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DEVELOPMENT OF A ROBUST ALGORITHM TO COMPUTE REACTIVE AZEOTROPES

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Abstract - In this paper, a novel approach for establishing the route for process intensification through the application of two developed softwares to characterize reactive mixtures is presented. A robust algorithm was developed to build up reactive phase diagrams and to predict the existence and the location of reactive azeotropes. The proposed algorithm does not depend on initial estimates and is able to compute all reactive azeotropes present in the mixture. It also allows verifying if there are no azeotropes, which are the major troubles in this kind of programming. An additional software was developed in order to calculate reactive residue curve maps. Results obtained with the developed program were compared with the published in the literature for several mixtures, showing the efficiency and robustness of the developed softwares.

Keywords: Chemical equilibria; Phase equilibria; Reactive distillation; Reactive azeotrope.

INTRODUCTION

In the last two decades, reactive distillation process has received growing attention due to its potential as an alternative to conventional separation processes for many complex liquid-phase systems. Actually, this process is known since the middle of the twenty century (for instance, Berman et al., 1948). However, only in the last 12 years, reactive distillation processes have received new commercial importance. Taylor and Krishna (2000) published a very good review about this subject, with more than 300 references.

The advantages achieved by performing simultaneously reaction and separation within the same apparatus lead to an important area of design: process intensification (Stankiewicz, 2003). This process shows many advantages, such as less energy consumption and/or waste formation, decreasing equipment volume, lower solvent use, and greater selectivity. These aspects can also be related with Green Chemical Engineering (Malone and Huss, 2003).

However, the non-linear coupling of reactions, transport phenomena and phase equilibrium increase the complexity in the design and in the operation of this kind of separation process. Recently, Almeida-Rivera et al. (2004) published some perspectives about reactive distillation processes. The authors analyzed several methods available for design and operation, and they suggested some guidelines to propose a reactive distillation process. These guidelines are separated in levels, and the first level is the feasibility analysis. Certainly, the first important task before the proposition of a feasible separation scheme is to study the system behavior. This can be made through system characterization. In order to proceed with this, some literature works must be referred.

Barbosa and Doherty (1988b), leaning on the books of Smith and Missen (1982) and Van Zeggeren

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*To whom correspondence should be addressed and Storey (1970), started with the studies about reactive distillation thermodynamics. One of the most important features inside of this series of papers published by Doherty's group is the introduction of a set of transformed composition variables. These new variables are, particularly, useful in the construction of thermodynamic diagrams.

Alternatively, Frey and Stichlmair (1999) and Stichlmair and Frey (1999) published another approach to study the thermodynamic and kinetic of reactive distillation processes. This methodology is based on reactive distillation lines, being, a priori, limited to three component mixtures.

Using the approach developed by Barbosa and Doherty (1988b), Maier et al. (2000) proposed a methodology based on interval analysis in order to locate reactive azeotropes. This method is particularly interesting, since it provides a powerful tool to predict all the reactive azeotropes. However, the extension of this methodology to heterogeneous mixture calculations is difficult due to the complexity of the mathematical formulation.

A robust computational program to calculate reactive azeotropes must be able to compute all azeotropes and to verify when the mixture is zeotropic. For instance, Okasinski and Doherty (1997) used arc-length continuation method to find reactive azeotropes as function of the reaction equilibrium constant. However, this technique does not answer if all azeotrope compositions were calculated. Moreover, since the system of equations is strongly nonlinear, one of the main problems in this case is to supply suitable initial estimates.

In this work, a robust algorithm to find out reactive azeotropes was developed, in order to characterize reactive mixtures, with any number of components. In the calculation of the reactive azeotrope composition, the program is self-started and it is able to compute all azeotropes present in the mixture, and also to verify if there are no azeotropes, showing its robustness.

Furthermore, a computational program to build up residue curve maps for nonreactive and reactive systems was developed, in Fortran language, establishing feasible splits and optimum distillation schemes. Thus, an important set of tool is available to establish the route for process intensification.

