical reactions boils at a constant temperature with no change in liquid and vapor compositions.

### 2.2.1 Thermodynamic Conditions for Reactive Azeotropy

Ung and Doherty<sup>9</sup> derived necessary and sufficient conditions for reactive azeotropes. For a system of  $N$  components with  $R$  chemical reactions, these conditions are: 1) equilibrium between all phases, 2) chemical equilibrium for all reactions, 3) the transformed vapor mole fraction is equal to the transformed liquid mole fraction for  $N - R - 2$  components, and 4) the mole fractions sum to unity and are bounded between 0 and 1.

The phase equilibrium expression for reactive azeotropes has the same form as the non-reactive case, equation (4). For an homogenous system the expression is:

$$\ln P_i^{sat} + \ln \gamma_i + \ln x_i - \ln y_i - \ln P = 0 \quad \forall i \in N. \quad (9)$$

For an heterogeneous system, the expression is written:

$$\ln P_i^{sat} + \ln \gamma_i^{L_j} + \ln x_i^{L_j} - \ln y_i - \ln P = 0 \quad \forall i \in N \quad \forall j \in P^L. \quad (10)$$

The second condition for reactive azeotropes is chemical equilibrium. The reaction equilibrium constant for each reaction  $r$  is defined by the following equation:

$$K_{eq}^r = \prod_{i=1}^N a_i^{\nu_i^r} \quad (11)$$

where, by convention, the stoichiometric coefficients,  $\nu_i^r$ , are negative for reactants and positive for products and zero for inert components. The variable  $a_i$  is the activity of component  $i$ , defined as  $a_i = x_i \gamma_i$ . Since the activity coefficient for most equations is defined as  $\ln \gamma_i$ , for convenience we take the logarithm of both sides of equation 11, which results in,

$$\ln K_{eq}^r = \sum_{i=1}^N \nu_i^r (\ln x_i + \ln \gamma_i). \quad (12)$$

Ung and Doherty<sup>12</sup> proposed transformed composition variables that can be thought of as reaction-invariant compositions. The transformed variables describe the composition of the system as if no reaction was occurring. To define the transformed composition variables,

a set of  $R$  reference components are chosen. For the remaining  $N - R$  components, the transformation is defined as:

$$X_i = \left( \frac{x_i - \nu_i^T \mathbf{N}^{-1} \mathbf{x}_{Ref}}{1 - \nu_{TOT}^T \mathbf{N}^{-1} \mathbf{x}_{Ref}} \right) \quad i = 1, \dots, N - R \quad (13)$$

$$Y_i = \left( \frac{y_i - \nu_i^T \mathbf{N}^{-1} \mathbf{y}_{Ref}}{1 - \nu_{TOT}^T \mathbf{N}^{-1} \mathbf{y}_{Ref}} \right) \quad i = 1, \dots, N - R \quad (14)$$

where  $X_i$  is the transformed liquid composition of component  $i$ ,  $\mathbf{x}_{Ref}$  is the liquid composition of the set of  $R$  reference components,  $\nu_i^T$  is the row vector of stoichiometric coefficients of component  $i$  for each reaction, and  $\nu_{TOT}^T$  is a row vector where each element corresponds to a reaction  $r$ , and is the sum of the stoichiometric coefficients for all components that participate in reaction  $r$ . The square matrix  $\mathbf{N}$  is formed from the stoichiometric coefficients of the  $R$  reference components in the  $R$  reactions where the rows correspond to components and the columns correspond to reactions. Based on this analysis, they showed that one of the conditions for reactive azeotropy is that the reaction-invariant liquid composition must be equal to the reaction-invariant vapor composition, (Ung and Doherty<sup>9</sup>). Using the transformed composition variables, the third condition for reactive azeotropes is written:

$$X_i = Y_i \quad i = 1, \dots, N - R - 1 \quad (15)$$

The final condition requires that the mole fractions in each phase sum to unity and have values between 0 and 1.

$$\begin{aligned} \sum_{i \in N} y_i &= 1 \\ \sum_{i \in N} x_i &= 1 \\ 0 &\leq y_i, x_i \leq 1 \quad \forall i \in N \end{aligned} \quad (16)$$

### 2.2.2 Reactive Azeotrope Mathematical Formulation

In order to enclose all reactive azeotropes, one must enclose all solutions to the system of nonlinear equations (9) or (10), and (12), (14), (15), and (16) listed in the previous section.

The definitions of the transformed composition variables (equation 14) are fractional terms where both the numerator and denominator are linear expressions involving several variables. In order to simplify the formulation of the problem, the definitions are substituted into equation 15. This yields,

$$\left( \frac{x_i - \nu_i^T \mathbf{N}^{-1} \mathbf{x}_{Ref}}{1 - \nu_{TOT}^T \mathbf{N}^{-1} \mathbf{x}_{Ref}} \right) = \left( \frac{y_i - \nu_i^T \mathbf{N}^{-1} \mathbf{y}_{Ref}}{1 - \nu_{TOT}^T \mathbf{N}^{-1} \mathbf{y}_{Ref}} \right) \quad i = 1, \dots, N - R. \quad (17)$$

When the expression is multiplied by the denominator of both sides, the following equation is obtained:

$$\begin{aligned}
& (x_i - y_i) - \nu_i^T \mathbf{N}^{-1}(\mathbf{x}_{Ref} - \mathbf{y}_{Ref}) \\
& + (\nu_i^T \mathbf{N}^{-1} \mathbf{x}_{Ref} - x_i)(\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{y}_{Ref}) \\
& - (\nu_i^T \mathbf{N}^{-1} \mathbf{y}_{Ref} - y_i)(\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{x}_{Ref}) = 0 \quad i = 1, \dots, N - R.
\end{aligned} \tag{18}$$

Note that the first two terms in equation (18) are a group of linear terms, while the third and fourth terms are groups of bilinear terms.

In order to enclose all solutions to the system of nonlinear equations (9) or (10), and (12), (18), (16), we formulate the problem as a global minimization, where the objective is to minimize a slack variable,  $s$ , that corresponds to the violation of the nonlinear constraints. For the most general case of heterogeneous reactive azeotropes, that is, a boiling mixture containing  $N$  components undergoing  $R$  reactions in  $P^L$  liquid phases, the global optimization problem is formulated as follows:



$$\begin{aligned}
& \min_{\mathbf{x}, \mathbf{y}, T, s} & s \\
\text{subject to} & \ln P + \ln y_i - \ln P_i^{sat} - \ln \gamma_i^{Lj} - \ln x_i^{Lj} - s \leq 0 & \forall i \in N \quad \forall j \in P^L \\
& -\ln P - \ln y_i + \ln P_i^{sat} + \ln \gamma_i^{Lj} + \ln x_i^{Lj} - s \leq 0 & \forall i \in N \quad \forall j \in P^L \\
& \ln K_{eq}^r - \sum_{i \in N} \nu_i^r (\ln x_i^{Lj} + \ln \gamma_i^{Lj}) - s \leq 0 & \forall r \in R \quad \forall j \in P^L \\
& -\ln K_{eq}^r + \sum_{i \in N} \nu_i^r (\ln x_i^{Lj} + \ln \gamma_i^{Lj}) - s \leq 0 & \forall r \in R \quad \forall j \in P^L \\
& (x_i - y_i) - \nu_i^T \mathbf{N}^{-1} (\mathbf{x}_{Ref} - \mathbf{y}_{Ref}) \\
& + (\nu_i^T \mathbf{N}^{-1} \mathbf{x}_{Ref} - x_i) (\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{y}_{Ref}) \\
& - (\nu_i^T \mathbf{N}^{-1} \mathbf{y}_{Ref} - y_i) (\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{x}_{Ref}) - s \leq 0 & i = 1, \dots, N - R - 1 \\
& -(x_i - y_i) + \nu_i^T \mathbf{N}^{-1} (\mathbf{x}_{Ref} - \mathbf{y}_{Ref}) \\
& - (\nu_i^T \mathbf{N}^{-1} \mathbf{x}_{Ref} - x_i) (\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{y}_{Ref}) \\
& + (\nu_i^T \mathbf{N}^{-1} \mathbf{y}_{Ref} - y_i) (\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{x}_{Ref}) - s \leq 0 & i = 1, \dots, N - R - 1 \\
& x_i - \sum_{j \in P^L} m^{Lj} x_i^{Lj} - s \leq 0 & \forall i \in N \\
& -x_i + \sum_{j \in P^L} m^{Lj} x_i^{Lj} - s \leq 0 & \forall i \in N \\
& \sum_{i \in N} y_i = 1 \\
& \sum_{i \in N} x_i^{Lj} = 1 & \forall j \in P^L \\
& \sum_{j \in P^L} m^{Lj} = 1 \\
& s \geq 0 \\
& 0 \leq y_i \leq 1 & \forall i \in N \\
& 0 \leq x_i^{Lj} \leq 1 & \forall i \in N \quad \forall j \in P^L \\
& 0 \leq m^{Lj} \leq 1 & \forall j \in P^L \\
& T^L \leq T \leq T^U
\end{aligned} \tag{19}$$

Note that the variable  $x_i^{Lj}$  denotes the mole fraction of component  $i$  in liquid phase  $j$  and the variable  $x_i$  is the overall fraction of component  $i$  in the liquid phases.

When there is only one liquid phase present in the system, the above formulation can be greatly simplified to the following formulation:

$$\begin{aligned}
& \min_{\mathbf{x}, \mathbf{y}, T, s} && s \\
\text{subject to} &&& \ln P + \ln y_i - \ln P_i^{sat} - \ln \gamma_i - \ln x_i - s \leq 0 \quad \forall i \in N \\
&&& -\ln P - \ln y_i + \ln P_i^{sat} + \ln \gamma_i + \ln x_i - s \leq 0 \quad \forall i \in N \\
&&& \ln K_{eq}^r - \sum_{i \in N} \nu_i^r (\ln x_i + \ln \gamma_i) - s \leq 0 \quad \forall r \in R \\
&&& -\ln K_{eq}^r + \sum_{i \in N} \nu_i^r (\ln x_i + \ln \gamma_i) - s \leq 0 \quad \forall r \in R \\
&&& (x_i - y_i) - \nu_i^T \mathbf{N}^{-1} (\mathbf{x}_{Ref} - \mathbf{y}_{Ref}) \\
&&& + (\nu_i^T \mathbf{N}^{-1} \mathbf{x}_{Ref} - x_i) (\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{y}_{Ref}) \\
&&& - (\nu_i^T \mathbf{N}^{-1} \mathbf{y}_{Ref} - y_i) (\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{x}_{Ref}) - s \leq 0 \quad i = 1, \dots, N - R - 1 \\
&&& - (x_i - y_i) + \nu_i^T \mathbf{N}^{-1} (\mathbf{x}_{Ref} - \mathbf{y}_{Ref}) \\
&&& - (\nu_i^T \mathbf{N}^{-1} \mathbf{x}_{Ref} - x_i) (\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{y}_{Ref}) \\
&&& + (\nu_i^T \mathbf{N}^{-1} \mathbf{y}_{Ref} - y_i) (\nu_{TOT}^T \mathbf{N}^{-1} \mathbf{x}_{Ref}) - s \leq 0 \quad i = 1, \dots, N - R - 1 \\
&&& \sum_{i \in N} y_i = 1 \\
&&& \sum_{i \in N} x_i = 1 \\
&&& s \geq 0 \\
&&& 0 \leq y_i \leq 1 \quad \forall i \in N \\
&&& 0 \leq x_i \leq 1 \quad \forall i \in N \\
&&& T^L \leq T \leq T^U
\end{aligned} \tag{20}$$

### 3 Procedure for Locating All Heterogeneous and Reactive Azeotropes

#### 3.1 Description

The method presented in this paper for enclosing all heterogeneous and reactive azeotropes is based on the work of Maranas and Floudas<sup>11</sup> for enclosing all solutions to systems of nonlinear equations. In this section, the global optimization procedure will be summarized. The problem is formulated by introducing a slack variable to the equilibrium constraint of the initial problem. This transforms the initial problem into a global optimization problem (8), (19), or (20). Each feasible solution to the original system of equations corresponds to a zero objective function value and denotes the existence of an azeotrope.

