Calculation of a double reactive azeotrope using stochastic optimization approaches

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Abstract. An homogeneous reactive azeotrope is a thermodynamic coexistence condition of two phases under chemical and phase equilibrium, where compositions of both phases (in the Ung-Doherty sense) are equal. This kind of nonlinear phenomenon arises from real world situations and has applications in chemical and petrochemical industries. The modeling of reactive azeotrope calculation is represented by a nonlinear algebraic system with phase equilibrium, chemical equilibrium and azeotropy equations. This nonlinear system can exhibit more than one solution, corresponding to a double reactive azeotrope. The robust calculation of reactive azeotropes can be conducted by several approaches, such as interval-Newton/generalized bisection algorithms and hybrid stochastic-deterministic frameworks. In this paper, we investigate the numerical aspects of the calculation of reactive azeotropes using two metaheuristics: the Luus-Jaakola adaptive random search and the Firefly algorithm. Moreover, we present results for a system (with industrial interest) with more than one azeotrope, the system isobutene/methanol/methyl-tert-butyl-ether (MTBE). We present convergence patterns for both algorithms, illustrating - in a bidimensional subdomain - the identification of reactive azeotropes. A strategy for calculation of multiple roots in nonlinear systems is also applied. The results indicate that both algorithms are suitable and robust when applied to reactive azeotrope calculations for this “challenging” nonlinear system.

1. Introduction
An azeotrope (in its classical statement) is a thermodynamic phenomenon where a boiling mixture produces a vapor with identical composition (the relative quantities of the mixture components, expressed in molar scales) when compared to the liquid phase. Azeotropic states can introduce confinement regions for separations that explore differences between boiling points of the mixture components. Ordinarily, the azeotrope condition is represented by the equalities of compositions for both phases in equilibrium, i.e.: \( x_i = y_i, i = 1, 2, \ldots, c \), where \( x_i \) and \( y_i \) represent liquid and vapor molar fractions, and \( c \) is the number of components. For reactive systems, it is possible to obtain a similar expression, but using a nonlinear transformation on the vector of molar fractions [1], producing a new set of compositional coordinates for liquid and vapor phases, \( X_i \) and \( Y_i \), respectively, which are equal in the reactive azeotropic condition:

\[
X_i = \frac{x_i - \nu_t^i N^{-1} x_{ref}}{1 - \nu_{tot}^i N^{-1} x_{ref}}; Y_i = \frac{y_i - \nu_t^i N^{-1} y_{ref}}{1 - \nu_{tot}^i N^{-1} y_{ref}}
\]
In this expression, \( \nu_i \) refers to the stoichiometric coefficient of component \( i \) in the chemical reaction, \( \nu_{i\text{sat}} \) is a vector with sums of stoichiometric coefficients for chemical reactions, \( N \) is a matrix of stoichiometric coefficients for reference components (the number of reference components is equal to the number of equilibrium chemical reactions that are chosen among the set of reacting species), \( x_{i\text{ref}} \) (resp., \( y_{i\text{ref}} \)) is the vector of molar fractions in liquid (resp., vapor) phase for the reference components. Reactive azeotropes can be observed even in ideal mixtures (vapor and liquid ideal phases), whereas ordinary homogeneous azeotropes are consequences of the nonidealities of liquid phase. Moreover, several systems show reactive azeotropes, and, in some cases, more than one azeotrope [2]. The reactive azeotrope calculation is characterized by a nonlinear set of algebraic equations, representing phase coexistence conditions, chemical equilibria and the azeotropy condition. Thus, this nonlinear system can be converted in an optimization problem and solved by classical (deterministic) nonlinear optimization methods or by using metaheuristics. Platt [7] presents an analysis of Differential Evolution algorithm and Luus-Jaakola method in a calculation of a single reactive azeotrope in a quaternary ideal system.

In this work we addressed the calculation of reactive azeotropes in a ternary non-ideal system (with two azeotropes) using two metaheuristics: the Luus-Jaakola (LJ) algorithm (an adaptive random search method) [3] and the Firefly algorithm (FF) [4]. We also studied some strategies to identify further solutions, using a modification of the objective function [5] or through a repulsion technique [6], in order to avoid solutions previously obtained. The main objective of this work is not to compare efficiency or robustness of LJ and FF algorithms, but to provide an useful framework for "hard" nonlinear systems with multiple roots.

