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Analysis and prediction of input multiplicity for the reactive flash separation using reaction-invariant composition variables

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ABSTRACT

In this study, we introduce a new approach for predicting and analyzing the input multiplicity in reactive flash separation processes. Specifically, we have identified necessary conditions to detect these multiple states in reactive flash separations using reaction-invariant composition variables. The presence of the input multiplicity is studied for the reactive systems of MTBE and TAME production to illustrate the capabilities of our methodology. For these reactive systems, we report the existence of multiple states for different operating conditions. In summary, our strategy can be applied with any reactive system and thermodynamic model, assuming that all reactions are reversible and in thermodynamic equilibrium and the operating conditions are away from the retrograde region. In general, our method is a robust procedure for the multiplicity analysis in flash separation of multi-reactive and multi-component systems.

Keywords: Reactive flash separation; Input multiplicity; Reaction-invariant composition variables

1. Introduction

Reactive separation schemes (e.g., reactive distillation, extraction and crystallization) are integrated unit operations widely used in the current chemical industry due to their well-known economical and operational advantages. Specifically, these separation systems may improve the process performance via the reduction of capital cost, the increment of selectivity and conversion, the decrement of heat demand, the suppression of side reactions and the avoidance of undesirable phase equilibrium conditions such as homogeneous azeotropy (Taylor and Krishna, 2000). However, the reliable modeling of reactive separation process is difficult due to the multicomponent nature of the reactive systems, the nonlinearity of the thermodynamic models caused by the interaction of simultaneous chemical and physical equilibrium, and also by the type of variables involved in defining the mathematical model, which are generally composition variables in molar units and extents of reaction. In particular, reactive separation processes exhibit a high non-linear behavior and, as a consequence, the multiplicity of solutions is often possible during the design and modeling of these separation schemes (Taylor and Krishna, 2000; Chen et al., 2002).

Multiplicity of solutions is an important feature of industrial processes and plays an important role in design, simulation and control of separation units (Monroy-Loperena, 2001). In process system engineering, it is important to predict all multiple states within the practical domain of operating variables, to know whether they are desirable, and to understand how the separation scheme responses to changes in the operating conditions (Tiscareño et al., 1998; Yang et al., 2006). According to the literature, reactive separation systems can exhibit two types of multiplicity: input and output multiplicity (Singh et al., 2005a; Malinen and Tanskanen, 2010). Input multiplicity occurs when two or more sets of input variables produce the same output conditions, while output multiplicity occurs when one set of input variables results in two or more independent sets of output variables (Singh et al., 2005a,b;

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Nomenclature

F	feed
V	vapor phase
L	liquid phase
c	number of components
r	number of independent chemical reactions
a_i	activity of component i
K_{eq}	reaction equilibrium constant
n_i	mole number of component i
N	invertible matrix of stoichiometric coefficients of reference components
P	pressure
T	temperature
v_i	stoichiometric coefficient of component i
x	mole fraction
X	transformed mole fraction
z	feed mole fraction
Z	transformed feed mole fraction
γ_i	activity coefficient of component i in the mixture
K_i	phase equilibrium constant of component i
$\hat{\phi}^V$	transformed amount fraction for vapor phase
ϕ^V	mole fraction of vapor phase
T_{bub}	bubble-point temperature
T_{dew}	dew-point temperature

Kumar and Kaistha, 2008; Malinen and Tanskanen, 2010); Fig. 1 illustrates these types of multiplicity. It is convenient to remark that the input variables of separation processes are those that can be manipulated by controllers. These variables include the reflux ratio, reboiler duty, and feed flow, among others. On the other hand, the output variables can be also controlled or used to describe the process conditions, e.g., the stage temperatures and compositions (Singh et al., 2005b). In particular, the input multiplicity (IM) is relevant and important because of it imposes significant control and operation problems than those obtained for output multiplicity (Vaca et al., 2006; Kumar and Kaistha, 2008).

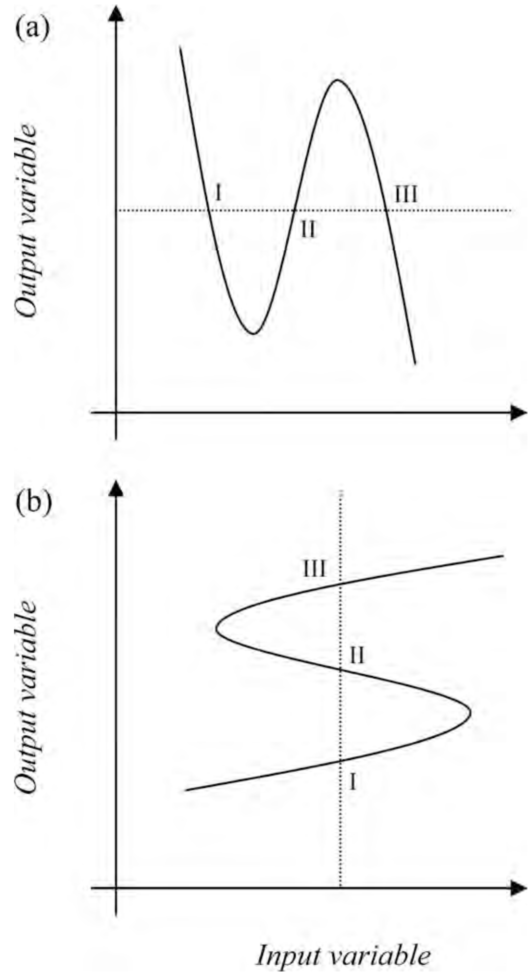


Fig. 1 – Types of multiplicity in reactive separation systems: (a) input multiplicity and (b) output multiplicity.