The multiple global minima of formulations (8), (19), and (20) are enclosed based on a branch and bound procedure. This procedure creates a convex relaxation of the prob-

lem by constructing tight convex lower bounding functions for each nonconvex term in the constraints. Then, the global minimum of the convex relaxed problem within some box constraints can be found using any commercially available local optimization algorithm.

When the convex relaxed problem is solved, there are two possibilities. If the solution of the relaxed problem is strictly positive inside some rectangular region, then because it is an underestimator, the solution of the original problem must also be strictly positive inside the region. This allows us to fathom (eliminate) parts of the total region which do not contain any solutions. The second outcome is that the solution is zero. In this case, the original problem may or may not have a solution in the current region and thus the region cannot be fathomed. Instead, the current region is partitioned into smaller regions and the procedure is repeated until all regions are fathomed, or a feasible solution is found.

It is critical to note that as the size of the current region decreases, the maximum separation between the original constraint functions and the convex relaxed functions also decreases. Therefore, any feasible point of the relaxed problem can become at least  $\epsilon$ -feasible for the original problem by tightening the bounds around the point.

In this work, each region which has a non-positive solution of the convex relaxed problem is partitioned into two smaller regions by bisecting the longest side of the initial region. At each iteration in the branch and bound procedure, the lower bound of the original problem is calculated by finding the infimum over all minima of the relaxed problem in each region which has not been fathomed. Thus, a simple way of improving the lower bound is to halve only the subrectangle responsible for the infimum of the minima of the relaxed problem at each iteration. Convergence is reached when none of the subrectangles inside the total region have a negative lower bound in which case there are no solutions, or when all of the remaining subrectangles with negative lower bounds have been refined to a prespecified size tolerance.

### 3.2 Novel Approach to Handle Trivial Solutions

In the problem of enclosing all heterogeneous azeotropes, we assume that there are two or more liquid phases present, and we solve for the compositions of the liquid phases and the temperature for every heterogeneous azeotrope. However, it is possible to find solutions that satisfy the conditions for heterogeneous azeotropes where the compositions of the liquid phases are identical. When this occurs, the solution is called a “trivial” solution. Trivial solutions frequently correspond to homogeneous azeotropes.

From the constraint that the composition of the vapor phase is identical to the overall composition of the liquid phase, we have,

$$y_i = \sum_{j \in P^L} m^{L_j} x_i^{L_j} \quad (21)$$

Since  $x_i^{L_j}$  is the same for every component  $i$  in each liquid phase  $j$ , then the liquid phase fractions,  $m^{L_j}$  can take any value between 0 and 1, as long as  $\sum_{j \in P^L} m^{L_j} = 1$ . Therefore, if one trivial solution exists, then there are an infinite number of trivial solutions to (8) and (19). This poses great difficulty for the branch and bound approach, since every region that contains a solution to the original system of nonlinear equations must be kept and partitioned until the size of the region has been reduced to a prespecified tolerance.

The primary difficulty with trivial solutions is that the number of convex lower bounding problems that must be solved becomes very large, which requires large amounts of computational effort. Our approach to the problem of trivial solutions greatly reduces the computational effort, while maintaining the theoretical guarantee that all heterogeneous azeotropes will be enclosed.

In our approach, when the current region is chosen, a quick check is performed to determine if it is possible for the region to contain a trivial solution. The check is as follows: for every liquid phase,  $L_1$ , if there is another liquid phase,  $L_2$ , where the bounds on the composition for every component in  $L_2$  overlap the bounds on the composition in  $L_1$ , then the region can potentially contain a trivial solution.

$$(x_i^{L_1 LBD}, x_i^{L_1 UBD}) \cap (x_i^{L_2 LBD}, x_i^{L_2 UBD}) \neq \emptyset \quad \forall i \in N \quad (22)$$

If the region may contain a trivial solution, then a lower bounding problem *is not* solved, but the region is retained, and the solution  $s_{sol}^{r, Iter}$  is set to zero and the solution point is set to the center of the region. If the region cannot contain a trivial solution a lower bounding problem is solved. The rest of the branch and bound procedure remains unchanged.

This approach has two advantages: 1) regions containing a trivial solution are not discarded until they have been reduced below the size tolerance, and 2) lower bounding problems are not solved until a region is guaranteed not to contain a trivial solution. Advantage 1 maintains the theoretical guarantee for enclosing all azeotropes, while advantage 2 keeps the problem computationally tractable. In the following section, the basic steps of the algorithm are outlined.

### 3.3 Algorithmic Steps for Enclosing All Heterogeneous and Reactive Azeotropes

#### STEP 0 - Initialization

A size tolerance  $\epsilon_r$  and feasibility tolerance  $\epsilon_f$  are selected and the iteration counter is set to one. In this computational studies in sections 5 and 6 the tolerances have been set to  $\epsilon_r = 1 \times 10^{-3}$  and  $\epsilon_f = 1 \times 10^{-6}$ . Global bounds are set for temperature  $T$ , and composition,  $\mathbf{x}$  and  $\mathbf{y}$  and the local bounds are set equal to the global bounds. In addition, an initial point is selected.

**STEP 1 - Feasibility and Convergence Check**

Let the current point be the solution of the lower bounding problem in the current region. If the solution of the lower bounding problem is  $s = 0$ , and the maximum violation of all nonconvex constraints of the original problem calculated at the current point is less than the feasibility tolerance  $\epsilon_f$ , then the current point is an  $\epsilon_f$ -solution of the original problem. The current rectangle is fathomed if it has been refined to the point where its diagonal is less than  $\epsilon_r$ .

**STEP 2 - Partitioning of Current Rectangle**

The current rectangle is partitioned into two smaller rectangles by bisecting the longest side in the current rectangle.

**STEP 3 - Check for Trivial Solutions**

For every pair of liquid phases, check

$$(x_i^{L_1 LBD}, x_i^{L_1 UBD}) \cap (x_i^{L_2 LBD}, x_i^{L_2 UBD}) \neq \emptyset \quad \forall i \in N \quad (23)$$

If the above statement is true, then the current region may contain a trivial solution. Set  $s_{sol}^{r, Iter} = 0$ , and set the solution point to the center of the current region. Proceed to STEP 5.

**STEP 4 - Solution of Convex Problems Inside Subrectangles**

Solve the convexified optimization problem in both subrectangles by using any convex nonlinear solver (e.g., MINOS 5.4<sup>13</sup>). If the solution  $s_{sol}^{r, Iter}$ , where  $r$  denotes a rectangle, is zero, then it is stored along with the value of the variables  $(\mathbf{x}, T)$  at the solution point. If  $s_{sol}^{r, Iter}$  is strictly positive then the element  $(r, Iter)$  is fathomed and the corresponding rectangle is no longer considered to contain a possible solution. Note that the global solution of the original nonconvex problem is known to be zero, thus no upper bounding problem needs to be solved.

**STEP 5 - Update Iteration Counter and Lower Bound**

The iteration counter is increased by one, and the lower bound of the solution is updated to be the minimum solution over the stored ones from previous iterations. Furthermore, the

solution selected as the new lower bound is erased from the stored set.

**STEP 6** - *Update Current Point and Current Bounds*

The current point is selected to be the solution point of the previously found minimum solution in **STEP 4**, and the current rectangle becomes the subrectangle containing the previously found solution,

**STEP 7** - *Check for Convergence*

If the lower bound of the solution is less than or equal to zero, then return to **STEP 1**. Otherwise, terminate.

A proof that this procedure is guaranteed to converge is given in Maranas and Floudas<sup>11</sup>. For the problem of finding all homogeneous reactive azeotropes, step 3 can be omitted, since there is only one liquid phase.

## 4 Identification of Nonconvex Terms

The formulation of the problem for enclosing all heterogeneous azeotropes, equation (8), and the formulation of the problem for enclosing all reactive azeotropes, equation (19), contain several nonconvex functions. If a local optimization approach is used to solve these problems, it is likely that some of the multiple global minima will be missed, or even that none will be found. Therefore, in order to guarantee that *all* global minima are enclosed, it is necessary to develop a convex relaxation of the problem. In the approach used in this paper, a lower bound on the solution of (8) and (19) is obtained by replacing each nonconvex constraint with a tight convex underestimator and then using a commercially available nonlinear solver such as MINOS5.4. The upper and lower bounds on the solutions are then refined using a branch and bound approach.

A convex relaxation is developed by partitioning each nonlinear function in the constraint equations into convex and nonconvex terms. Tight convex lower bounding functions are then developed and replace each nonconvex term in the constraints.

Note that the formulations for enclosing all reactive azeotropes, (19) and (20), contain an additional set of nonlinear constraints that the formulation for heterogeneous non-reactive azeotropes, (8) does not contain. These additional equations are the chemical reaction equilibrium constraints. However, the nonconvex terms that arise from the additional equations are identical to the nonconvex terms in the phase equilibrium constraint. The nonconvex terms correspond to the logarithm of composition,  $\ln x_i$ , and to the activity coefficient equation,  $\ln \gamma_i$ . Therefore, once convex lower bounding functions have been developed for the heterogeneous azeotrope case, the same analysis can be applied to the reactive azeotrope case.

For many activity coefficient equations, the binary interaction parameters, such as  $\tau_{ij}$  and  $G_{ij}$  in the NRTL equation, can be considered as functions of temperature. However, for most systems, the temperature dependence of the Antoine equation for the vapor pressure outweighs the temperature dependence of the activity coefficient equation. Therefore, in this analysis, the interaction parameters are considered to be constants, and are calculated using a reference temperature located between the upper and lower bounds for the system being modeled. In section 5 the effect of using constant values for the binary interaction parameters is studied in detail.

## 4.1 Saturated Vapor Pressure Equation

In this work, the saturated vapor pressure is calculated using the Antoine equation:

$$\ln P_i^{sat} = a_i - \frac{b_i}{T + c_i} \quad (24)$$

where  $a_i$ ,  $b_i$ , and  $c_i$  are constants. The parameters  $a_i$  and  $b_i$  are always positive, while  $c_i$  may be positive or negative but  $|c_i| < T$ . In the problem of enclosing all heterogeneous azeotropes, Problem (8), and the problem of enclosing all reactive azeotropes, Problem (19) and (20), this term appears in the constraints as both  $(-\ln P_i^{sat})$  and  $(+\ln P_i^{sat})$ . It can be easily shown that the term:

$$-\frac{b_i}{T + c_i} \quad (25)$$

is concave in  $T$ . As a result, in the first set of constraints of (8) which have  $(-\ln P_i^{sat})$ , this term is convex and no underestimation is needed. In the second set of constraints however, this term is concave and a convex underestimator is required. A convex underestimator for this concave term is simply a line segment between the values of the term at each limit. That is,

$$-\frac{b_i}{T + c_i} \geq -\frac{b_i}{T^L + c_i} + \frac{-\frac{b_i}{T^U + c_i} + \frac{b_i}{T^L + c_i}}{T^U - T^L}(T - T^L) \quad (26)$$

where  $T^L$ ,  $T^U$  are the lower and upper bounds on the temperature in the current region.

## 4.2 Wilson Equation

Wilson<sup>14</sup> developed an equation to model the fluid phase excess Gibbs free energy for vapor-liquid systems. It is well known that the Wilson equation fails to predict liquid-liquid behavior, therefore it is not possible to use the Wilson equation for enclosing all heterogeneous

azeotropes. The Wilson equation is often used to model solutions containing polar and non-polar components and can be useful for examining homogeneous reactive and non-reactive systems. The Wilson activity coefficient equation is:

$$\ln \gamma_i = 1 - \ln \left( \sum_{j \in N} x_j \Lambda_{ij} \right) - \sum_{j \in N} \frac{x_j \Lambda_{ji}}{\sum_{k \in N} x_k \Lambda_{jk}} \quad (27)$$

where  $\Lambda_{ij}$  is the nonsymmetric binary interaction parameter between components  $i$  and  $j$  with  $\Lambda_{ii} = 1$ .