2. Problem Formulation and Numerical Methods
The reactive homogeneous azeotrope is a phase coexistence condition where the compositional coordinates for liquid and vapor phases, in Ung-Doherty sense, are equal. Thus, we can represent an homogeneous reactive azeotrope in a mixture with \( r \) equilibrium reactions as [1]:

\[
X_i = Y_i \quad i = 1, 2, \ldots, c-r-1.
\]

Simultaneous chemical and phase equilibrium problem is expressed by the following equations:

\[
\begin{align*}
&P_{y_i} - x_i \gamma_i P_{i\text{sat}} = 0 \quad i = 1, 2, \ldots, c \\
&\sum_{i=1}^{c} x_i - 1 = 0 \\
&\sum_{i=1}^{c} y_i - 1 = 0 \\
&\ln(K) - \nu^l \ln(a) = 0 \quad i = 1, 2, \ldots, r
\end{align*}
\]  

(2)

In Eqs. (2), \( P \) is the system pressure, \( \gamma_i \) is the activity coefficient for component \( i \) (calculated via Wilson model) and \( P_{i\text{sat}} \) is the saturation pressure for specie \( i \) (evaluated by Antoine equation). Also in Eqs. (2), \( K \) is the vector of chemical equilibrium constants, \( \nu \) is a matrix of stoichiometric coefficients (dimension \( c \times r \)). In monoreactive problems, \( \nu \) is a vector with the stoichiometric coefficients of each component participating in the equilibrium chemical reaction and, obviously, \( K \) is a scalar quantity. The vector \( a \) is the vector of activities; the activity of component \( i \) is defined as \( a_i = \gamma_i x_i \). Physical parameters are found in [2].

An analysis of degrees of freedom for this nonlinear system indicates \( c+2+r \) equations. The thermodynamic coordinates are: \( x, y, T \) and \( P \), performing \( 2c+2 \) variables. Thus, the number of degrees of freedom for the phase coexistence problem is \( (2c+2) - (c+r+2) = c-r \). If one consider pressure (or temperature) previously specified, we obtain \( c-r-1 \). This quantity is satisfied by the reactive azeotrope conditions. The vector of unknowns will be referred as: \( \theta^l = [x_1 \ x_2 \ldots x_c \ y_1 \ y_2 \ldots y_c \ T] \). The nonlinear system appears as:

\[
F_l(\theta) = 0, \quad l = 1, 2, \ldots, 2c+1,
\]

where \( F_l \) refers to each nonlinear equation formed by Eqs.(2) and the reactive azeotrope condition. Thus, a related optimization problem can be constructed, by the scalar function

\[
f(\theta) = \sum_{l=1}^{2c+1} (F_l(\theta))^2.
\]

A minimizer \( \theta \) of the function \( f(\theta) \) that produces a null minimum is also a solution of the nonlinear system represented by Eqs. (2) plus reactive azeotrope equations.
Table 1. Reactive azeotropes – isobutene + methanol + MTBE – $K = 49.0$.

| Component    | $x_{i1}^{az1}$ | $y_{i1}^{az1}$ | $T^{az1}$ | $x_{i2}^{az2}$ | $y_{i2}^{az2}$ | $T^{az2}$ |
|--------------|----------------|----------------|-----------|----------------|----------------|-----------|
| isobutene (1)| 0.0446038      | 0.1727712      | 392.2444  | 0.0138208      | 0.0748231      | 391.17559 |
| methanol (2) | 0.1197971      | 0.2378773      | -         | 0.4037263      | 0.4406101      | -         |
| MTBE (3)     | 0.8355991      | 0.5893516      | -         | 0.5824529      | 0.4845668      | -         |

As pointed previously, this nonlinear optimization problem was solved by two metaheuristics: the LJ method [3] and the FF algorithm [4]. The LJ method is an adaptive random search algorithm, with a double-loop structure and a contraction strategy for the search region. Here, we used $n_{int} = 1000$ (internal iterations), $n_{out} = 1000$ (number of contractions of search region), $\epsilon = 0.997$ (contraction factor). The FF algorithm mimetizes the behaviour of fireflies in nature. FF algorithm parameters used are: $\gamma = 2$ (light absorption coefficient), $\beta_0 = 0.5$ (attraction of two collapsed fireflies), $\alpha = 0.05$ (except for temperature, where $\alpha = 5$) (random movement parameter), number of fireflies = 30, generations = 500. More details on LJ and FF algorithms can be found in [3, 4]. In order to calculate multiple roots (minima), some additional steps are necessary, usually a modification in the objective-function. In this work, we evaluate two possible modifications in the objective-function (fitness): the proposal of Hirsch et al. [5] and the repulsion technique employed by Parsopoulos and Vrahatis [6].

