A method for flash calculations in reactive mixtures

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RESUMEN

En este trabajo se reporta un método alternativo para realizar cálculos flash en sistemas reactivos, el cual ha sido desarrollado empleando la teoría de transformación de variables de Ung y Doherty (1995). En este método se utiliza un enfoque de resolución simultánea de ecuaciones para realizar los cálculos de equilibrio bifásico en este tipo de sistemas. El comportamiento numérico del método propuesto es evaluado empleando varios casos de estudio y los resultados obtenidos indican que éste es eficiente y generalmente puede converger a las composiciones de equilibrio.

Palabras clave: Equilibrio Químico. Equilibrio de fases. Cálculos flash. Variables transformadas.

SUMMARY

This paper introduces an alternative method for performing flash calculations in reacting systems, which has been developed using the theory of variable transformation of Ung and Doherty (1995). We use a simultaneous equation solving approach to perform two phase equilibrium calculations in chemically reactive systems. The numerical performance of proposed method is tested using several cases of study and our results show that it is efficient and generally can converge to the equilibrium compositions.

Key words: Chemical equilibrium. Phase equilibrium. Flash calculations. Transformed variables.

RESUM

En aquest treball, es comunica un mètode alternatiu per realitzar càlculs flash en sistemes reactius, que ha estat desenvolupat emprant la teoria de transformació de variables de Ung i Doherty (1995). En aquest mètode, s'utilitza un enfocament de resolució simultània d'equacions per realitzar els càlculs d'equilibri bifàsic en aquest tipus de sistemes. El comportament numèric del mètode proposat s'avalua emprant diversos casos d'estudi i els resultats obtinguts indiquen que aquest és eficient i generalment pot convergir a les composicions d'equilibri.

Mots clau: Equilibri químic. Equilibri de fases. Càlculs flash. Variables transformades.

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INTRODUCTION

The description of phase equilibrium in reacting mixtures is an important topic involved in several chemical engineering applications and it is the theoretical basis for design, analysis and synthesis of reactive separation processes (Pérez-Cisneros *et al*., 1997). During the last years, there has been a growing interest for developing new methods for describing the thermodynamic behavior of mixtures under physical and chemical equilibrium. Until now, several methods have been proposed to address phase stability and equilibrium problems in reactive systems (Castillo and Grossmann, 1981; Castier *et al*., 1989; Michelsen, 1989; Xiao *et al*., 1989; Smith *et al*., 1993; McDonald and Floudas, 1995; Ung and Doherty, 1995; Seider and Widagdo, 1996; Pérez-Cisneros *et al*., 1997; Stateva and Wakeham, 1997; Phoenix and Heidemann, 1998; Jalali and Seader, 1999; Platt and de Medeiros, 1999; Wasylkiewicz and Ung, 2000). These approaches can be classified as equation solving methods or Gibbs energy minimization techniques. If the mathematical formulation of chemical equilibrium problem is considered, we can also classify these methods as stoichiometric or non-stoichiometric (Smith *et al*., 1993).

The phase equilibrium problem with several chemical reactions is highly non linear and multivariable (Seider and Widagdo, 1996). By consequence, there are numerical problems associated with the equilibrium calculations. Specifically, we have initialization problems, the presence of trivial solutions or local minimums of Gibbs free energy and also the numerical methods may present slow convergence or divergence (Smith *et al*., 1993). Generally, published methods use reaction extents and mole fractions as independent variables and they may present some numerical problems if a proper initialization scheme or reliable solution technique is not considered. In addition, some methods can not handle the presence of inert components (Ung and Doherty, 1995). The inert components do not participate in any of the reactions, but have an influence on the phase equilibrium.

A suitable choice to reduce the problem dimensionality and to favor the numerical performance of solution algorithms consists in using techniques of variable transformation (Ung and Doherty, 1995; Pérez-Cisneros *et al*., 1997). However, this approach has not received much attention from chemical engineers regardless of its advantages.

The objective of this paper is to introduce an alternative algorithm for performing flash calculations in reactive systems. We propose a simultaneous equation solving method to perform two phase equilibrium calculations in chemically reactive systems. This method has been developed using the theory of transformed variables of Ung and Doherty (1995). We show the numerical performance of our method using several examples.