PROBLEM FORMULATION

According to Barbosa and Doherty (1987), the material balance equations that describe the distillation of reactive systems can be simplified by introducing the following set of transformed composition variables:

$$X_i = \frac{x_i - s_i x_{ref}}{1 - s_T x_{ref}} \qquad i=1, \ldots, c-R \tag{1}$$

$$Y_i = \frac{y_i - s_i y_{ref}}{1 - s_T y_{ref}} \qquad i=1, \ldots, c-R \tag{2}$$

where x_i and y_i are the nontransformed mole fractions of component i in the liquid and in the vapor phases, respectively, x_{ref} and y_{ref} are the mole fraction compositions of the reference components in the liquid and in the vapor phases, respectively, s_i is the stoichiometry factor of component i, s_T is the sum of all stoichiometry factors in the reaction, and c and R are the number of components and reactions, respectively. The reference component must be adequately chosen, according to Okasinski and Doherty (1997) statements.

By using this set of equations, one of the criteria to find reactive azeotropes is (Barbosa and Doherty, 1988b):

$$X_i = Y_i \quad i=1, \ldots, c-R \tag{3}$$

In order to calculate the composition of reactive azeotropes, Eq. (3) must be solved together with phase (Eq. (4)) and reaction equilibria (Eq. (5)) assumptions, which can be expressed, considering the vapor phase as an ideal mixture (at low pressures) and the liquid phase as nonideal, by:

$$Py_i = P_i^{sat} \gamma_i x_i \tag{4}$$

$$K_r = \exp\left(\frac{-\Delta G_r(T)}{RT}\right) = \prod_{i=1}^{C} \left(x_i \gamma_i\right)^{s_i} \tag{5}$$

where P is the total pressure of the system, P_i^{sat} is the saturation pressure for component i, γ_i is the activity coefficient for component i, ΔG_r is the Gibbs free energy, R is the universal gas constant, and T is the absolute temperature.

ALGORITHM OF THE DEVELOPED SOFTWARES

In order to have a set of tools to characterize reactive systems, it was developed computational programs to calculate reactive azeotropes and to build up reactive residue curve maps, according to the equations described above.

Reactive Azeotrope Calculations

The set of equations listed above (Eqs. (3), (4), and (5)) presents a strong nonlinear behavior. Normally, the procedures to solve this kind of problem in the published literature need right choice of the initial estimates. Moreover, it is not known, a priori, the number of azeotropic points, or even if the reactive mixture is really azeotropic.

In this work, the developed program is able to bypass these problems, since it, firstly, builds up the reactive phase diagram, covering the whole range of compositions, from zero to one. The azeotropic condition is tested in each point, using a grid-based methodology, guaranteeing that all azeotropes are calculated.

The set of nonlinear algebraic equations are solved using a modified Powell hybrid algorithm and a finite-difference approximation for the Jacobian.

When it is found a point that lies within an established criterion ($X_i - Y_i = 10^{-10}$), this point should be the initial estimate to find the actual azeotropic composition, which is calculated using an optimization procedure, through SQP (Sequential Quadratic Programming) method.

Furthermore, it was developed a new function to find out azeotropic compositions, making the convergence easier. The objective function (Eq. (6)) takes into account the difference between the liquid and the vapor transformed composition variables plus the difference between bubble (T_{bubble}) and dew (T_{dew}) point temperatures, since both statements, $X_i = Y_i$ and $T_{bubble} = T_{dew}$, must be satisfied.

$$F_{obj} = \sum_{i=1}^{c} \left(\frac{X_i - Y_i}{X_i} \right)^2 + \left(\frac{T_{bubble} - T_{dew}}{T_{bubble}} \right)^2 \qquad (6)$$

These two main aspects, the independence of initial estimates and the new objective function, make the developed algorithm very robust and with an easier convergence. Moreover, since this methodology is based on simpler mathematical functions, it will be certainly easier to be applied to heterogeneous systems. These studies are being carried out, applying the proposed global phase stability analysis developed by Wasylkiewicz and Ung (2000).

Summarizing, the basic procedure in this methodology is:

1) to compute the phase diagram by stepping through a grid of values of the independent composition variable(s);

2) if it is found a point that is near to the reactive azeotropic condition, then this value is taken as an initial estimate for solving the azeotrope composition more precisely, starting an optimization procedure.