The Wilson expression for the activity coefficients contains three different nonconvex terms. The first nonconvex term is  $(\ln \sum_{j \in N} x_j \Lambda_{ij})$ . The second and third nonconvex terms are:

$$s_j^1 = \frac{x_j}{\sum_{k \in N} x_k \Lambda_{jk}} \quad (28)$$

and,

$$s_j^2 = -\frac{x_j}{\sum_{k \in N} x_k \Lambda_{jk}}. \quad (29)$$

A convex lower bounding function must be developed for each of these nonconvex terms. The first nonconvex term is concave in  $x_i$ , for  $i = 1, 2, \dots, N$ . Therefore, this term can be underestimated by the following expression:

$$\ln \sum_{j \in N} x_j \Lambda_{ij} \geq \ln m_i^L + \frac{\ln \frac{m_i^U}{m_i^L}}{(m_i^U - m_i^L)} (\sum_{j \in N} x_j \Lambda_{ij} - m_i^L) \quad (30)$$

where,

$$\begin{aligned} m_i^L &= \min \sum_{j \in N} x_j \Lambda_{ij} \\ \text{s.t. } &\sum_{j \in N} x_j = 1 \\ &x_j^L \leq x_j \leq x_j^U \end{aligned} \quad (31)$$

and,

$$\begin{aligned} m_i^U &= \max \sum_{j \in N} x_j \Lambda_{ij} \\ \text{s.t. } &\sum_{j \in N} x_j = 1 \\ &x_j^L \leq x_j \leq x_j^U \end{aligned} \quad (32)$$



For the second type of nonconvex terms found in the Wilson formulation, 28 and (29), we follow the method presented in Maranas and Floudas<sup>11</sup> for products of univariate functions. The convex underestimators for these terms are:

$$s_j^1 \geq \max \left\{ \frac{x_j^L}{\sum_{k \in N} x_k \Lambda_{jk}} + \frac{x_j}{m_j^U} - \frac{x_j^L}{m_j^U}, \right. \\ \left. \frac{x_j^U}{\sum_{k \in N} x_k \Lambda_{jk}} + \frac{x_j}{m_j^L} - \frac{x_j^U}{m_j^L} \right\}.$$

$$s_j^2 \geq \max \left\{ -\frac{x_j}{m_j^L} + \frac{x_j^L \sum_{k \in N} x_k \Lambda_{jk}}{m_j^L m_j^U} - \frac{x_j^L}{m_j^U}, \right. \\ \left. -\frac{x_j}{m_j^U} + \frac{x_j^U \sum_{k \in N} x_k \Lambda_{jk}}{m_j^L m_j^U} - \frac{x_j^U}{m_j^L} \right\}.$$

Using the convex underestimating functions, we have developed a method for enclosing all homogeneous reactive azeotropes with the Wilson activity coefficient equation.

### 4.3 NRTL Equation

The NRTL equation was derived by Renon and Prausnitz<sup>15</sup> for fluid phase activity coefficients using the Non-Randomness assumption and Scott's Two-Liquid theory. The NRTL formula for the activity coefficient is:

$$\ln \gamma_i = \frac{\sum_{j \in N} \tau_{ji} G_{ji} x_j}{\sum_{j \in N} G_{ji} x_j} + \sum_{j \in N} \frac{G_{ij} x_j}{\sum_{k \in N} G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_{k \in N} \tau_{kj} G_{kj} x_k}{\sum_{k \in N} G_{kj} x_k} \right) \quad (33)$$

The NRTL activity coefficient expression contains two types of nonconvex terms that are fractional in composition.

$$\pm \frac{x_i}{\sum_{j \in N} G_{ji} x_j} \quad \text{and} \quad \pm \frac{x_i x_j}{\left( \sum_{k \in N} G_{ki} x_k \right)^2} \quad (34)$$

Tight convex lower bounding functions for both of the terms shown above have been derived and are provided in Appendix A. The convex lower bounding functions can be applied for both the heterogeneous and reactive azeotrope formulations.

## 4.4 UNIQUAC Equation

The UNIQUAC equation was originally developed by Abrams and Prausnitz<sup>16</sup>. They postulated that the excess Gibbs energy depended on two effects: a combinatorial contribution due to the differences in the sizes and shapes of the components, and a residual contribution due to the energetic interactions between the components. The original equation was modified by Anderson and Prausnitz<sup>17</sup> in order to improve predictions for systems containing polar molecules such as water and alcohols. The activity coefficient for the UNIQUAC equation is given as:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (35)$$

where,

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j \in N} l_j x_j \quad (36)$$

and,

$$\ln \gamma_i^R = q'_i \left( 1 - \ln \left( \sum_{j \in N} \tau_{ji} \theta'_j \right) - \sum_{j \in N} \frac{\tau_{ij} \theta'_j}{\sum_{k \in N} \theta'_k \tau_{kj}} \right) \quad (37)$$

The combinatorial and residual contributions to the activity coefficient are represented by  $\gamma_i^C$  and  $\gamma_i^R$  respectively. The  $\tau_{ij}$  are non-symmetric binary interaction parameters,  $q_i$ ,  $q'_i$ , and  $r_i$  are structural parameters of the pure components, and  $z$  is a lattice coordination number. The values  $l_i$ ,  $\theta_i$ ,  $\theta'_i$ , and  $\phi_i$  are defined in terms of the parameters described above and are given by:

$$\begin{aligned} l_i &= \frac{z}{2}(r_i - q_i) - (r_i - 1) & \forall i \in N \\ \theta_i &= \frac{q_i x_i}{\sum_{j \in N} q_j x_j} & \forall i \in N \\ \theta'_i &= \frac{q'_i x_i}{\sum_{j \in N} q'_j x_j} & \forall i \in N \\ \phi_i &= \frac{r_i x_i}{\sum_{j \in N} r_j x_j} & \forall i \in N \end{aligned} \quad (38)$$

When the definitions of these parameters are substituted into the  $\ln \gamma_i^C$  and  $\ln \gamma_i^R$  expressions, and these two are added together to form the complete  $\ln \gamma_i$  equation some simplifications can be made. The final expression is:

$$\begin{aligned} \ln \gamma_i = & \left( \frac{z}{2} q_i - 1 \right) \ln \left( \sum_{j \in N} r_j x_j \right) - \frac{z}{2} q_i \ln \left( \sum_{j \in N} q_j x_j \right) - r_i \frac{\sum_{j \in N} l_j x_j}{\sum_{j \in N} r_j x_j} \\ & - q'_i \ln \left( \sum_{j \in N} \tau_{ji} q'_j x_j \right) + q'_i \ln \left( \sum_{j \in N} q'_j x_j \right) - q'_i \sum_{j \in N} \frac{\tau_{ij} q'_j x_j}{\sum_{k \in N} \tau_{kj} q'_k x_k} \\ & + \left( \ln r_i + \frac{z}{2} q_i \ln \left( \frac{q_i}{r_i} \right) + l_i + q'_i \right) \end{aligned}$$

As is evident, this expression contains many nonconvex terms. The first four nonconvex terms are log terms:

$$\ln \left( \sum_{j \in N} r_j x_j \right), \quad \ln \left( \sum_{j \in N} q_j x_j \right), \quad \ln \left( \sum_{j \in N} q'_j x_j \right), \quad \text{and} \quad \ln \left( \sum_{j \in N} \tau_{ji} q'_j x_j \right) \quad (39)$$

The last four nonconvex term are fractional terms:

$$+ \frac{\sum_{j \in N} l_j x_j}{\sum_{l \in N} r_l x_l}, \quad - \frac{\sum_{j \in N} l_j x_j}{\sum_{l \in N} r_l x_l}, \quad + \frac{\sum_{j \in N} \tau_{ij} q'_j x_j}{\sum_{l \in N} \tau_{lj} q'_l x_l}, \quad \text{and} \quad - \frac{\sum_{j \in N} \tau_{ij} q'_j x_j}{\sum_{l \in N} \tau_{lj} q'_l x_l} \quad (40)$$

Note that the binary interaction parameter,  $\tau_{ij}$ , is considered to be a constant in this analysis, as described in Section 4.

Tight convex lower bounding functions for all of the nonconvex terms that arise from the UNIQUAC equation have been derived and are provided in Appendix B. The convex lower bounding functions can be applied for both the heterogeneous and reactive azeotrope formulations.

## 4.5 UNIFAC Equation

In some cases, one would like to predict the azeotropes for a system where there is insufficient equilibrium data to obtain accurate binary interaction parameter values. As a result, several solution-of-groups methods have been developed to allow equilibrium predictions in these systems. Solution-of-groups methods consider the molecules in the chemical system as

groupings of elements. For example, 1-propanol contains one  $CH_3$  group, one  $CH_2$  group, and one  $CH_2OH$  group. The interactions between the molecules can then be approximated by determining the interactions between the groups that make up the molecules.

The most widely used solution-of-groups method is the UNIFAC equation, originally developed by Fredenslund et al.<sup>18</sup>, primarily because the group-interaction parameters for many pairs of groups have been calculated and compiled and are updated periodically, Gmehling et al.<sup>19</sup>. As its name indicates, the UNIFAC (UNIQUE Functional Group Activity Coefficients) method is based on the UNQUAC equation. Like the UNQUAC equation, the natural logarithm of the UNIFAC activity coefficient is the sum of a combinatorial contribution and a residual contribution:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (41)$$

The combinatorial part,  $\ln \gamma_i^C$ , uses only pure-component data, and therefore no modifications of the UNQUAC combinatorial part, Equation (36), are needed. However, in the UNIFAC method, the residual part is calculated as the sum of the energetic interactions of the *groups*, rather than the molecules themselves.

First, the pure component parameters,  $q_i$  and  $r_i$ , are defined as:

$$q_i = \sum_{g \in G} v_{gi} Q_g \quad \text{and} \quad r_i = \sum_{g \in G} v_{gi} R_g \quad (42)$$

where  $G$  is the set of all groups in the system;  $v_{gi}$  is the number of groups  $g$  contained in component  $i$ ;  $Q_g$  is the group area parameter; and  $R_g$  is the group volume parameter.

The residual part of the UNIFAC equation is given by the following expression:

$$\begin{aligned} \ln \gamma_i^R = \sum_{g \in G} Q_g v_{gi} & \left\{ - \sum_{m \in G} \frac{\Psi_{gm} \sum_{j \in N} Q_m v_{mj} x_j}{\sum_{l \in G} \Psi_{lm} \sum_{k \in N} Q_l v_{lk} x_k} \right. \\ & - \ln \left( \sum_{m \in G} \Psi_{mg} \sum_{j \in N} Q_m v_{mj} x_j \right) \\ & + \ln \left( \sum_{j \in N} q_j x_j \right) \\ & + \ln \left( \sum_{m \in G} \Psi_{mg} Q_m v_{mi} \right) \\ & - \ln q_i \\ & \left. + \sum_{m \in G} \frac{\Psi_{gm} Q_m v_{mi}}{\sum_{l \in G} \Psi_{lm} Q_l v_{li}} \right\} \end{aligned} \quad (43)$$

where the temperature-dependent group-interaction parameter,  $\Psi_{gm}$ , is given by

$$\Psi_{gm} = \exp\left(-\frac{a_{gm}}{T}\right) \quad (44)$$

and the group-interaction parameter,  $a_{gm}$ , is determined from experimental phase equilibrium data. Similar to the NRTL and UNIQUAC equations, the group interaction parameters are treated as constants with respect to temperature in this paper. By introducing a few substitutions, the residual contribution can be simplified to

$$\begin{aligned} \ln \gamma_i^R = & - \sum_{g \in G} \kappa_{gi} \ln \left( \sum_{j \in N} \alpha_{gj} x_j \right) \\ & + \sum_{g \in G} \kappa_{gi} \ln \left( \sum_{j \in N} q_j x_j \right) \\ & - \sum_{g \in G} \frac{\sum_{j \in N} \beta_{gij} x_j}{\sum_{k \in N} \alpha_{gk} x_k} \\ & + \delta_i \end{aligned} \quad (45)$$

where the constants  $\kappa_{gi}$ ,  $\alpha_{gj}$ ,  $\beta_{gij}$ , and  $\delta_i$  are given by

$$\begin{aligned} \kappa_{gi} &= Q_g v_{gi} \\ \alpha_{gj} &= \sum_{m \in G} \kappa_{mj} \Psi_{mg} \\ \beta_{gij} &= \sum_{m \in G} \kappa_{mi} \kappa_{gj} \Psi_{mg} \\ \delta_i &= \sum_{g \in G} \kappa_{gi} \cdot \ln \left( \frac{\sum_{m \in G} \kappa_{mi} \Psi_{mg}}{q_i} \right) \\ &+ \sum_{g \in G} \kappa_{gi} \sum_{m \in G} \frac{\kappa_{mi} \Psi_{gm}}{\sum_{l \in G} \kappa_{li} \Psi_{lm}} \end{aligned}$$

The UNIFAC equation contains several nonconvex terms. As was the case for the UNIQUAC equation, these terms fall into two categories: logarithmic terms, and fractional terms. In addition, since the combinatorial part of the UNIFAC equation is identical to the UNIQUAC equation, the nonconvex terms that arise from this part are also identical. These equations are the first two expressions in (39), and the first two expressions in (40). The nonconvex terms from the residual part are the following:

$$\ln \left( \sum_{j \in N} \alpha_{gj} x_j \right), \quad \text{and} \quad \ln \left( \sum_{j \in N} q_j x_j \right) \quad (46)$$

and

$$+\frac{\beta_{gij}x_j}{\sum_{k \in N} \alpha_{gk}x_k}, \quad \text{and} \quad -\frac{\beta_{gij}x_j}{\sum_{k \in N} \alpha_{gk}x_k} \quad (47)$$

Tight convex lower bounding functions for all of the nonconvex terms that arise from the UNIFAC equation have been derived and are provided in Appendix C. The convex lower bounding functions can be applied for both the heterogeneous and reactive azeotrope formulations.