PHASE EQUILIBRIUM CONDITIONS EXPRESSED IN TERMS OF TRANSFORMED COMPOSITION VARIABLES

Ung and Doherty (1995) have proposed the use of transformed composition variables with the goal of developing a simpler thermodynamic framework for treating reactive systems. The transformed variables restrict the solution space to the compositions that are already in chemical equilibrium, reduce the dimension of the composition space by the number of independent reactions and make the phase diagrams look similar to those of non-reactive mixtures. These characteristics allow that all of the procedures used to obtain thermodynamic properties of non-reactive mixtures can be extended to reactive systems and, by con-

sequence, the non-reactive flash algorithms can be easily modified to account for the equilibrium reactions (Wasylkiewicz and Ung, 2000).

The transformed mole fraction of Ung and Doherty (1995) are defined as

$$X_i = \frac{x_i - v_i N^{-1} \overrightarrow{x_{ref}}}{1 - v_{TOT} N^{-1} \overrightarrow{x_{ref}}} \quad i = 1,.., c - R \tag{1}$$

where c is the component number, $\overrightarrow{x_{ref}}$ is the column vector of R reference component mole fractions, v_i is the row vector of stoichiometric coefficients of component i for each reaction, v_{TOT} is a row vector where each element corresponds to reaction r and it is the sum of the stoichiometric coefficients for all components that participate in reaction r and N is a square matrix formed from the stoichiometric coefficients of the reference components in the R reactions (Ung and Doherty, 1995). To evaluate thermodynamic properties, which are expressed on mole fraction basis, the reference mole fractions $\overrightarrow{x_{ref}}$ are calculated using Equation (1) and from the equilibrium constants for each reaction K_{eq}^r by solving a system of R nonlinear equations given by

$$K_{eq}^r = \prod_{i=1}^{c} a_i^{v_i^r} \quad r = 1,.., R \tag{2}$$

where a_i is the activity of component i and v_i^r is the stoichiometric coefficient of component i in reaction r, respectively. When we know the R reference mole fractions, for a set of $c - R$ specified transformed variables X_i, the corresponding mole fractions of $c - R$ non-reference components are calculated using Equation (1).

For a multicomponent multireaction mixture, the dimensionless transformed molar Gibbs free energy of mixing can be defined as

$$\frac{\Delta \hat{g}}{R_g T} = \frac{\hat{g} - \hat{g}_0}{R_g T} = \sum_{i=1}^{c-R} X_i \left(\frac{\Delta \hat{\mu}_i \{X\}}{R_g T} \right) = \sum_{i=1}^{c-R} X_i \ln(x_i \gamma_i \{X\}) = \sum_{i=1}^{c-R} X_i \ln \left(\frac{x_i \hat{\varphi}_i \{X\}}{\varphi_i} \right) \tag{3}$$

where R_g is the gas universal constant, T is the temperature, $\frac{\Delta \hat{\mu}_i}{R_g T} = \frac{\hat{\mu}_i \{X\} - \mu_i^o}{R_g T}$ is the transformed chemical potential of component i, $\hat{g}_0$ is the pure component free energy, $\hat{g}$ is the transformed molar Gibbs free energy, φ_i is the fugacity coefficient of pure component, $\hat{\varphi}_i$ is the fugacity coefficient of component i in the mixture and γ_i is the activity coefficient of component i, respectively. We note that $\hat{\varphi}_i$ and γ_i are functions of the transformed composition variables X.

Consider a feed with a global transformed composition Z that splits in two phases, then $\frac{\Delta \hat{g}}{R_g T}$ is given by

$$\frac{\Delta \hat{g}}{R_g T} = \Phi^\alpha \sum_{i=1}^{c-R} X_i^\alpha \left(\frac{\Delta \hat{\mu}_i^\alpha}{R_g T} \right) + \Phi^\beta \sum_{i=1}^{c-R} X_i^\beta \left(\frac{\Delta \hat{\mu}_i^\beta}{R_g T} \right) \tag{4}$$