Calculation of Reactive Residue Curve Maps

The set of differential equations to build up reactive residue curve maps has been derived by Barbosa and Doherty (1988a) and it is given by:

$$\frac{dX_i}{d\tau} = X_i - Y_i \qquad i = 1, \ ..., \ c - R - 1 \qquad (7)$$

where τ is the warped time.

Starting from an initial value for X_i, it is necessary to calculate the corresponding value of Y_i using the phase and reaction equilibrium relationships (Eqs. (3) and (4)). The set of nonlinear equations is solved using the same mathematical procedure described above for reactive azeotrope composition calculations. Since Y_i was calculated, it is possible to integrate Eq. (7), applying a Runge-Kutta method.. These steps are carried out until a singular point is reached. The singular points occur when the composition of a pure component is reached or when $X_i = Y_i$, which corresponds to reactive azeotrope. Fig. 1 shows the proposed algorithm to build up reactive residue curve maps.

Other important feature of this kind of programming is the initial liquid mole composition that is supplied to build up composition diagrams and residue curve maps. In quaternary systems, for a fixed pressure, the remaining degrees of freedom are equal to 2, and it must be specified two initial liquid mole compositions. However, it is not really known if the composition range will be from zero to one, because the composition of one or more than one component can be lesser than unity, due to the chemical equilibrium. So, it is important that the initial compositions be supplied in terms of the transformed variable compositions, since one of the advantages of the transformed composition variables is that even in the midst of reaction none of them lie on restricted intervals, and all can span the whole range of values from zero to one (Ung and Doherty, 1995).

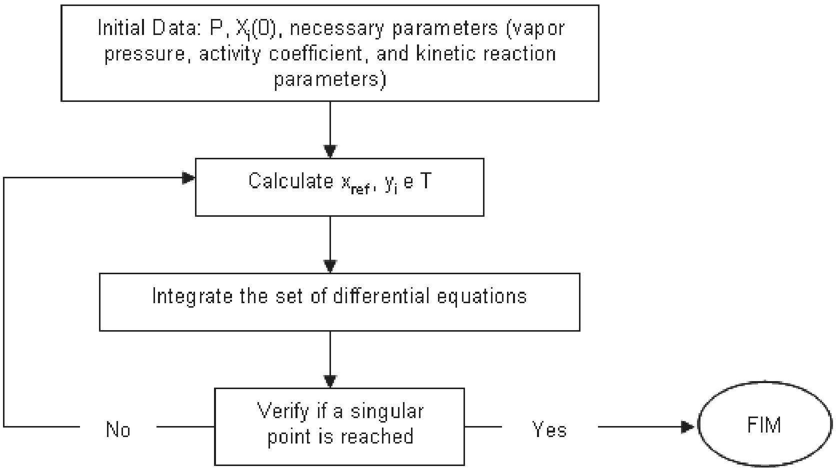

Figure 1: Schematic algorithm to build up reactive residue curve maps.

RESULTS

In order to analyze the performance of the developed software in a wide range of situations, two different systems were considered. Both of them were previously studied and published in the open literature (Barbosa and Doherty, 1988b, and Maier et al., 2000) and all results obtained in this work can be compared with the values computed by other methodologies used by the referred authors. Models and parameters were used in the same way that they were reported in Barbosa and Doherty (1988b), and in Maier et al. (2000), making the comparison between the results more effective.

Case Study 1: Hypothetical Ideal Systems A + B ↔ C and A + B ↔ C + D

These systems were, firstly, proposed by Barbosa e Doherty (1988b). For the ternary mixture, the authors considered two different hypothetical values for ΔG^0, -0.8314 kJ/mol and -8.314 kJ/mol. Vapor and liquid phases are considered ideal. For ternary and quaternary mixtures, components C and D were chosen as the reference ones, respectively. Total pressure for these systems is equal to 101.32 kPa.

For the smallest ΔG^0 value, the program finds that there is not any azeotrope in all the composition range. However, considering a ΔG^0 value ten times greater than in the first case an azeotrope is found. The fact that reactive azeotropes occur in ideal system was previously detected and explained by Barbosa and Doherty (1988b).

Table 1 shows the calculated azeotrope compositions, and the values reported in Barbosa and Doherty (1988b). All results are similar. Blank lines indicate that the value was not mentioned by the authors.