## 4.6 Bilinear Terms

Bilinear terms appear in the formulations for both the heterogeneous and the reactive azeotrope problems. In each case, the bilinear term is replaced by a new variable, and lower bounds and upper bounds on the new variable are introduced using the results of Al-Khayyal and Falk<sup>20</sup> and McCormick<sup>21</sup>. This method is described in Appendix D.

## 5 Computational Studies for Enclosing All Heterogeneous Azeotropes

The proposed approach for enclosing all heterogeneous azeotropes in a multicomponent mixture is written in GAMS and was run on a Hewlett Packard J-2240 machine. The solver MINOS5.4<sup>13</sup> is used as a subroutine. All times reported are the total cpu time in seconds needed to enclose all azeotropes in the system. A convergence tolerance of  $1 \cdot 10^{-6}$  was used for all examples. For each system experimental data reported in Gmehling et al.<sup>22</sup> are listed for all of the known heterogeneous azeotropes.

In comparing the computational results for the examples with the experimental data, it is noted that in some cases the equations will fail to predict a known azeotrope, or will predict azeotropes where none exist. This demonstrates the importance of obtaining reliable estimates of the pure-component and binary-interaction parameters for the system being studied. In addition, it is well known that no single thermodynamic model provides superior results for every system. The purpose of the following examples is to demonstrate the performance of the global optimization based approach for several different activity coefficient equations. No attempt is made to determine the most accurate model or set of parameters for the systems presented.

The binary interaction parameters in the NRTL, UNIQUAC and UNIFAC equations are functions of temperature. In the NRTL equation, the equations for the parameters,  $\tau_{ij}$  and  $G_{ij}$  are:

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}$$

$$G_{ij} = \exp -\alpha_{ij}\tau_{ij}$$

where  $g_{ij}$  and  $\alpha_{ij}$  are constant binary interaction parameters. In the UNIQUAC equation, the equation for the parameter,  $\tau_{ij}$  is:

$$\tau_{ij} = \exp -\frac{u_{ij} - u_{jj}}{RT}$$

where  $u_{ij}$  is a constant binary interaction parameter. In the UNIFAC equation, the expression for the parameter,  $\Psi_{gm}$  is:

$$\Psi_{gm} = \exp \left( -\frac{a_{gm}}{T} \right)$$

where  $a_{gm}$  is a constant binary group-interaction parameter. For most systems, the temperature dependence of the Antoine equation for the vapor pressure outweighs the temperature dependence of the activity coefficient equation. Therefore, in this analysis, the interaction parameters are considered to be constants, and are calculated using a reference temperature located between the upper and lower bounds for the system being modeled. In order to study the effect that this simplification has on the prediction of azeotropes, results have been obtained using the full temperature dependence of the binary interaction parameters. Tables are provided which show the difference between solutions obtained with and without temperature dependence.

An iterative scheme for determining the temperature dependent binary interaction parameters has been suggested by a reviewer. In this approach, an initial reference temperature,  $T_0$  is specified. The binary interaction parameters are calculated using  $T_0$ . The global optimization procedure for enclosing all azeotropes is applied. Then, for each azeotrope that is found, the following iterative approach is used. The new reference temperature,  $T_1$ , is set to the temperature of the azeotrope from the initial solution. The binary interaction parameters are recalculated using  $T_1$ . Then the global optimization approach is applied again, where the variable bounds (composition and temperature) are set to tight intervals around the previous location of the azeotrope. If the new azeotrope temperature is within some tolerance of the previous temperature, then the procedure is terminated. Otherwise, the reference temperature is updated again, and another iteration is performed.

## 5.1 Ethanol/Benzene/Cyclohexane/Water

This quaternary system was used by Eckert and Kubicek<sup>8</sup> to illustrate their homotopy-continuation approach for finding all heterogeneous azeotropes. Experimental data show

that this system contains two binary heterogeneous azeotropes, two ternary heterogeneous, azeotropes, and one quaternary heterogeneous azeotrope. In addition, the system contains four binary homogeneous azeotropes and one ternary homogeneous azeotrope. In this example, the NRTL, UNIQUAC, and UNIFAC equations are used to model the liquid phase activity coefficients.

### 5.1.1 Binary Systems

The results for the binary system Benzene-Water are shown in Table 1. Both the UNIQUAC and UNIFAC equations predict vapor compositions for the single heterogeneous azeotrope that are very close to the experimentally reported values. The GAMS implementation required 21 to 24 seconds for the UNIQUAC and UNIFAC models and 41 seconds for the NRTL model.

The results for the other binary system, Cyclohexane-Water, are shown in Table 2. For this system, the UNIQUAC equation did not predict any heterogeneous azeotropes for any literature values of the binary interaction parameters for Cyclohexane-Water. It is interesting to note that the UNIFAC equation predicted a heterogeneous azeotrope that is very close to the experimental values. In general, one expects the UNIQUAC equation to perform better than the UNIFAC, since UNIQUAC parameters are obtained from experimental data, while UNIFAC parameters are empirically determined from molecular group contributions. The computational effort for the three implementations ranges from 10 to 25 seconds.

### 5.1.2 Ternary Systems

For the first ternary system, Ethanol-Benzene-Water, (see Table 3), the UNIFAC and UNIQUAC equations provide predictions that are close to the experimental values, while the heterogeneous azeotrope predicted by the NRTL equation is far from the experimental values. The computational effort is increased for this larger system, but remains reasonable, ranging from 100 to 140 seconds.

The second ternary system is Ethanol-Cyclohexane-Water, and the results are shown in Table 4. The UNIQUAC and UNIFAC equations provide good predictions while the NRTL equation is far from the experimental values. It is interesting to note that even though Cyclohexane-Water is a subset of this ternary system for which the UNIQUAC equation performed poorly, for the ternary system, the UNIQUAC equation performs well. The CPU times required for all implementations are less than 100 seconds, ranging from 88 to 96 seconds.



### 5.1.3 Quaternary System

The final heterogeneous azeotrope in the system is a quaternary azeotrope between Ethanol-Benzene-Cyclohexane-Water. The results are shown in Table 5. Following the pattern of the previous azeotropes in this system, the UNIQUAC and UNIFAC equations provide predictions of the azeotrope that are much closer to the experimental values than the NRTL equation. Note that even for this large system, the computational effort for the GAMS implementation is very reasonable, requiring 221 seconds for the NRTL equation, 242 seconds for the UNIQUAC equation, and 257 seconds for the UNIFAC equation.

Note that our results with the NRTL equation differ significantly from the results of Eckert and Kubicek<sup>8</sup>. This is most likely due to the fact that different binary interaction parameters were used to obtain the results in this work.

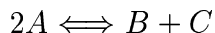
### 5.1.4 Temperature Dependence of Binary Interaction Terms

Tables 6 through 19 compare the results obtained by solving the problem temperature dependent binary interaction parameters with those obtained using constant parameters. The results clearly show that using constant values for the binary interaction parameters has very little effect on the solution obtained. In the majority of cases, the differences for mole fractions are in the third decimal place, and the differences for the temperatures are in the fourth significant digit. There were no cases where a new azeotrope was located by using temperature-dependent binary interaction parameters.

## 6 Computational Studies for Enclosing All Reactive Azeotropes

### Example 1: Hypothetical Ternary System I

This example was used by Okasinski and Doherty<sup>10</sup> in order to study the behavior of reactive azeotropes. The mixture contains three components undergoing one reaction,

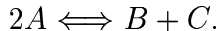


The system contains only one liquid phase. In this example, the Wilson equation is used to model the liquid phase activity coefficients, and we have used the Antoine equation and Wilson equation parameters provided by Okasinski and Doherty<sup>10</sup>.

Table 20 shows the results of the proposed approach for enclosing all reactive azeotropes for three different values of the equilibrium constant. Okasinski and Doherty<sup>10</sup> report that there is one reactive azeotrope for all values of the equilibrium constant, and this is verified in our results. As the equilibrium constant is increased, the composition of the reactive azeotrope moves towards higher B composition, and the temperature of the azeotrope decreases slightly. The computational effort ranged from 7 to 15 seconds for this ternary example.

### Example 2: Hypothetical Ternary System II

This is another example of a hypothetical single-reaction system used by Okasinski and Doherty<sup>10</sup>. The mixture contains three components undergoing the reaction:



The system contains only one liquid phase. In this example, the Wilson equation is used to model the liquid phase activity coefficients, and the Antoine equation and Wilson equation parameters provided by Okasinski and Doherty<sup>10</sup> are used.

This is an interesting system because at small values of the equilibrium constant, two reactive azeotropes exist. When the equilibrium constant is increased beyond 0.027, both reactive azeotropes disappear. The results are shown in Table 21 for  $K_{eq} = 0.001$  and  $K_{eq} = 0.025$ . In both cases, the approach for enclosing all reactive azeotropes located both reactive azeotropes. The computational effort for this example is substantially larger than for the ternary system in Example 1, since more than one reactive azeotrope is present. For  $K_{eq} = 0.001$ , 423 seconds were required for the GAMS implementation. Interestingly, as the azeotropes move closer together in composition and temperature space for  $K_{eq} = 0.025$ , the computational effort is reduced, to 99 seconds.

### Example 3: MTBE System with no inert

The MTBE system has been well-studied in the literature for design of reactive distillation columns. Methanol and isobutene react to form methyl *tert*-butyl ether (MTBE).



At a pressure of 8 atm, this system contains two homogeneous non-reactive azeotropes. In this example, the Wilson equation is used to model the liquid phase activity coefficients, and

the Antoine equation and Wilson equation parameters provided by Okasinski and Doherty<sup>10</sup> are used.

Results for three different values of the equilibrium constant are shown in Table 22. At a small value of  $K_{eq}$ , only one reactive azeotrope exists, which contains a high concentration of the reactant isobutene. Okasinski and Doherty<sup>10</sup> report that in the region,  $0.145 < K_{eq} < 31.9$ , no reactive azeotropes exist. At  $K_{eq} = 32.0$ , our approach shows that two new reactive azeotropes appear, with low isobutene concentration. The two azeotropes have similar compositions and temperatures. As the equilibrium constant is increased, the reactive azeotropes move further apart, as is shown for  $K_{eq} = 49.0$ . When only one azeotrope exists, only 30 seconds of CPU time are required. For the cases with two azeotropes, 114 seconds and 104 seconds are required.

#### Example 4: MTBE System with n-Butane inert

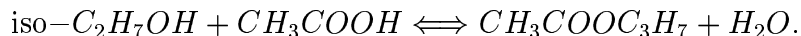
In this example, an inert has been added to the MTBE system. The Wilson equation is used to model the liquid phase activity coefficients, and the Antoine equation and Wilson equation parameters provided by Okasinski and Doherty<sup>10</sup> are used.