subject to

$$Z_i - \Phi^\alpha X_i^\alpha - \Phi^\beta X_i^\beta = 0 \quad i = 1,..., c - R \tag{5}$$

where X_i^α and X_i^β are the equilibrium transformed mole fractions of component i. The transformed mole phase fractions Φ^α and Φ^β are defined as

$$\Phi^j = \phi^j \frac{1 - v_{TOT} N^{-1} \overrightarrow{x_{ref}^j}}{1 - v_{TOT} N^{-1} \overrightarrow{z_{ref}}} \quad j = \alpha, \beta \tag{6}$$

subject to $\Phi^\alpha + \Phi^\beta = 1$ where ϕ^j is the conventional mole fraction of phase j whose feasible domain is (0, 1) and $\overrightarrow{z_{ref}}$

is the column vector of R reference component mole fractions in the feed Z. At equilibrium, $\frac{\Delta \hat{g}}{R_g T}$ must be at the global minimum for a stable phase equilibrium. Then, the stationary condition of this equilibrium problem is

$$\frac{\Delta \hat{\mu}_i^\alpha}{R_g T} = \frac{\Delta \hat{\mu}_i^\beta}{R_g T} \quad i = 1,..., c - R \tag{7}$$

This equation can be expressed in terms of fugacity or activity coefficients as follows

$$\frac{\Delta \hat{\mu}_i}{R_g T} = \ln\left(\frac{x_i \hat{\varphi}_i \{X\}}{\varphi_i}\right) = \ln(x_i \gamma_i \{X\}) \quad i = 1,..., c - R \tag{8}$$

Using Equations (7) and (8), we can deduce the following relation for mole fractions at two phase equilibrium

$$x_i^\beta = x_i^\alpha \left(\frac{\hat{\varphi}_i^\alpha}{\hat{\varphi}_i^\beta}\right) = x_i^\alpha \left(\frac{\gamma_i^\alpha}{\gamma_i^\beta}\right) \quad i = 1,..., c - R \tag{9}$$

We define the transformed phase equilibrium constant as

$$\hat{K}_i = \frac{\hat{\varphi}_i^\alpha \{X^\alpha\}}{\hat{\varphi}_i^\beta \{X^\beta\}} = \frac{\gamma_i^\alpha \{X^\alpha\}}{\gamma_i^\beta \{X^\beta\}} \quad i = 1,..., c - R \tag{10}$$

Equation (1) is used to define x_i as function of X_i, then

$$x_i^j = X_i^j \left(1 - \nu_{TOT} N^{-1} \vec{x}_{ref}\right) + \nu_i N^{-1} \vec{x}_{ref}^j \quad i=1,..., c-R; \, j=\alpha,\beta \tag{11}$$

We write the phase equilibrium conditions in terms of transformed variables, using Equations (9) - (11), as follows

$$X_i^\beta = X_i^\alpha \hat{K}_i \theta + \delta_i \quad i = 1,..., c - R \tag{12}$$

and

$$\theta = \frac{1 - \nu_{TOT} N^{-1} \vec{x}_{ref}^\alpha}{1 - \nu_{TOT} N^{-1} \vec{x}_{ref}^\beta} \tag{13}$$

$$\delta_i = \frac{\nu_i N^{-1} \left(\hat{K}_i \vec{x}_{ref}^\alpha - \vec{x}_{ref}^\beta\right)}{1 - \nu_{TOT} N^{-1} \vec{x}_{ref}^\beta} \quad i = 1,..., c - R \tag{14}$$

Thus, Equations (12) – (14), subject to the transformed material balance and mole fraction restrictions, form our new equilibrium conditions for flash calculations in reacting systems. In the next section, we describe an approach to solve these conditions.

PROPOSED METHOD FOR REACTIVE FLASH CALCULATIONS

A) Solution method

We use a simultaneous equation solving method to find the phase equilibrium conditions in a reacting mixture. This approach is generally used for performing flash calculations in non-reactive systems since it is conceptually simple and straightforward. The popular Newton method is used because it provides quadratic convergence when the initial estimates are close to the solution and is readily available in several computer programs (Teh and Rangaiah, 2002). Two phase equilibrium conditions in reacting mixtures are calculated by simultaneously solving Equations (5) and (12) – (14). We have $2(c - R) - 1$ non-linear equations with the following unknowns: $c - R - 1$ transformed mole fractions of both phases at equilibrium and the transformed phase mole fraction Φ^α or $\Phi^\beta = 1 - \Phi^\alpha$. By numerical reasons, we consider convenient using ϕ^j instead of Φ^j as unknown because the feasible domain of that variable is always known: $\phi^j \in (0, 1)$.