Figs. 2 and 3 show temperature-composition diagrams for the considered systems under transformed composition variables. In Fig. 3, it is possible to visualize the azeotrope occurrence for ΔG^0=-8.314 kJ/mol.

Another way to characterize and to visualize the system behavior is through residue curve maps. Figs. 4 and 5 show residue curve maps for this system under both situations, ΔG^0= -0.8314 kJ/mol and ΔG^0= -8.314 kJ/mol, respectively. As it can be seen in Fig. 4, this residue curve map has two singular points: a stable node, corresponding to pure component A, and an instable node, corresponding to pure component B. Pure component C is not a singular point, because the assumption that the reaction reaches the equilibrium instantaneously, which means that pure component C can never be obtained, since it will react immediately to give a mixture of A, B and C. However, considering a greater value for ΔG^0, the residue curve converges to the azeotropic point (Fig. 5). Thus, in a reactive distillation process under this last situation, the residue product will be at the reactive azeotropic composition.

For the hypothetical quaternary system, it is found one azeotropic composition, considering ΔG^0 equal to 0.8314 kJ/mol. Table 2 shows the obtained composition values, and those obtained by Barbosa e Doherty (1988b), showing that all the results are, also, similar.

Table 1: Comparison between reactive azeotrope compositions for the hypothetical ideal ternary mixture A + B ↔ C at 101.32 kPa.

Variables	This work	Barbosa e Doherty (1988b)
x_A	0.0697	0.0697
x_B	0.4956	0.4955
y_A	0.1737	0.1738
y_B	0.5520	0.5519
T (K)	394.81	

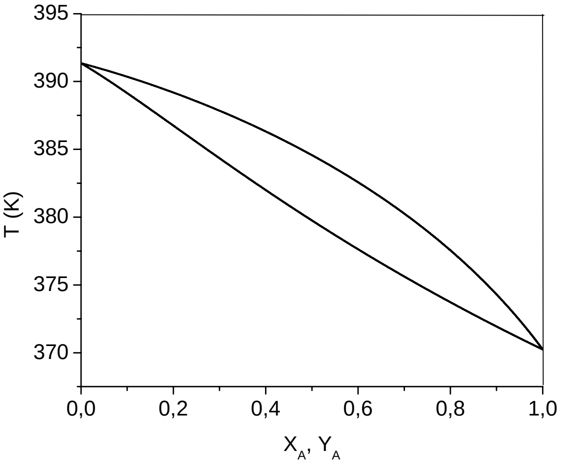

Figure 2: Reactive phase diagram for the hypothetical ideal system at 101.32 kPa and ΔG^0= -0.8314 kJ/mol.

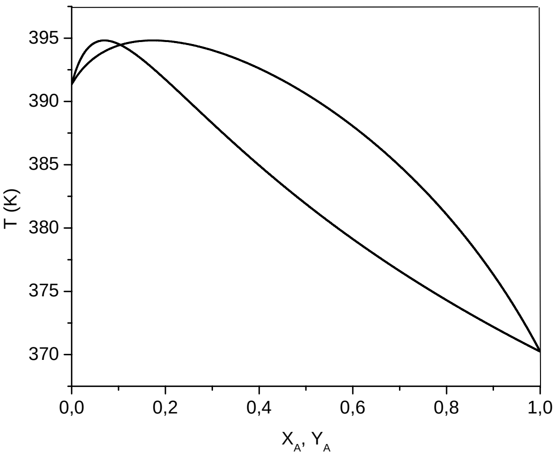

Figure 3: Reactive phase diagram for the hypothetical ideal system at 101.32 kPa and ΔG^0= -8.314 kJ/mol.

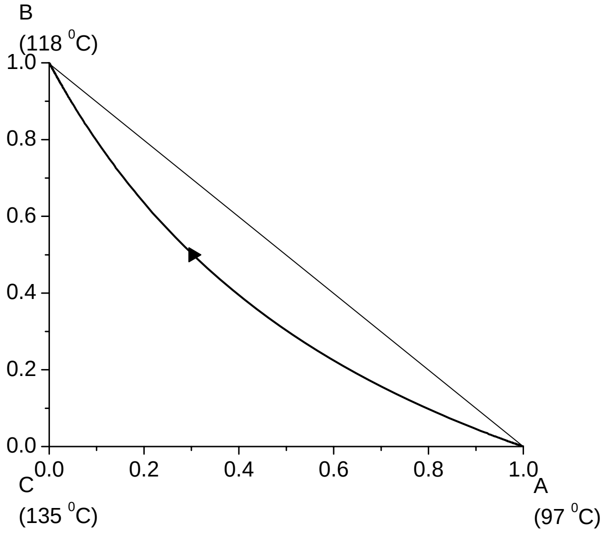

Figure 4: Reactive residue curve map for the hypotetical ideal mixture A+B↔C, at 101.32 kPa, with ΔG^0= -0.8314 kJ/mol.