The results for this four-component example are shown in Table 23. For a value of the equilibrium constant of  $K_{eq} = 27.0$ , the approach for enclosing all reactive azeotropes finds two azeotropes. One azeotrope has very low n-butane composition, and corresponds to the “pseudo”-reactive azeotrope reported by Ung and Doherty<sup>9</sup>. The second azeotrope has very high n-butane composition. This corresponds to the saddle reactive azeotrope just inside the composition triangle, as reported by Ung and Doherty<sup>9</sup>. The computational effort of 150 seconds is very reasonable, even for this larger, difficult example.

#### Example 5: Isopropyl Acetate System

Isopropyl acetate is formed through the acid-catalyzed esterification reaction between isopropanol and acetic acid:



A reactive azeotrope was recently discovered for this system, which is the first reactive azeotrope to be confirmed experimentally, Song et al.<sup>23</sup>. The equilibrium constant for this

reaction is reported to be 8.7 by Lee and Kuo<sup>24</sup>. In this work, we have attempted to predict the reactive azeotrope using the proposed method with the NRTL, UNIQUAC, and UNIFAC equations. Binary interaction parameters for the NRTL equation were obtained from Manning<sup>25</sup>. Table 24 shows that the NRTL equation predicts a reactive azeotrope for  $K_{eq} = 8.7$  that is very close to the experimental results reported by Song et al.<sup>23</sup>. Binary interaction parameters for the UNIQUAC equation were obtained from the DECHEMA vapor-liquid equilibrium data series (Gmehling and Onken<sup>26</sup>) with the exception of the isopropanol-isopropyl acetate and isopropyl acetate-water interactions. These were calculated from the UNIFAC group contribution parameters. Table 24 shows that the UNIQUAC and UNIFAC activity coefficient equations do not predict a reactive azeotrope for  $K_{eq} = 8.7$ . However, when the equilibrium constant is increased above 15.0, a reactive azeotrope appears for the UNIQUAC equation. The reactive azeotrope predicted by the UNIQUAC equation for  $K_{eq} = 20.0$  is shown in table 24 and is close to the homogeneous non-reactive azeotrope between isopropyl alcohol and water. The computational requirement for locating the reactive azeotropes was 66 seconds for the NRTL equation and 37 seconds for the UNIQUAC equation. In the cases where a reactive azeotrope does not exist, the computational effort is reduced to 22 seconds for the UNIQUAC equation and 29 seconds for the UNIFAC equation.

## 7 Conclusions

This work has presented a deterministic global optimization method for enclosing all heterogeneous azeotropes in non-reacting mixtures containing  $N$  components and  $P^L$  liquid phases. A method based on the same global optimization approach has been developed for computing all reactive azeotropes in mixtures containing  $N$  components undergoing  $R$  chemical reactions. The global optimization method is based on a branch and bound algorithm to iteratively solve a formulation of the original problem in which the nonconvex constraints are replaced by valid convex underestimating functions. A novel approach has been developed for avoiding the computational difficulty that arises from “trivial” solutions. The problem may contain multiple global minima, and there is a one-to-one correspondence between global minima where the objective value is zero and heterogeneous azeotropes. Nonconvex terms for the saturated vapor pressure equation  $\ln P_i^{sat}$ , the Wilson equation, the NRTL equation, the UNIQUAC equation, and the UNIFAC equation have been identified and convex underestimating terms derived for each. While only four thermodynamic models were used, this method can be extended to include the modified Wilson, and ASOG activity coefficient models, as well as equation of state models.

The novel contribution of this approach is that it offers a theoretical guarantee of enclosing all heterogeneous and reactive azeotropes, while at the same time the computational effort

is modest. In addition, the approach is not limited to a small number of components, reactions, or liquid phases. The effectiveness of this method was demonstrated for several chemical systems and three different thermodynamic models of the liquid phase activity coefficients. In all examples, the method found all azeotropes for the systems studied.

*Acknowledgements:* The authors would like to thank Professors Doherty and Malone, and Bob Huss from the Department of Chemical Engineering at the University of Massachusetts for providing the NRTL parameters for the isopropyl acetate reactive system. The authors thank an anonymous reviewer for the excellent suggestion on the iterative procedure for the temperature dependence of the binary interaction parameters. The authors also acknowledge financial support from the National Science Foundation. Professor Floudas acknowledges partial support from the European Commission (JOE3-CT97-0085) during his sabbatical at the Chemical Process Engineering Research Institute, CPERI.

## References

- (1) Fidkowski, Z. T.; Malone, M. F.; Doherty, M. F. Computing Azeotropes in Multicomponent Mixtures. *Comp. Chem. Engng.* **1993**, *17* (12), 1141.
- (2) Harding, S. T.; Maranas, C. D.; McDonald, C. M.; Floudas, C. A. Locating All Azeotropes in Homogeneous Azeotropic Systems. *IEEC Res.* **1997**, *36* (1), 160.
- (3) Maier, R. W.; Brennecke, J.; Stadtherr, M. Reliable Computation of Homogeneous Azeotropes. *AIChE J.* **1998**, *44*, 1745.
- (4) Widagdo, S.; Seider, W. D. Azeotropic Distillation. *AIChE Journal* **1996**, *42*, 96.
- (5) Wasylkiewicz, S.; Castillo, F. Pressure Sensitivity Analysis of Azeotropes and its Application in Synthesis of Distillation Column Sequences for Separation of Multicomponent Azeotropic Mixtures. In *Second Conference on Process Integration, Modeling and Optimization for Energy Saving and Pollution Reduction*, **1999**, 701–706.
- (6) Chapman, R. G.; Goodwin, S. P. A General Algorithm for the Calculation of Azeotropes in Fluid Mixtures. *Fluid Phase Equilibria* **1993**, *85*, 55.
- (7) Michelsen, M. L. The Isothermal Flash Problem: Part I. Stability. *Fluid Phase Equilibria* **1981**, *9*, 1.
- (8) Eckert, E.; Kubicek, M. Computing Heterogeneous Azeotropes in Multicomponent Mixtures. *Comp. Chem. Engng.* **1997**, *21*, 347.

- (9) Ung, S.; Doherty, M. Necessary and Sufficient Conditions for Reactive Azeotropes in Multireaction Mixtures. *AIChE J.* **1995**, *41* (11), 2383.
- (10) Okasinski, M.; Doherty, M. Thermodynamic Behavior of Reactive Azeotropes. *AIChE J.* **1997**, *43* (9), 2227.
- (11) Maranas, C. D.; Floudas, C. A. Finding All Solutions of Nonlinearly Constrained Systems of Equations. *Journal of Global Optimization* **1995**, *7* (2), 153.
- (12) Ung, S.; Doherty, M. Vapor-Liquid Phase Equilibrium in Systems with Multiple Chemical Reactions. *Chem. Eng. Sci.* **1995**, *50*, 23.
- (13) Murtagh, B. A.; Saunders, M. A. *MINOS 5.0 User's Guide*; Systems Optimization Laboratory Dept. of Operations Research, Stanford University, CA. 1988.
- (14) Wilson, G. M. Vapor Liquid Equilibrium XI: A New Expression for the Excess Gibbs Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127.
- (15) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14* (1), 135.
- (16) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21* (1), 116.
- (17) Anderson, T. F.; Prausnitz, J. M. Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria. 1: Vapor-Liquid Equilibria. *Ind. Eng. Chem. Proc. Des. Dev.* **1978**, *17*, 552.
- (18) Fredenslund, A.; Jones, R.; Prausnitz, J. Group Contribution Estimation of Activity Coefficients in Non-ideal Mixtures. *AIChE J.* **1975**, *21*, 1086.
- (19) Gmehling, J.; Tiegs, D.; Knipp, U. A Comparison of the Predictive Capability of Different Group Contribution Methods. *Fluid Phase Equilibria* **1990**, *54*, 147.
- (20) Al-Khayyal, F. A.; Falk, J. E. Jointly Constrained Biconvex Programming. *Maths Ops Res.* **1983**, *8*, 273.
- (21) McCormick, G. Computability of Global Solutions to Factorable Nonconvex Programs: Part I – Convex Underestimating Problems. *Math. Programming* **1976**, *10*, 147.
- (22) Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data*; VCH, 1994.

- (23) Song, W.; Huss, R.; Doherty, M.; Malone, M. Discovery of a Reactive Azeotrope. *Nature* **1998**, *388*, 561.
- (24) Lee, L.; Kuo, M. Phase and Reaction Equilibrium of the Acetic Acid-Isopropanol-Isopropyl Acetate-Water System at 760mmHg. *Fluid Phase Equilibria* **1996**, *123*, 147.
- (25) Manning, J. *Kinetics and Feasibility of Reactive Distillation in Isopropyl Acetate Synthesis*; Master's thesis Department of Chemical Engineering, University of Massachusetts Amherst, Massachusetts 1999.
- (26) Gmehling, J.; Onken, U. *Vapor-liquid equilibrium data collection*; vol. I, Part 1 of *Chemistry Data Series* DECHEMA, 1977.

## A Convex Underestimating Functions for the NRTL Equation

In the NRTL equation formulation of the problem of enclosing all heterogeneous and reactive azeotropes, three different types of nonconvex terms are encountered:

$$\begin{aligned}
 +p_i &= \frac{w_i}{y_i} \\
 -p_i &= -\frac{w_i}{y_i} \\
 +q_i &= \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j} \\
 -q_i &= -\sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j} \\
 +r_i &= \sum_{j \in N} G_{ij} \frac{x_j w_j}{y_j y_j} \\
 -r_i &= -\sum_{j \in N} G_{ij} \frac{x_j w_j}{y_j y_j}
 \end{aligned}$$

where

$$\begin{aligned}
 y_i &= \sum_{j \in N} G_{ji} x_j \\
 w_i &= \sum_{j \in N} \tau_{ji} G_{ji} x_j
 \end{aligned}$$

so  $x_i, y_i \geq 0$ , but  $w_i$  can be positive or negative.

Following the method of Maranas and Floudas<sup>11</sup> for fractional terms, the first two types of nonconvex term can be underestimated by:

$$\begin{aligned} \frac{w_i}{y_i} &\geq \max \left\{ \begin{aligned} &\left[ \frac{w_i^L}{y_i} + \frac{w_i}{y_i^U} - \frac{w_i^L}{y_i^U} \quad \text{if } w_i^L \geq 0 \right] \\ &\left[ \frac{w_i}{y_i^U} - \frac{w_i^L y_i}{y_i^L y_i^U} + \frac{w_i^L}{y_i^L} \quad \text{if } w_i^L < 0 \right] \end{aligned} \right. \\ &\quad \left. \begin{aligned} &\left[ \frac{w_i^U}{y_i} + \frac{w_i}{y_i^L} - \frac{w_i^U}{y_i^L} \quad \text{if } w_i^U \geq 0 \right] \\ &\left[ \frac{w_i}{y_i^L} - \frac{w_i^U y_i}{y_i^L y_i^U} + \frac{w_i^U}{y_i^U} \quad \text{if } w_i^U < 0 \right] \end{aligned} \right\} \\ -\frac{w_i}{y_i} &\geq \max \left\{ \begin{aligned} &\left[ -\frac{w_i^L}{y_i} - \frac{w_i}{y_i^L} + \frac{w_i^L}{y_i^L} \quad \text{if } w_i^L \leq 0 \right] \\ &\left[ -\frac{w_i}{y_i^L} + \frac{w_i^L y_i}{y_i^L y_i^U} - \frac{w_i^L}{y_i^U} \quad \text{if } w_i^L > 0 \right] \end{aligned} \right. \\ &\quad \left. \begin{aligned} &\left[ -\frac{w_i^U}{y_i} - \frac{w_i}{y_i^U} + \frac{w_i^U}{y_i^U} \quad \text{if } w_i^U \leq 0 \right] \\ &\left[ -\frac{w_i}{y_i^U} + \frac{w_i^U y_i}{y_i^L y_i^U} - \frac{w_i^U}{y_i^L} \quad \text{if } w_i^U > 0 \right] \end{aligned} \right\} \end{aligned}$$

where

$$\begin{aligned} w_j^L &= \min_{k \in N} \tau_{kj} G_{kj} x_k \\ w_j^U &= \max_{k \in N} \tau_{kj} G_{kj} x_k \\ y_j^L &= \min_{k \in N} G_{kj} x_k \\ y_j^U &= \max_{k \in N} G_{kj} x_k \end{aligned}$$

and in the second type of nonconvex term, each fractional term in the summation can be underestimated by:

$$\begin{aligned} \frac{x_j}{y_j} &\geq \max \left\{ \begin{aligned} &\frac{x_j^L}{y_j} + \frac{x_j}{y_j^U} - \frac{x_j^L}{y_j^U}, \\ &\frac{x_j^U}{y_j} + \frac{x_j}{y_j^L} - \frac{x_j^U}{y_j^L} \end{aligned} \right\} \\ -\frac{x_j}{y_j} &\geq \max \left\{ \begin{aligned} &-\frac{x_j}{y_j^L} + \frac{x_j^L y_j}{y_j^L y_j^U} - \frac{x_j^L}{y_j^U}, \\ &-\frac{x_j}{y_j^U} + \frac{x_j^U y_j}{y_j^L y_j^U} - \frac{x_j^U}{y_j^L} \end{aligned} \right\} \end{aligned}$$