Due to numerical performance of Newton method, suitable initial values are required to favor its convergence. The procedure used to initialize the reactive flash calculations is described in the following sentences.

B) Initialization strategy

A key factor to favor the convergence in the calculation of equilibrium compositions is the initialization procedure. As indicated above, it is convenient to use suitable initial values to improve the performance of numerical methods involved in flash calculations. Several researchers have proposed different approaches to estimate initial values for performing equilibrium calculations in reactive and non-reactive mixtures. The classical approach is based on the results of phase stability analysis (Michelsen, 1982; Wasylkiewicz and Ung, 2000; Iglesias-Silva et al. 2003). Following Iglesias-Silva et al. (2003), we have used one of the stationary points obtained from phase stability analysis, applying the Reactive Tangent Plane Distance Function RTPF (Wasylkiewicz and Ung, 2000), to start the flash calculations. Phase stability of a reactive mixture is evaluated by minimizing the next function

$$RTPDF = \sum_{i=1}^{c-R} X_i \left(\hat{\mu}_i \{X\} - \hat{\mu}_i \{Z\}\right) \tag{15}$$

where $\hat{\mu}_i \{Z\}$ is the transformed chemical potential of component i at the transformed feed composition. In the present study, the stationary point that globally minimizes the RTPDF function is used as initial value for one of the phase composition combined with reasonable estimations in the rest of the transformed compositions. This approach has been successfully applied in two phase equilibrium calculations in non-reactive mixtures and the results showed that it is a proper initialization strategy (Iglesias-Silva et al. 2003). The RTPDF function is globally minimized using the Simulated Annealing (SA) method. Bonilla-Petriciolet et al. (2006) has tested the SA method with several reactive systems and found that it is robust for reactive phase stability analysis. Specifically, we use the algorithm proposed by Corana et al. (1987). However, another global optimization method, deterministic or stochastic, can be used for this purpose.

On the other hand, the initial value for the transformed phase mole fraction is calculated using an analytical solution of the material balance which is given by

$$\Phi^\alpha = \frac{X_{c-R}^\beta - Z_{c-R}}{X_{c-R}^\beta - X_{c-R}^\alpha} \tag{16}$$

where X_{c-R}^α and X_{c-R}^β are the initial values proposed for the equilibrium compositions of component $c–R$, respectively. For this estimation, we consider that $X_1^\alpha < Z_1 < X_1^\beta$.

RESULTS AND DISCUSSION

To test the numerical performance of our method, five examples with different dimensionality and thermodynamic models are considered (see Table 1). These systems have been studied by other researchers in the context of reac-

and phase stability analysis (Ung and Doherty, 1995; Okasinski and Doherty, 1997; Okasinski and Doherty, 2000; Maier *et al*. 2000; Harding and Floudas, 2000; Bonilla-Petriciolet *et al*. 2006). We have assumed that all systems present two phases at equilibrium. It is important to note that we are not interested on evaluating the capability of thermodynamic models to represent the phase equilibrium behavior of systems under analysis. Considering this fact, all conditions used for our examples are only for demonstration purposes.

In our study, all examples are solved using different feed conditions (temperature, pressure, chemical equilibrium constants and feed compositions). We have defined a tolerance value of 1×10^{-06} for the convergence of proposed method where

$$\text{Tolerance} = \sqrt{\sum_{i=1}^{2(c-R)-1} F_i^2} \qquad (17)$$

being F_i the equations that form our equilibrium conditions. Our first example is a ternary system that follows an equilibrium decomposition reaction $2A \leftrightarrow B + C$ with liquid – vapor equilibrium. The system pressure is 4 atm and we have assumed a reaction equilibrium constant independent of temperature ($K_{eq} = 7.0$). Under these conditions, this system has a homogeneous reactive azeotrope: $X_1 = 0.035549$ and 357.913 K. Phase equilibrium compositions for different feed conditions are calculated and results are reported in Table 2. In this table, we report the mean number of $\hat{K}$-value evaluations. In general, our method shows a good performance in the flash calculations and requires few evaluations of $\hat{K}$-values to reach the equilibrium compositions for the specified tolerance.