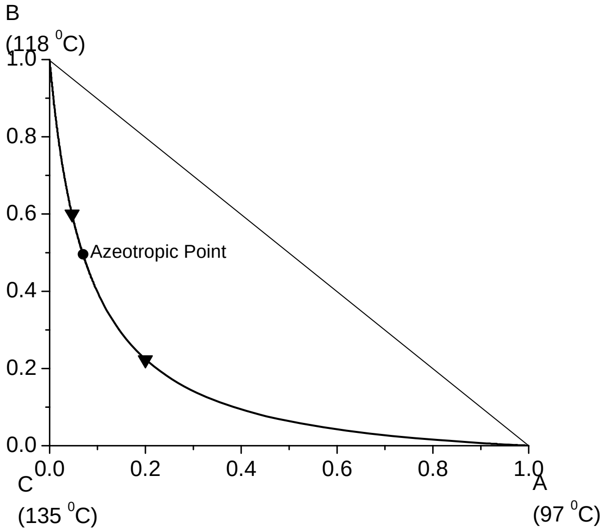

Figure 5: Reactive residue curve map for the hypotetical ideal mixture A+B↔C, at 101.32 kPa, with ΔG^0= -8.314 kJ/mol.

Table 2: Comparison between reactive azeotrope compositions for the hypothetical ideal quaternary mixture A + B ↔ C + D at 101.32 kPa.

Variables	This work	Barbosa e Doherty (1988b)
x_A	0.1884	0.1884
x_B	0.3583	0.3583
x_C	0.2151	0.2152
y_A	0.0733	0.0733
y_B	0.2433	0.2432
y_C	0.3302	0.3303
T (K)	362.7	-

Case Study 2: Isobutene + Methanol ↔ MTBE

Fig. 6 shows the nonreactive residue curve map for the system under consideration. The binary azeotrope between methanol and tert-butyl methyl ether (MTBE) is a saddle point and between isobutene and methanol an unstable node appears, leading to the occurrence of a distillation boundary. This distillation boundary splits the diagram in two different regions of distillation, making the separation of the ternary mixture impossible.

These verifications make the reactive distillation an alternative process to obtain MTBE. So, this reactive system was studied in order to understand its behavior. Gibbs free energy values where calculated as a function of the temperature, according with Eq. (7) (Barbosa and Doherty, 1988b).

$$\frac{\Delta G^0}{R} = -4254.05 + 10.0982 \times T + 0.2667 \times T \times \ln(T) \qquad (7)$$

Fig. 7 shows the reactive residue curve map for this system, where it can be seen that, under atmospheric pressure, this reactive mixture does not present any azeotrope, showing how the chemical equilibrium influences the phase equilibrium. This conclusion is in agreement with the results of Barbosa and Doherty (1988b). Fig. 8 shows the reactive phase diagram for isobutene/methanol/MTBE at 101.3 kPa, confirming that this reactive system is zeotropic.

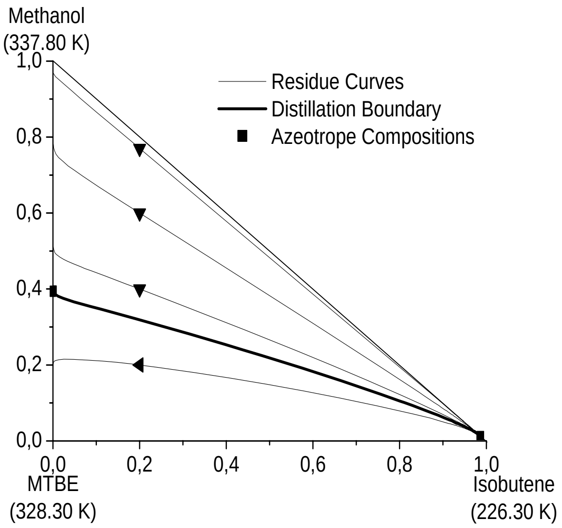

Figure 6: Nonreactive residue curve map for the system Isobutene + Methanol ↔ MTBE at 101.32 kPa.