Therefore, since  $\sum_j (\max x_j) = \max \left( \sum_j x_j \right)$ , the convex underestimator for the second term is:



$$\begin{aligned}
\sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j} &\geq \max \left\{ \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j^L}{y_j} + \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j^U} - \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j^L}{y_j^U}, \right. \\
&\quad \left. \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j^U}{y_j} + \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j^L} - \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j^U}{y_j^L} \right\} \\
-\sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j} &\geq \max \left\{ -\sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j^L} + \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j^L y_j}{y_j^L y_j^U} - \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j^L}{y_j^U}, \right. \\
&\quad \left. -\sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j^U} + \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j^U y_j}{y_j^L y_j^U} - \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j^U}{y_j^L} \right\}
\end{aligned}$$

The third term is more difficult to underestimate, but a convex underestimator can be constructed by successively finding the convex lower bounding function for pairs of univariate functions in a recursive manner until no pairs are left. The recursive procedure for constructing convex underestimators from pairs of univariate functions, as shown by Maranas and Floudas<sup>11</sup>, can be used for the third nonconvex term from the NRTL equation as illustrated below.

First, the fractional term  $\left(\frac{x_j}{y_j}\right)$  is considered. Since  $x_j^L$  and  $x_j^U$  are both always greater than zero, this term can be underestimated by:

$$\frac{x_j}{y_j} \geq \lambda_j^2 = \max \left\{ \frac{x_j^L}{y_j} + \frac{x_j}{y_j^U} - \frac{x_j^L}{y_j^U}, \right. \\
\left. \frac{x_j^U}{y_j} + \frac{x_j}{y_j^L} - \frac{x_j^U}{y_j^L} \right\}$$

and since  $(x_j - x_j^L)$  is always positive,  $\lambda_j^2$  is always positive. Next, a convex underestimating function is constructed for the term  $\left(\frac{\lambda_j^2}{y_j}\right)$ :

$$\frac{\lambda_j^2}{y_j} \geq \lambda_j^1 = \max \left\{ \frac{\lambda_j^{2,L}}{y_j} + \frac{\lambda_j^2}{y_j^U} - \frac{\lambda_j^{2,L}}{y_j^U}, \right. \\
\left. \frac{\lambda_j^{2,U}}{y_j} + \frac{\lambda_j^2}{y_j^L} - \frac{\lambda_j^{2,U}}{y_j^L} \right\}$$

where  $\left(\lambda_j^{2,L} = \frac{x_j^L}{y_j^U}\right)$  and  $\left(\lambda_j^{2,U} = \frac{x_j^U}{y_j^L}\right)$ .

Finally, convex underestimating functions for the terms  $(\lambda_j^1 w_j)$  and  $(\lambda_j^1 (-w_j))$  are constructed:

$$\begin{aligned}
\lambda_j^1 w_j &\geq \max \left\{ w_j^L \lambda_j^1 + w_j \lambda_j^{1,L} - w_j^L \lambda_j^{1,L}, \right. \\
&\quad \left. w_j^U \lambda_j^1 + w_j \lambda_j^{1,U} - w_j^U \lambda_j^{1,U} \right\} \\
\lambda_j^1 (-w_j) &\geq \max \left\{ -w_j^U \lambda_j^1 - w_j \lambda_j^{1,L} + w_j^U \lambda_j^{1,L}, \right. \\
&\quad \left. -w_j^L \lambda_j^1 - w_j \lambda_j^{1,U} + w_j^L \lambda_j^{1,U} \right\}
\end{aligned}$$

where  $\left( \lambda_j^{1,L} = \frac{\lambda_j^{2,L}}{y_j^U} = \frac{x_j^L}{y_j^U y_j^U} \right)$  and  $\left( \lambda_j^{1,U} = \frac{\lambda_j^{2,U}}{y_j^L} = \frac{x_j^U}{y_j^L y_j^L} \right)$ . Combining these terms gives a convex underestimating function for the each fractional term in the summation.

$$\begin{aligned}
\frac{x_j w_j}{y_j y_j} &\geq \max \left\{ w_j^L \lambda_j^1 + \frac{w_j x_j^L}{y_j^U y_j^U} - \frac{w_j^L x_j^L}{y_j^U y_j^U}, \right. \\
&\quad \left. w_j^U \lambda_j^1 + \frac{w_j x_j^U}{y_j^L y_j^L} - \frac{w_j^U x_j^U}{y_j^L y_j^L} \right\} \\
-\frac{x_j w_j}{y_j y_j} &\geq \max \left\{ -w_j^U \lambda_j^1 - \frac{w_j x_j^L}{y_j^U y_j^U} + \frac{w_j^U x_j^L}{y_j^U y_j^U}, \right. \\
&\quad \left. -w_j^L \lambda_j^1 - \frac{w_j x_j^U}{y_j^L y_j^L} + \frac{w_j^L x_j^U}{y_j^L y_j^L} \right\}
\end{aligned}$$

and  $\lambda_j^1$ ,  $\lambda_j^2$ ,  $y_j^L$ ,  $y_j^U$ ,  $w_j^L$ , and  $w_j^U$  are as defined above. Now, by the same argument as was given for the second type of nonconvex term, the convex underestimator for the third type of term is:

$$\begin{aligned}
\sum_{j \in N} G_{ij} \frac{x_j w_j}{y_j y_j} &\geq \max \left\{ \sum_{j \in N} G_{ij} w_j^L \lambda_j^1 + \sum_{j \in N} G_{ij} \frac{w_j x_j^L}{y_j^U y_j^U} - \sum_{j \in N} G_{ij} \frac{w_j^L x_j^L}{y_j^U y_j^U}, \right. \\
&\quad \left. \sum_{j \in N} G_{ij} w_j^U \lambda_j^1 + \sum_{j \in N} G_{ij} \frac{w_j x_j^U}{y_j^L y_j^L} - \sum_{j \in N} G_{ij} \frac{w_j^U x_j^U}{y_j^L y_j^L} \right\} \\
-\sum_{j \in N} G_{ij} \frac{x_j w_j}{y_j y_j} &\geq \max \left\{ -\sum_{j \in N} G_{ij} w_j^U \lambda_j^1 - \sum_{j \in N} G_{ij} \frac{w_j x_j^L}{y_j^U y_j^U} + \sum_{j \in N} G_{ij} \frac{w_j^U x_j^L}{y_j^U y_j^U}, \right. \\
&\quad \left. -\sum_{j \in N} G_{ij} w_j^L \lambda_j^1 - \sum_{j \in N} G_{ij} \frac{w_j x_j^U}{y_j^L y_j^L} + \sum_{j \in N} G_{ij} \frac{w_j^L x_j^U}{y_j^L y_j^L} \right\}
\end{aligned}$$

## B Convex Underestimating Functions for the UNIQUAC Equation

The problem of enclosing all heterogeneous and reactive azeotropes using the UNIQUAC equation contains many nonlinear terms. The nonconvex terms can be grouped into two

basic categories. The first group has the form:

$$\ln \left( \sum_{j \in N} c_j x_j \right)$$

The nonconvex terms in this group are:

$$\ln \left( \sum_{j \in N} r_j x_j \right), \quad \ln \left( \sum_{j \in N} q_j x_j \right), \quad \ln \left( \sum_{j \in N} q'_j x_j \right), \quad \text{and} \quad \ln \left( \sum_{j \in N} \tau_{ji} q'_j x_j \right)$$

These are all concave terms, thus convex underestimating functions can easily be constructed. When terms of this form appear as  $(-\ln \sum_{j \in N} c_j x_j)$  they are convex and do not need underestimators. The convex underestimators for the first three terms above are written:

$$\ln \left( \sum_{j \in N} c_j x_j \right) \geq \ln m^L + \frac{\ln \left\{ \frac{m^U}{m^L} \right\}}{(m^U - m^L)} \left( \sum_{j \in N} c_j x_j - m^L \right)$$

for  $c_j = r_j, q_j$ , or  $q'_j$  and where,

$$\begin{aligned} m^U &= \max \sum_{j \in N} c_j x_j \\ \text{s.t.} \quad &\sum_{j \in N} x_j = 1 \\ &x_j^L \leq x_j \leq x_j^U \end{aligned}$$

and,

$$\begin{aligned} m^L &= \min \sum_{j \in N} c_j x_j \\ \text{s.t.} \quad &\sum_{j \in N} x_j = 1 \\ &x_j^L \leq x_j \leq x_j^U \end{aligned}$$

The convex underestimator for the fourth term is very similar:

$$\ln \left( \sum_{j \in N} c_{ij} x_j \right) \geq \ln m_i^L + \frac{\ln \left\{ \frac{m_i^U}{m_i^L} \right\}}{(m_i^U - m_i^L)} \left( \sum_{j \in N} c_{ij} x_j - m_i^L \right)$$

for  $c_{ij} = \tau_{ji} q'_j$  and where,

$$\begin{aligned}
m_i^U &= \max \sum_{j \in N} \tau_{ji} q'_j x_j \\
\text{s.t. } &\sum_{j \in N} x_j = 1 \\
&x_j^L \leq x_j \leq x_j^U
\end{aligned}$$

and,

$$\begin{aligned}
m_i^L &= \min \sum_{j \in N} \tau_{ji} q'_j x_j \\
\text{s.t. } &\sum_{j \in N} x_j = 1 \\
&x_j^L \leq x_j \leq x_j^U
\end{aligned}$$

The second group of nonconvex terms are fractional terms of the form:

$$c \cdot \frac{x_j}{\sum_{l \in N} d_l x_l} \quad (48)$$

This group includes the terms:

$$+\frac{\sum_{j \in N} l_j x_j}{\sum_{l \in N} r_l x_l}, \quad -\frac{\sum_{j \in N} l_j x_j}{\sum_{l \in N} r_l x_l}, \quad +\frac{\sum_{j \in N} \tau_{ij} q'_j x_j}{\sum_{l \in N} \tau_{lj} q'_l x_l}, \quad \text{and} \quad -\frac{\sum_{j \in N} \tau_{ij} q'_j x_j}{\sum_{l \in N} \tau_{lj} q'_l x_l}$$

For terms of this type, the sign of the constant in the numerator determines the formula that is used for the underestimating function. For the UNIQUAC equation, the parameters  $q_j, q'_j, r_j$ , and  $\tau_{ij}$  are always positive, while  $l_j$  may be either positive or negative. Therefore the constant  $c = +\tau_{ij} q'_j$  will always be positive and  $c = -\tau_{ij} q'_j$  will always be negative. However, the sign of the constant for the first two terms,  $c = +l_j$  and  $c = -l_j$  must be determined before the underestimating function is constructed. When  $c$  is positive, the underestimating function for a linear fractional term is given by:

$$\frac{cx_j}{\sum_{j \in N} d_j x_j} \geq \max \left\{ \frac{cx_j^L}{\sum_{l \in N} d_l x_l} + \frac{cx_j}{m^U} - \frac{cx_j^L}{m^U}, \right. \\
\left. \frac{cx_j^U}{\sum_{l \in N} d_l x_l} + \frac{cx_j}{m^L} - \frac{cx_j^U}{m^L} \right\}$$