The second example is a reacting ternary mixture $A_1 + A_2 \leftrightarrow A_3$ with liquid – liquid equilibrium. This system was introduced by Ung and Doherty (1995) in the developing of their approach of variable transformation. We have studied this

system at 323.15 Kelvin and using different values for the reaction equilibrium constant. Table 3 shows the results of flash calculations for different feeds. In this case, the $\hat{K}$-value evaluations ranged from 14 to 34 in all performed calculations.

Our third example is the reaction of isobutene, methanol and methyl ter-butyl ether. This system shows a vapor – liquid equilibrium at 8 atm. Again, we have considered a reaction equilibrium constant independent of temperature. Different temperatures and feed compositions are considered in flash calculations where the results are reported in Table 4. For all tested conditions, the new method requires less than 35 $\hat{K}$-value evaluations to find the equilibrium compositions.

In the fourth example, we use the same reaction as before but include n-butane as an inert. We have studied this system at 100 °C and 10 atm. However, in this case, the reaction equilibrium constant is dependent of temperature (see Table 1). Some tie-lines calculated for this mixture are reported in Figure 1 and details of flash calculations appear in Table 5. For this system, we report the slopes of tie-lines X'_{12}, which are calculated using

$$X'_{12} = \frac{X_2^\alpha - X_2^\beta}{X_1^\alpha - X_1^\beta} \qquad 18)$$

The $\hat{K}$-value evaluations ranged from 20 to 66 for all feeds considered in this reactive mixture.

Our final example is the quaternary mixture acetic acid + n-butanol ↔ water + n-butyl acetate. We have assumed a liquid – liquid equilibrium at 25 °C and UNIQUAC model is used to predict the thermodynamic properties. Phase equilibrium diagram of this system is shown in Figure 2 while the numerical performance of our method is reported in Table 6. With respect to $\hat{K}$-value evaluations, it ranged from 20 to 82 for all compositions.

Finally, phase stability analysis of calculated equilibrium compositions was performed using RTPDF and Simulated Annealing method. All reported compositions are stable.

TABLE I

Reactive systems, transformed variables, thermodynamic models and parameters used as examples in flash calculations.

System	Thermodynamic models	Transformed variables
$2\,A_1 \leftrightarrow A_2 + A_3$	Ideal solution and Antoine equation. $K_{eq} = 7.0$ Model parameters taken from Okasinski and Doherty (1997).	$X_1 = x_1 + 2x_3$ $X_2 = x_2 - x_3 = 1 - X_1$
$A_1 + A_2 \leftrightarrow A_3$	Margules solution model. Model parameters taken from Ung and Doherty (1995).	$X_1 = \dfrac{x_1 + x_3}{1 + x_3}$ $X_2 = \dfrac{x_2 + x_3}{1 + x_3} = 1 - X_1$
$A_1 + A_2 \leftrightarrow A_3$ (1) Isobutene, (2) Methanol and (3) Methyl ter-butyl ether	Wilson solution model and Antoine equation $K_{eq} = 0.04$ Model parameters taken from Maier *et al*. (2000).	$X_1 = \dfrac{x_1 + x_3}{1 + x_3}$ $X_2 = \dfrac{x_2 + x_3}{1 + x_3} = 1 - X_1$
$A_1 + A_2 \leftrightarrow A_3$ and A_4 as an inert (1) Isobutene, (2) Methanol, (3) Methyl ter-butyl ether and (4) n-Butane	Wilson solution model and Antoine equation. $\Delta G / R = 4205.05 + 10.0982T - 0.2667T \ln T$ where T [=] K Model parameters taken from Maier *et al*. (2000).	$X_1 = \dfrac{x_1 + x_3}{1 + x_3} \quad X_2 = \dfrac{x_2 + x_3}{1 + x_3}$ $X_4 = \dfrac{x_4}{1 + x_3} = 1 - X_1 - X_2$
$A_1 + A_2 \leftrightarrow A_3 + A_4$ (1) Acetic Acid, (2) n-Butanol, (3) Water and (4) n-Butyl acetate	UNIQUAC solution model. $\ln K_{eq} = \dfrac{450}{T} + 0.8$ where T [=] K Model parameters taken from Wasylkiewicz and Ung (2000).	$X_1 = x_1 + x_4 \quad X_2 = x_2 + x_4$ $X_3 = x_3 - x_4 = 1 - X_1 - X_2$