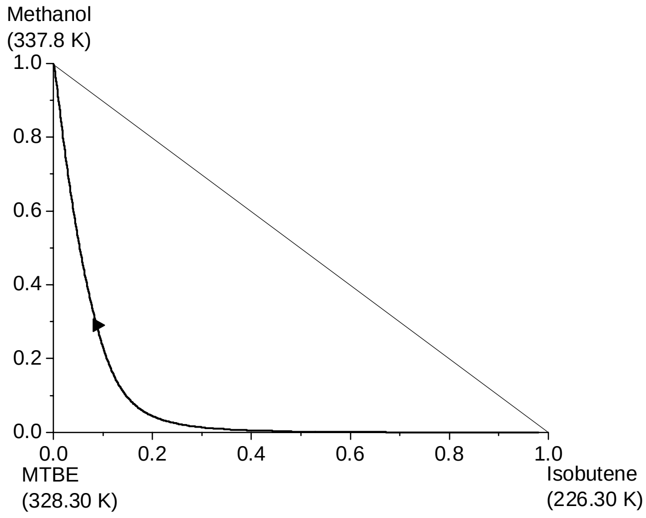

Figure 7: Reactive residue curve map for the system Isobutene + Methanol ↔ MTBE at 101.32 kPa.

Maier et al. (2000) studied this same system at 810.56 kPa (8 atm) and with different constant values for the equilibrium constant (K_r). Similar results were obtained in this work. When K_r is equal to 49.0, the mixture forms two azeotropes at different compositions. Fig. (9) shows the reactive phase equilibrium diagram for this case, and the calculated azeotropic composition values are reported in Table 3.

In actual processes to produce MTBE through reactive distillation, the source of iC4 consists of C4 cuts available from steam or catalytic crackers. In order to analyze this multicomponent system, it is considered that C4 stream consists, basically, of isobutene and n-butenes, being n-butenes inert components in the reaction.

For this quaternary system (ethanol/isobutene/MTBE/n-butene) the search of azeotropes were carried out at pressures of 1013.2, 2026.4 and 4052.8 kPa (10, 20, and 40 atm). Although in this high pressure it is not correct to consider the vapor as an ideal mixture, this assumption will be still considered, in order to compare the obtained results with those published by Maier et al. (2000). Tables 4, 5, and 6 show the results at 1013.2, 2026.4, and 4052.8 kPa, respectively, and once more the calculated values are in agreement with those calculated by Maier et al. (2000).

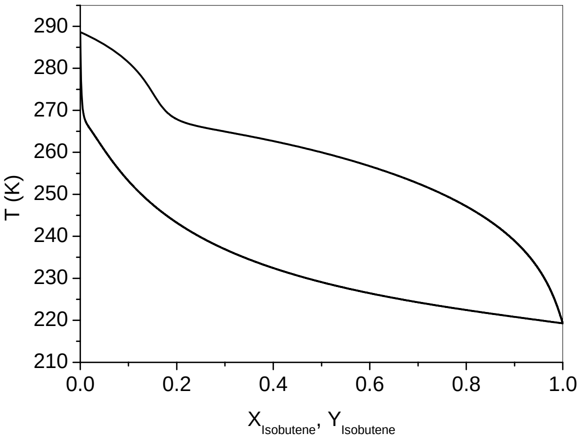

Figure 8: Reactive phase diagram for the system isobutene/methanol/MTBE at 101.32 kPa.