When  $c$  is negative, the underestimating function is given by:

$$\frac{cx_j}{\sum_{j \in N} d_j x_j} \geq \max \left\{ -\frac{cx_j}{m^L} + \frac{cx_j^L \cdot \sum_{l \in N} d_l x_l}{m^L m^U} - \frac{cx_j^L}{m^U}, \right. \\ \left. -\frac{cx_j}{m^U} + \frac{cx_j^U \sum_{l \in N} d_l x_l}{m^L m^U} - \frac{cx_j^U}{m^L} \right\}$$

where,

$$m^U = \max \sum_{l \in N} d_l x_l \\ \text{s.t.} \quad \sum_{l \in N} x_l = 1 \\ x_l^L \leq x_l \leq x_l^U$$

and,

$$m^L = \min \sum_{l \in N} d_l x_l \\ \text{s.t.} \quad \sum_{l \in N} x_l = 1 \\ x_l^L \leq x_l \leq x_l^U$$

## C Convex Underestimating Functions for the UNIFAC Equation

The problem of enclosing all heterogeneous and reactive azeotropes using the UNIFAC equation contains several nonconvex terms. Most of the terms are identical to the nonconvex terms from the UNIQUAC equation, as discussed in Section 4.5. Convex lower bounding functions for these terms are derived in Appendix B. Of the remaining nonconvex terms, the first term has the same logarithmic form as discussed for the UNIQUAC equation.

$$\ln \left( \sum_{j \in N} \alpha_{gj} x_j \right)$$

This is a concave term, thus the convex lower bounding function is given by the following equation:

$$\ln \left( \sum_{j \in N} \alpha_{gj} x_j \right) \geq \ln m_g^L + \frac{\ln \left\{ \frac{m_g^U}{m_g^L} \right\}}{(m_g^U - m_g^L)} \left( \sum_{j \in N} \alpha_{gj} x_j - m_g^L \right)$$

where

$$\begin{aligned} m_g^U &= \max \sum_{j \in N} \alpha_{gj} x_j \\ \text{s.t. } &\sum_{j \in N} x_j = 1 \\ &x_j^L \leq x_j \leq x_j^U \end{aligned}$$

and,

$$\begin{aligned} m_g^L &= \min \sum_{j \in N} \alpha_{gj} x_j \\ \text{s.t. } &\sum_{j \in N} x_j = 1 \\ &x_j^L \leq x_j \leq x_j^U \end{aligned}$$

The last two nonconvex terms for the UNIFAC equation are fractional terms.

$$+\frac{\beta_{gij}x_j}{\sum_{k \in N} \alpha_{gk}x_k}, \quad \text{and} \quad -\frac{\beta_{gij}x_j}{\sum_{k \in N} \alpha_{gk}x_k}$$

For the UNIFAC equation, the parameter  $\beta_{gij}$  is always positive. Therefore, for the positive fractional term, the underestimating function is given by:

$$+\frac{\beta_{gij}x_j}{\sum_{k \in N} \alpha_{gk}x_k} \geq \max \left\{ \frac{\beta_{gij}x_j^L}{\sum_{k \in N} \alpha_{gk}x_k} + \frac{\beta_{gij}x_j}{m_g^U} - \frac{\beta_{gij}x_j^L}{m_g^U}, \right. \\ \left. \frac{\beta_{gij}x_j^U}{\sum_{k \in N} \alpha_{gk}x_k} + \frac{\beta_{gij}x_j}{m_g^L} - \frac{\beta_{gij}x_j^U}{m_g^L} \right\}$$

For the negative fractional term, the underestimating function is given by:

$$-\frac{\beta_{gij}x_j}{\sum_{k \in N} \alpha_{gk}x_k} \geq \max \left\{ -\frac{\beta_{gij}x_j}{m_g^L} + \frac{\beta_{gij}x_j^L \cdot \sum_{k \in N} \alpha_{gk}x_k}{m_g^L m_g^U} - \frac{\beta_{gij}x_j^L}{m_g^U}, \right. \\ \left. -\frac{\beta_{gij}x_j}{m_g^U} + \frac{\beta_{gij}x_j^U \cdot \sum_{k \in N} \alpha_{gk}x_k}{m_g^L m_g^U} - \frac{\beta_{gij}x_j^U}{m_g^L} \right\}$$

where,

$$\begin{aligned}
m_g^U &= \max \sum_{k \in N} \alpha_{gk} x_k \\
\text{s.t.} \quad &\sum_{k \in N} x_k = 1 \\
&x_k^L \leq x_k \leq x_k^U
\end{aligned}$$

and,

$$\begin{aligned}
m_g^L &= \min \sum_{k \in N} \alpha_{gk} x_k \\
\text{s.t.} \quad &\sum_{k \in N} x_k = 1 \\
&x_k^L \leq x_k \leq x_k^U
\end{aligned}$$

## D Convexification of Bilinear Terms

Bilinear terms appear in the formulations for both the heterogeneous and the reactive azeotrope problems. For example, the constraint that the composition of the vapor phase is equal to the overall composition of the liquid phase given by equation (6) contains bilinear terms of the form,

$$m^{Lj} x_i^{Lj}. \quad (49)$$

In order to convexify the constraint, every bilinear term is replaced by one new variable, and lower bounds and upper bounds on the new variable are introduced using the results of Al-Khayyal and Falk<sup>20</sup> and McCormick<sup>21</sup>. Using this approach, equation (6) becomes,

$$y_i - \sum_{j \in P^L} w^{Lj} = 0 \quad (50)$$

where  $w^{Lj}$  has replaced the bilinear term  $m^{Lj} x_i^{Lj}$ . The upper and lower bounds on the new variable are provided by four constraints,

$$w^{Lj} \geq (m^{Lj})^{LBD} x_i^{Lj} + m^{Lj} (x_i^{Lj})^{LBD} - (m^{Lj})^{LBD} (x_i^{Lj})^{LBD} \quad (51)$$

$$w^{Lj} \geq (m^{Lj})^{UBD} x_i^{Lj} + m^{Lj} (x_i^{Lj})^{UBD} - (m^{Lj})^{UBD} (x_i^{Lj})^{UBD} \quad (52)$$

$$w^{Lj} \leq (m^{Lj})^{UBD} x_i^{Lj} + m^{Lj} (x_i^{Lj})^{LBD} - (m^{Lj})^{UBD} (x_i^{Lj})^{LBD} \quad (53)$$

$$w^{Lj} \leq (m^{Lj})^{LBD} x_i^{Lj} + m^{Lj} (x_i^{Lj})^{UBD} - (m^{Lj})^{LBD} (x_i^{Lj})^{UBD} \quad (54)$$

Note that equation (50) is a linear equality constraint, and the four new constraints are linear inequalities.

Heterogeneous azeotropes: Benzene – Water system				
GAMS Implementation; $P = 1.0$ atm				
Azeotrope	$x^{L1}$	$x^{L2}$	$y$	
NRTL Equation				
B	0.0046	0.7669	0.6421	$T = 346.79$ K
W	0.9954	0.2331	0.3579	$CPU = 41.38$
UNIQUAC Equation				
B	0.0032	0.9991	0.7043	$T = 342.31$ K
W	0.9968	0.0009	0.2957	$CPU = 21.18$
UNIFAC Equation				
B	0.0006	0.9951	0.7028	$T = 342.36$ K
W	0.9994	0.0049	0.2972	$CPU = 23.95$
Experimental Data				
B	—	—	0.704	$T = 342.45$ K
W	—	—	0.296	

Table 1: Results for Example 1; Benzene-Water



Heterogeneous azeotropes: Cyclohexane – Water system				
GAMS Implementation; $P = 1.0$ atm				
Azeotrope	$x^{L1}$	$x^{L2}$	$y$	
NRTL Equation				
C	0.8621	0.6834	0.6892	$T = 343.37$ K
W	0.1379	0.3166	0.3108	$CPU = 18.91$
UNIQUAC Equation				
No azeotrope predicted			$CPU = 10.83$	
UNIFAC Equation				
C	0.0030	0.6676	0.6121	$T = 348.67$ K
W	0.9970	0.3324	0.2973	$CPU = 25.26$
Experimental Data				
C	—	—	0.701	$T = 342.55$ K
W	—	—	0.299	

Table 2: Results for Example 1; Cyclohexane-Water

Heterogeneous azeotropes: Ethanol – Benzene – Water system				
GAMS Implementation; $P = 1.0$ atm				
Azeotrope	$x^{L1}$	$x^{L2}$	$y$	
NRTL Equation				
E	0.1156	0.0927	0.0939	$T = 344.84$ K
B	0.0224	0.6252	0.5927	$CPU = 101.55$
W	0.8620	0.2821	0.3134	
UNIQUAC Equation				
E	0.1111	0.1842	0.1673	$T = 339.70$ K
B	0.0011	0.7683	0.5912	$CPU = 126.99$
W	0.8878	0.0475	0.2414	
UNIFAC Equation				
E	0.3783	0.1008	0.1968	$T = 339.50$ K
B	0.0651	0.8806	0.5986	$CPU = 140.10$
W	0.5566	0.0186	0.2046	
Experimental Data				
E	—	—	0.228	$T = 338.00$ K
B	—	—	0.539	
W	—	—	0.233	

Table 3: Results for Example 1; Ethanol-Benzene-Water

Heterogeneous azeotropes: Ethanol – Cyclohexane – Water system				
GAMS Implementation; $P = 1.0$ atm				
Azeotrope	$x^{L1}$	$x^{L2}$	$y$	
NRTL Equation				
E	0.0002	0.0003	0.0010	$T = 343.29$ K
C	0.0070	0.8741	0.6912	$CPU = 88.34$
W	0.9928	0.1257	0.3078	
UNIQUAC Equation				
E	0.5471	0.2112	0.3207	$T = 337.05$ K
C	0.0435	0.7539	0.5223	$CPU = 96.23$
W	0.4093	0.0349	0.1570	
UNIFAC Equation				
E	0.0004	0.0005	0.0010	$T = 348.65$ K
C	0.0030	0.6662	0.6114	$CPU = 92.28$
W	0.9966	0.3333	0.3876	
Experimental Data				
E	—	—	0.302	$T = 335.75$ K
C	—	—	0.522	
W	—	—	0.176	

Table 4: Results for Example 1; Ethanol-Cyclohexane-Water

Heterogeneous azeotropes: Ethanol – Benzene – Cyclohexane – Water system				
GAMS Implementation; $P = 1.0$ atm				
Azeotrope	$x^{L1}$	$x^{L2}$	$y$	
NRTL Equation				
E	0.1619	0.0517	0.0801	$T = 344.76$ K
B	0.3678	0.6452	0.5716	$CPU = 220.84$
C	0.0044	0.0061	0.0043	
W	0.4659	0.2970	0.3439	
UNIQUAC Equation				
E	0.3735	0.1785	0.2232	$T = 334.60$ K
B	0.0368	0.4161	0.3293	$CPU = 241.63$
C	0.0107	0.3631	0.2824	
W	0.5790	0.0422	0.1651	
UNIFAC Equation				
E	0.1576	0.1039	0.1116	$T = 337.41$ K
B	0.0080	0.5739	0.4932	$CPU = 256.62$
C	0.0131	0.2071	0.1794	
W	0.8212	0.1151	0.2158	
Experimental Data				
E	—	—	0.224	$T =$ not provided
B	—	—	0.163	
C	—	—	0.380	
W	—	—	0.233	

Table 5: Results for Example 1; Ethanol-Benzene-Cyclohexane-Water

Benzene – Water				
NRTL				
	$T_{ref} = 330$ K		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.0046	0.7669	0.0060	0.7677
$x_2$	0.9954	0.2331	0.9940	0.2323
$y_1$	0.6421		0.6438	
$y_2$	0.3579		0.3562	
$T$	346.79 K		346.71 K	

Table 6: Analysis of Temperature Dependence of NRTL Binary Interaction Parameters; Benzene – Water system

Benzene – Water UNIQUAC				
	$T_{ref} = 333.15 \text{ K}$		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.0032	0.9991	0.0033	0.9989
$x_2$	0.9968	0.0009	0.9967	0.0011
$y_1$	0.7043		0.7043	
$y_2$	0.2957		0.2957	
$T$	342.31 K		342.31 K	

Table 7: Analysis of Temperature Dependence of UNIQUAC Binary Interaction Parameters; Benzene – Water system