TABLE II

Numerical performance of proposed method in flash calculations for the reaction $2 A_1 \leftrightarrow A_2 + A_3$ at 4 atm and $K_{eq} = 7.0$ (Ideal solution and Antoine equation).

Feed conditions		Equilibrium compositions		
Z_1	T, ºC	X_1^α	X_1^β	Mean No. of $\hat{K}$-value evaluations
1.992	320	1.9896	1.9984	238
1.87	325	1.7488	1.9221	36
1.6	330	1.4823	1.7947	29
1.55	335	1.2229	1.6261	36
1.26	340	0.9753	1.4144	30
0.777	345	0.7377	1.1533	20
0.734	350	0.5045	0.8317	20
0.33	355	0.2589	0.4213	16
0.164	357	0.1391	0.2052	14

TABLE III

Numerical performance of proposed method in flash calculations for the reaction $A_1 + A_2 \leftrightarrow A_3$ at 323.15 K (Margules solution model).

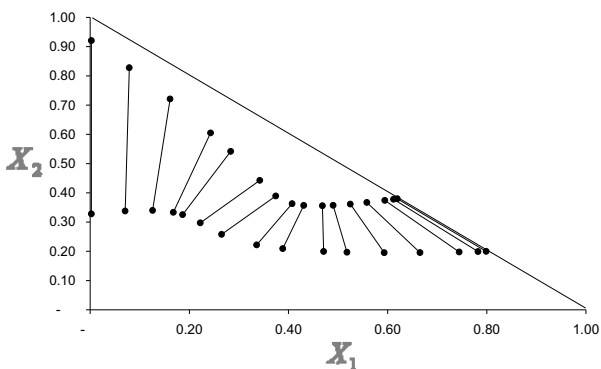| Feed conditions		Equilibrium compositions		
Z_1	K_{eq}	X_1^α	X_1^β	Mean No. of $\hat{K}$-value evaluations
0.6	3.5	0.4975	0.8401	18
0.7	3	0.4936	0.8069	17
0.5	2.5	0.4863	0.7400	14
0.55	4	0.5000	0.8606	22
0.776	5	0.5030	0.8851	16
0.6329	7.5	0.5065	0.9124	23
0.75	10	0.5080	0.9243	16

Figure 1. Phase diagram is transformed mole fractions for the reaction (1) Isobutene + (2) Methanol $\leftrightarrow$ (3) Methyl ter-butyl ether and (4) n-Butane as inert at 100ºC and 10 atm.

TABLE IV

Numerical performance of proposed method in flash calculations for the reaction Isobutene + Methanol $\leftrightarrow$ Methyl ter-butyl ether at 8 atm (Wilson solution model and Antoine equation).

Feed conditions		Equilibrium compositions		
Z_1	T, ºC	X_1^α	X_1^β	Mean No. of $\hat{K}$-value evaluations
0.903	61	0.8797	0.9260	23
0.7	65	0.3721	0.8956	18
0.5	70	0.2419	0.8665	19
0.7	80	0.1357	0.7967	18
0.2	90	0.0841	0.7042	17
0.4	100	0.0520	0.5819	18
0.2	110	0.0294	0.4226	17
0.08	120	0.0121	0.2177	17
0.03	125	0.0048	0.0952	14

TABLE V

Numerical performance of proposed method in flash calculations for the reaction Isobutene + Methanol $\leftrightarrow$ Methyl ter-butyl ether and n-Butane at 100ºC and 10 atm (Wilson solution model and Antoine equation).