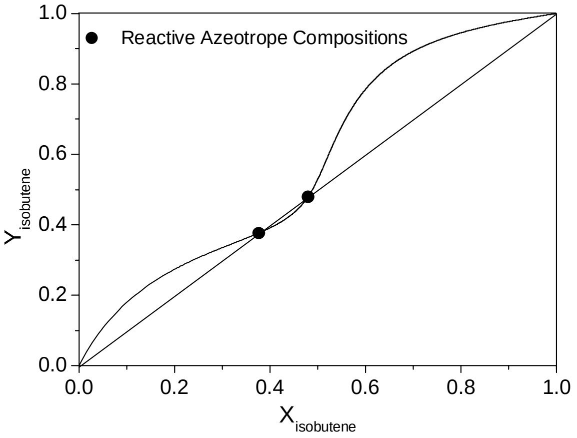

Figure 9: Reactive phase diagram for the system isobutene/methanol/MTBE at 810.56 kPa.

Table 3: Comparison between reactive azeotrope compositions for the isobutene/methanol/MTBE at 810.56 kPa with a fixed K_r value equal to 49.0.

	This work		Maier et al. (2000)		This work		Maier et al. (2000)	
Components	x_i	y_i	x_i	y_i	x_i	y_i	x_i	y_i
Isobutene	0.0138	0.0748	0.01	0.07	0.0446	0.1728	0.04	0.17
Methanol	0.4038	0.4407	0.40	0.44	0.1198	0.2381	0.12	0.24
MTBE	0.5824	0.4845	0.58	0.49	0.8356	0.5893	0.84	0.59

Table 4: Comparison between reactive azeotrope compositions for the isobutene/methanol/MTBE/n-butane at 1013.2 kPa.

	This work		Maier et al. (2000)	
Components	x_i	y_i	x_i	y_i
Isobutene	0.0053	0.0634	0.0055	0.0066
Methanol	0.0004	0.0015	0.0003	0.0015
MTBE	0.0014	0.0003	0.0015	0.0003
n-Butane	0.9929	0.9918	0.9927	0.9916
Temperature (K)	353.97		354.0	

Table 5: Comparison between reactive azeotrope compositions for the isobutene/methanol/MTBE/n-butane at 2026.4 kPa.

	This work		Maier et al. (2000)	
Components	x_i	y_i	x_i	y_i
Isobutene	0.0282	0.0336	0.0287	0.0342
Methanol	0.0017	0.0072	0.0014	0.0070
MTBE	0.0076	0.0020	0.0077	0.0020
n-Butane	0.9625	0.9572	0.9622	0.9568
Temperature (K)	390.33		388.4	

Table 6: Comparison between reactive azeotrope compositions for the isobutene/methanol/MTBE/n-butane at 4052.8 kPa.

	This work		Maier et al. (2000)	
Components	x_i	y_i	x_i	y_i
Isobutene	0.1549	0.1800	0.1478	0.1708
Methanol	0.0068	0.0363	0.0066	0.0334
MTBE	0.0458	0.0147	0.0409	0.0128
n-Butane	0.7925	0.7690	0.8047	0.7830
Temperature (K)	434.67		434.75	

CONCLUSIONS

Obtained results show that the developed software is able to compute one or more than one azeotrope present in ternary or quaternary mixtures, or even for mixtures with any number of components. It also allows verifying when the reactive mixture is zeotropic. Reactive azeotropes for ideal and nonideal and for ternary and quaternary mixtures were calculated. The CPU time is lesser than 0.5 s for all studied cases, showing the robustness of the developed software. Furthermore, the introduction of a previous step to calculate the initial estimates and the new objective function makes the convergence much easier.

NOMECLATURE

Symbols

C	component number	(-)
P	total pressure	(Pa)
P_i^{sat}	saturation pressure of component I	(-)
R	reaction number	
R	universal gas constant	(J mol^{-1} K^{-1})
s_i	Stoichiometric coefficients for component i in each reaction	(-)
s_T	sum of stoichiometric coefficients for each reaction	(-)
T	absolute temperature	(K)
X_i	transformed liquid mole fraction of a non-reference component *i*	(-)
x_i	liquid mole fraction of component i	(-)
x_{ref}	liquid mole fractions for R reference components	(-)
y_i	vapor mole fraction of component i	(-)
Y_i	transformed vapor mole fraction of a non-reference component *i*	(-)
y_{ref}	vapor mole fractions for *R* reference components	(-)

Greek Symbols

ΔG_r	variation of Gibbs free energy for reaction r	(J mol^{-1})
γ_i	activity coefficient of component *i*	(-)

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