Benzene – Water				
UNIFAC				
	$T_{ref} = 333.15 \text{ K}$		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.0006	0.9951	0.0006	0.9945
$x_2$	0.9994	0.0049	0.9994	0.0055
$y_1$	0.7028		0.7027	
$y_2$	0.2972		0.2973	
$T$	342.36 K		342.38 K	

Table 8: Analysis of Temperature Dependence of UNIFAC Binary Interaction Parameters; Benzene – Water system

Cyclohexane – Water				
NRTL				
	$T_{ref} = 330$ K		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.8621	0.6834	0.8610	0.6843
$x_2$	0.1379	0.3166	0.1390	0.3157
$y_1$	0.6892		0.6870	
$y_2$	0.3108		0.3130	
$T$	343.37 K		343.53 K	

Table 9: Analysis of Temperature Dependence of NRTL Binary Interaction Parameters; Cyclohexane – Water system



Cyclohexane – Water UNIFAC				
	$T_{ref} = 333.15 \text{ K}$		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.0030	0.6676	0.0035	0.6572
$x_2$	0.9970	0.3324	0.9965	0.3428
$y_1$	0.6121		0.6091	
$y_2$	0.3879		0.3909	
$T$	348.67 K		348.87 K	

Table 10: Analysis of Temperature Dependence of UNIFAC Binary Interaction Parameters; Cyclohexane – Water system

Ethanol – Benzene – Water NRTL				
	$T_{ref} = 330$ K		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.1156	0.0927	0.1205	0.0936
$x_2$	0.0224	0.6252	0.0275	0.6237
$x_3$	0.8620	0.2821	0.8520	0.2826
$y_1$	0.0939		0.0950	
$y_2$	0.5927		0.5938	
$y_3$	0.3134		0.3112	
$T$	344.84 K		344.77 K	

Table 11: Analysis of Temperature Dependence of NRTL Binary Interaction Parameters; Ethanol – Benzene – Water system

Ethanol – Benzene – Water UNIQUAC				
	$T_{ref} = 333.15 \text{ K}$		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.1111	0.1842	0.1174	0.1877
$x_2$	0.0011	0.7683	0.0013	0.7631
$x_3$	0.8878	0.0475	0.8813	0.0492
$y_1$	0.1673		0.1716	
$y_2$	0.5912		0.5885	
$y_3$	0.2414		0.2399	
$T$	339.70 K		339.65 K	

Table 12: Analysis of Temperature Dependence of UNIQUAC Binary Interaction Parameters; Ethanol – Benzene – Water system

Ethanol – Benzene – Water UNIFAC				
	$T_{ref} = 333.15 \text{ K}$		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.3783	0.1008	0.3732	0.1043
$x_2$	0.0651	0.8806	0.0632	0.8757
$x_3$	0.5566	0.0186	0.5636	0.0200
$y_1$	0.1968		0.1962	
$y_2$	0.5986		0.5979	
$y_3$	0.2046		0.2059	
$T$	339.50 K		339.55 K	

Table 13: Analysis of Temperature Dependence of UNIFAC Binary Interaction Parameters; Ethanol – Benzene – Water system

Ethanol – Cyclohexane – Water NRTL				
	$T_{ref} = 330$ K		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.0002	0.0003	0.0002	0.0003
$x_2$	0.0070	0.8741	0.0084	0.8743
$x_3$	0.9928	0.1257	0.9913	0.1254
$y_1$	0.0010		0.0010	
$y_2$	0.6912		0.6882	
$y_3$	0.3078		0.3108	
$T$	343.29 K		343.54 K	

Table 14: Analysis of Temperature Dependence of NRTL Binary Interaction Parameters; Ethanol – Cyclohexane – Water system

Ethanol – Cyclohexane – Water UNIQUAC				
	$T_{ref} = 333.15 \text{ K}$		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.5471	0.2112	0.5458	0.2129
$x_2$	0.0435	0.7539	0.0432	0.7515
$x_3$	0.4093	0.0349	0.4109	0.0355
$y_1$	0.3207		0.3209	
$y_2$	0.5223		0.5217	
$y_3$	0.1570		0.1573	
$T$	337.05 K		337.10 K	

Table 15: Analysis of Temperature Dependence of UNIQUAC Binary Interaction Parameters; Ethanol – Cyclohexane – Water system

Ethanol – Cyclohexane – Water UNIFAC				
	$T_{ref} = 343.15 \text{ K}$		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.0004	0.0005	0.0004	0.0005
$x_2$	0.0030	0.6662	0.0035	0.6557
$x_3$	0.9966	0.3333	0.9961	0.3438
$y_1$	0.0010		0.0010	
$y_2$	0.6114		0.6084	
$y_3$	0.3876		0.3906	
$T$	348.65 K		348.85 K	

Table 16: Analysis of Temperature Dependence of UNIFAC Binary Interaction Parameters; Ethanol – Cyclohexane – Water system

Ethanol – Benzene – Cyclohexane – Water NRTL				
	$T_{ref} = 330$ K		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.1619	0.0517	0.1023	0.0413
$x_2$	0.3678	0.6452	0.4874	0.6365
$x_3$	0.0044	0.0061	0.0037	0.0049
$x_4$	0.4659	0.2970	0.4067	0.3173
$y_1$	0.0801		0.0710	
$y_2$	0.5716		0.5612	
$y_3$	0.0043		0.0051	
$y_4$	0.3439		0.3627	
$T$	344.76 K		344.64 K	

Table 17: Analysis of Temperature Dependence of NRTL Binary Interaction Parameters; Ethanol – Benzene – Cyclohexane – Water system



Ethanol – Benzene – Cyclohexane – Water UNIQUAC				
	$T_{ref} = 333.15 \text{ K}$		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.3735	0.1785	0.3728	0.1776
$x_2$	0.0368	0.4161	0.0368	0.4165
$x_3$	0.0107	0.3631	0.0106	0.3642
$x_4$	0.5791	0.0422	0.5798	0.0417
$y_1$	0.2232		0.2222	
$y_2$	0.3293		0.3297	
$y_3$	0.2824		0.2834	
$y_4$	0.1651		0.1647	
$T$	334.60 K		334.50 K	

Table 18: Analysis of Temperature Dependence of UNIQUAC Binary Interaction Parameters; Ethanol – Benzene – Cyclohexane – Water system

Ethanol – Benzene – Cyclohexane – Water UNIFAC				
	$T_{ref} = 343.15$ K		Temp Dependent BIP's	
	$L_1$	$L_2$	$L_1$	$L_2$
$x_1$	0.1576	0.1039	0.1569	0.1043
$x_2$	0.0080	0.5739	0.0081	0.5750
$x_3$	0.0131	0.2071	0.0132	0.2054
$x_4$	0.8212	0.1151	0.8218	0.1152
$y_1$	0.1116		0.1119	
$y_2$	0.4932		0.4936	
$y_3$	0.1794		0.1778	
$y_4$	0.2158		0.2167	
$T$	337.41 K		337.50 K	

Table 19: Analysis of Temperature Dependence of UNIFAC Binary Interaction Parameters; Ethanol – Benzene – Cyclohexane – Water system

Reactive azeotropes: Hypothetical 3-Component Example I			
Wilson Equation; $P = 1.0$ atm			
$K_{eq} = 0.100$			
Azeotrope	$x_i$	$y_i$	
A	0.1495	0.1491	$T = 456.42$ K
B	0.8504	0.8488	$Iter = 216$
C	0.0001	0.0021	$CPU = 10.85$ sec
$K_{eq} = 1.000$			
Azeotrope	$x_i$	$y_i$	
A	0.1057	0.0916	$T = 456.11$ K
B	0.8939	0.9010	$Iter = 291$
C	0.0004	0.0074	$CPU = 14.64$ sec
$K_{eq} = 1000.0$			
Azeotrope	$x_i$	$y_i$	
A	0.0026	0.0015	$T = 455.00$ K
B	0.9973	0.9966	$Iter = 139$
C	0.0001	0.0019	$CPU = 7.62$ sec

Table 20: Results for Reactive Example 1

Reactive azeotropes: Hypothetical 3-Component Example II			
Wilson Equation; $P = 1.0$ atm			
$K_{eq} = 0.001$			
Azeotrope 1	$x_i$	$y_i$	
A	0.9659	0.9353	$T = 354.66$ K
B	0.0211	0.0364	
C	0.0130	0.0283	
Azeotrope 2	$x_i$	$y_i$	
A	0.6723	0.6704	$T = 352.85$ K
B	0.3270	0.3279	$Iter = 1237$
C	0.0007	0.0016	$CPU = 423.54$
$K_{eq} = 0.025$			
Azeotrope 1	$x_i$	$y_i$	
A	0.7507	0.6895	$T = 456.11$ K
B	0.2233	0.2539	
C	0.0260	0.0566	
Azeotrope 2	$x_i$	$y_i$	
A	0.7994	0.7188	$T = 456.11$ K
B	0.1646	0.2049	$Iter = 1597$
C	0.0360	0.0763	$CPU = 98.63$ sec

Table 21: Results for Reactive Example 2

Reactive azeotropes: MTBE system with no inert Wilson Equation; $P = 1.0$ atm GAMS Implementation			
$K_{eq} = 0.050$			
Azeotrope 1	$x_i$	$y_i$	
I	0.9373	0.9385	$T = 334.26$ K
M	0.0400	0.0577	$Iter = 610$
MTBE	0.0226	0.0038	$CPU = 30.74$
$K_{eq} = 32.0$			
Azeotrope 1	$x_i$	$y_i$	
I	0.0385	0.1606	$T = 389.5946$ K
M	0.2243	0.3229	
MTBE	0.7372	0.5165	
Azeotrope 2	$x_i$	$y_i$	
I	0.0326	0.1442	$T = 389.5915$ K
M	0.2669	0.3514	$Iter = 1895$
MTBE	0.7003	0.5044	$CPU = 113.88$ sec
$K_{eq} = 49.0$			
Azeotrope 1	$x_i$	$y_i$	
I	0.0327	0.1336	$T = 391.90$ K
M	0.1703	0.2955	
MTBE	0.7970	0.5709	
Azeotrope 2	$x_i$	$y_i$	
I	0.0159	0.0812	$T = 389.5915$ K
M	0.3599	0.4185	$Iter = 1791$
MTBE	0.6242	0.5003	$CPU = 103.73$ sec

Table 22: Results for Reactive Example 3

Reactive azeotropes: MTBE with Inert Wilson Equation; $P = 1.0$ atm GAMS Implementation			
$K_{eq} = 27.00$			
Azeotrope 1	$x_i$	$y_i$	
I	0.0346	0.1462	$T = 398.47$ K
M	0.2976	0.3787	
MTBE	0.6676	0.4748	
N	0.0002	0.0003	
Azeotrope 2	$x_i$	$y_i$	
I	0.0065	0.0082	$T = 355.887$ K
M	0.0007	0.0024	$Iter = 1654$
MTBE	0.0022	0.0005	$CPU = 150.28$ sec
N	0.9906	0.9889	

Table 23: Results for Reactive Example 4

Reactive azeotropes: Isopropyl Acetate System			
$P = 1.0$ atm; GAMS Implementation			
NRTL Equation: $K_{eq} = 8.7$			
Azeotrope	$x_i$	$y_i$	
IpOH	0.5398	0.4954	$T = 352.71$ K
AA	0.0540	0.0096	$Iter = 2031$
IpAc	0.1989	0.2433	$CPU = 66.50$
W	0.2072	0.2516	
UNIQUAC Equation; $K_{eq} = 8.7$			
No Azeotrope			$CPU = 22.17$
UNIFAC Equation; $K_{eq} = 8.7$			
No Azeotrope			$CPU = 28.88$
UNIQUAC Equation; $K_{eq} = 20.0$			
Azeotrope	$x_i$	$y_i$	
IpOH	0.5498	0.5357	$T = 350.06$ K
AA	0.0154	0.0010	$Iter = 924$
IpAc	0.0225	0.0364	$CPU = 36.92$
W	0.4123	0.4269	
Experimental Results			
From Song et al. <sup>23</sup> ; $K_{eq} = 8.7$			
Azeotrope	$x_i$	$y_i$	
IpOH	0.565	0.491	$T = 351.75$ K
AA	0.054	0.00	
IpAc	0.214	0.270	
W	0.167	0.239	

Table 24: Results for Reactive Example 5