Z	X'_{12}	Mean No. of $\hat{K}$-value evaluations
(0.278, 0.365, 0.357)	1.2106	26
(0.3, 0.3, 0.4)	1.2028	30
(0.35, 0.25, 0.4)	1.9706	28
(0.4, 0.25, 0.35)	3.4749	26
(0.47, 0.25, 0.28)	– 65.9879	31
(0.5, 0.3, 0.2)	– 5.7654	38
(0.55, 0.3, 0.15)	– 2.4315	38
(0.7, 0.25, 0.05)	– 1.1764	24
(0.699, 0.3, 0.001)	– 1.0034	26
(0.2, 0.45, 0.35)	3.6138	45
(0.15, 0.6, 0.25)	10.7573	22
(0.075, 0.6, 0.325)	58.4336	25
(0.22, 0.4, 0.38)	2.2320	26
(0.6, 0.3, 0.1)	– 1.5955	36

TABLE VI

Numerical performance of proposed method in flash calculations for the reaction Acetic Acid + n-Butanol ↔ Water + n-Butyl acetate at 25ºC (UNIQUAC solution model).

Z	X'_{12}	Mean No. of $\hat{K}$-value evaluations
(0.01, 0.4, 0.59)	46.0950	26
(0.05, 0.4, 0.55)	9.2152	31
(0.1, 0.2, 0.7)	2.6796	41
(0.15, 0.3, 0.55)	2.4648	37
(0.15, 0.5, 0.35)	3.7574	33
(0.2, 0.3, 0.5)	1.8920	34
(0.3, 0.3, 0.4)	1.3410	31
(0.3, 0.4, 0.3)	1.6227	28
(0.397, 0.294, 0.309)	1.0649	31
(0.394, 0.274, 0.332)	1.0323	31
(0.3, 0.15, 0.55)	0.9693	43

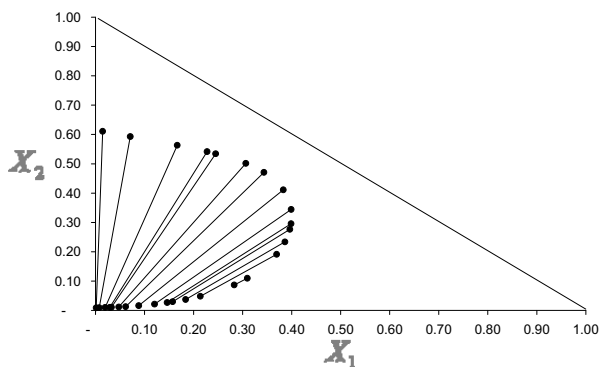**Figure 2.** Phase diagram in transformed mole fractions for the reaction (1) Acetic Acid + (2) n-Butanol ↔ (3) Water + (4) n-Butyl acetate at 25ºC.

CONCLUSIONS

In this study, we introduce an alternative method for performing flash calculations in multicomponent multireactive mixtures. This method is based on the transformed variables of Ung and Doherty (1995) which allow an easy numerical implementation of solution strategies and reduces the problem dimensionality. Our results show, using the proposed initialization strategy, that our method has an acceptable performance in flash calculations. However, due to the numerical nature of Newton method, if the starting values of the transformed compositions are far away from the solution, there may be a convergence problem in the numerical scheme in getting the phase equilibrium compositions. Considering this fact, in further studies, it is convenient to apply other solution strategies and develop more robust initialization schemes for flash calculations in multireactive systems. Also, we will extend the application of our method with other thermodynamic models such as equations of state.

NOTATION

c	number of components
K_{eq}	chemical equilibrium constant
$\hat{K}$	transformed phase equilibrium constant
P	Pressure given in atm
ref	reference component
R	reaction number
R_g	universal gas constant
T	Temperature given in ºC or K
v_i^γ	stoichiometric coefficient of component i
X	transformed mole fraction
X'_{12}	slope of tie-line
x	mole fraction
Z	transformed feed composition
z	feed mole composition

Greek letters

α,β	phase at equilibrium
μ	chemical potential
γ	activity coefficient
φ	fugacity coefficient
Φ	transformed phase mole fraction
ϕ	phase mole fraction

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