3. Results and Discussions

We present results for the reactive system isobutene (1) + methanol (2) $\rightleftharpoons$ MTBE (3), at $P = 8$ atm, considering $K = 49$ [2]. In this situation, this reactive system shows two azeotropes, as presented in Table 1. Here, we consider MTBE (component 3) as the reference component, accordingly to Eqs. (1). Figure 1 shows a typical execution of Firefly algorithm in this problem, in a two-dimensional projection (in fact, the problem is in $\mathbb{R}^5$). The two azeotropes correspond to the two stationary points in the diagram (a maximum and a minimum). Our computational experiments indicate that the Azeotrope 1 is found more easier than Azeotrope 2. In this scenario, we consider that, in a typical execution, Azeotrope 1 is found.

![Figure 1. Typical FF execution ($X_1, Y_1 \times T$ projection). o: initial fireflies; □: final fireflies.](image1)

![Figure 2. (a) Typical LJ execution ($X_1, Y_1 \times T$ projection). (b) Amplification of the neighbourhood of azeotropes.](image2)

Then, some strategy to calculate further solutions is necessary. Here, we tested the
modification of the objective-function proposed by [5]. After the localization of \( k \) roots, \( \{\theta_1, \theta_2, ..., \theta^k\} \), the new objective-function is defined as: 
\[
\mathcal{F}(\theta) = \sum (F_i(\theta))^2 + \beta \sum_{j=1}^{k} \exp(-|\theta - \theta_j|) \chi_{\rho}(|\theta - \theta_j|) \]
where \( \chi_{\rho}(\delta) = 1 \), if \( \delta \leq \rho \), or \( \chi_{\rho}(\delta) = 0 \), otherwise. Qualitatively, in the last expression, \( \beta \) should be a large value and \( \rho \) a small one. In these numerical experiments, we used \( \beta = 1 \times 10^3 \) and \( \rho = 0.1 \). First, the LJ/FF algorithm is applied with a random estimate. After the localization of the first azeotrope, the objective-function is modified and the algorithm is executed again. The procedure stops when the value of the objective-function in the optimum is larger than a tolerance (in fact, we are searching for null minima). The use of the technique proposed by Hirsch et al. [5] is useful, but, in some instances, the algorithms converged to local minima. Indeed, this kind of approach produces several local minima, in a “mexican hat” form, as pointed by Parsopoulos and Vrahatis [6]. Considering this scenario, the repulsion procedure proposed by these authors [6] is based on the calculation of an Euclidean norm \( d_{ij} = ||\theta_i - \theta^*_j|| \), where \( \theta^*_j \) is a minimizer previously found (in our numerical experiments, we used a Manhattan norm, or \( \ell^1 \) norm). If this norm is less than a specified control parameter \( r_{ij} \) (0.1 in our case), the current point is repelled from the center of the repulsion area, using an expression like as \( \theta_j \leftarrow \theta_j + p_{ij}(\theta_i - \theta^*_j)/d_{ij} \), where \( p_{ij} \) is a scale factor (equal to one in our computational experiments).

In order to avoid the “mexican hat effect”, we used the repulsion approach [6] to obtain a second azeotrope. A typical execution of LJ algorithm with this modification, and considering that the first azeotrope identified was Azeotrope 1, is presented in Figure 2. Clearly, the algorithm promotes a convergence to Azeotrope 2. We execute both algorithms for 20 instances using the repulsion technique. For LJ algorithm we observed a mean objective-function equal to \( 2.03 \times 10^{-3} \) (best value: \( 6.26 \times 10^{-5} \)), and for FF algorithm we obtain a mean value of \( 1.32 \times 10^{-3} \) (best value: \( 9.37 \times 10^{-4} \)). Obviously, a simple evaluation of mean values does not represent a performance or statistical comparison between algorithms, but it is useful to demonstrate that both methods produce final results in the neighbourhood of Azeotrope 2. Indeed, with a deterministic method applied after the stochastic algorithm (Newton or Simplex methods, for instance) one can easily obtain an accurate value for Azeotrope 2. For azeotropic temperature, for example, FF founds a mean value of 391.42 K (with standard deviation equal to 0.25) and LJ obtains 391.27 K (and 0.27 for standard deviation). Clearly, we observed a convergence pattern to Azeotrope 2.

4. Conclusions
In this work, we addressed the problem of calculation of reactive azeotropes in a ternary nonideal system, using two metaheuristics – the LJ algorithm [3] and the FF algorithm [4]. In this case, there are two reactive azeotropes, in opposite sides of compositional domain. We applied some repulsion strategies in order to produce a robust framework capable to obtain both azeotropes.

Acknowledgments
Gustavo M. Platt is grateful to Fundação Carlos Chagas Filho de Apoio à Pesquisa do Estado do Rio de Janeiro (FAPERJ), by the financial support for this research. Matheus O. Andrade is also grateful to FAPERJ, by the undergraduate research grant.

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