Theoretical and experimental studies have shown the existence of multiple states in reactive separation processes especially for reactive distillation columns (Hauan et al., 1997; Eldarsi and Douglas, 1998; Güttinger and Morari, 1999a,b; Taylor and Krishna, 2000; Chen et al., 2002; Baur et al., 2003; Singh et al., 2005a,b; Yang et al., 2006; Kumar and Kaistha, 2008; Svandová et al., 2009; Ramzan et al., 2010). Several authors have studied and analyzed the presence of multiplicity in reactive distillation columns using several operative variables and design parameters such as the system configuration, the selection of both thermodynamic and kinetic models, the reflux ratio, and the location of feed inlets, among others (Taylor and Krishna, 2000). Literature indicates that the existence and possible explanation of multiplicity in reactive distillation columns have been investigated by several authors for well-known reactive systems involved in the production of fuel ethers like MTBE and TAME (Mohl et al., 1999). Different numerical methods have been used to detect and predict the presence of multiple states in these separation systems where homotopy continuation approaches have been widely applied for predicting and analyzing the multiplicity via bifurcation diagrams (Güttinger and Morari, 1999a,b; Taylor and Krishna, 2000; Rodríguez et al., 2001, 2004; Chen et al., 2002; Malinen and Tanskanen, 2010). However, to the best of our knowledge, only few studies have been conducted on multiplicity in reactive flash separations (Rodríguez et al., 2001, 2004; Lakerveld et al., 2005; Ruiz et al., 2006). Note that the flash separation problem is one of the most important chemical engineering problems and is recurrent in the modeling and design of separation systems based on vapor–liquid phase equilibrium. Despite significant progress on design and modeling of reactive distillation columns have been achieved, more general results are needed concerning the presence of multiplicity in reactive flash operation. It is convenient to remark that the reliable determination and analysis of the existence of multiple states in reactive separation schemes is a challenging task and it is more complex than those involved for conventional non-reactive separation schemes because of the presence of chemical reactions increases the complexity and dimensionality of flash problems. Therefore, proper and reliable numerical strategies are required for modeling reactive systems and predicting the presence of multiple solutions in reactive separation processes.

Therefore, in this study we introduce a new approach to predict the existence of input multiplicity in reactive flash separations. This approach is based on the application of reaction-invariant composition variables of Ung and Doherty (1995a,b). Note that these variables allow that the classical procedures for analyzing and modeling non-reactive mixtures can be extended to systems with chemical reactions. The presence of the input multiplicity is studied for the

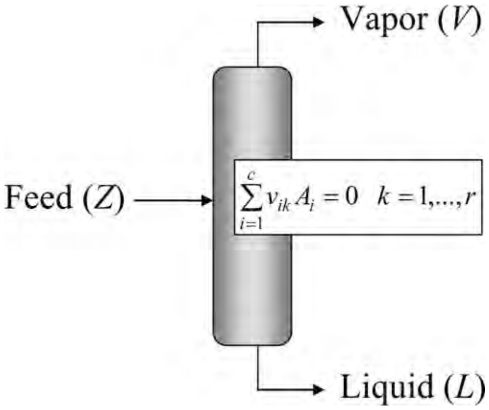


Fig. 2 – Schematic diagram of a reactive flash separation.

reactive systems of MTBE and TAME production to illustrate the capabilities of our methodology. For these reactive systems, we report the existence of multiple states for different operating conditions using our approach. Finally, we show that necessary K-based conditions for the existence of multiple solutions in non-reactive flash operation, previously reported by Tiscareño et al. (1998) and Monroy-Loperena (2001), can be useful for multiplicity analysis of reactive flash separation in tested reactive systems.

2. Problem formulation of input multiplicity in reactive flash separation

2.1. Model description

In general, a flash problem consists of finding the correct number and types of phases and their corresponding equilibrium compositions such that the Gibbs free energy of the system is at the global minimum. The chemical equilibrium constraints must be considered to determine the phase distribution and compositions of reactive systems. In this study, we will analyze the case of two-phase flash separation with a reactive vapor–liquid equilibrium.

Given a temperature T and pressure P, consider a reactive flash separation process for a system of c components with an initial composition $n_0 = (n_{1,0},\ldots,n_{c,0})$ that undergoes r independent chemical reactions (see Fig. 2). Using this formulation for the PT flash problem, we can discard the energy balance from the analysis and this thermodynamic problem is posed as a Gibbs free energy minimization problem. Under these conditions, the problem for modeling the reactive vapor–liquid equilibrium is to solve the system of non-linear equations obtained from the stationary conditions of the Gibbs free energy minimization problem, which involves the material balance, phase and chemical equilibrium, and consistency equations. Usually, this problem is formulated using conventional composition variables (i.e., mole numbers) as independent variables and unknowns (Lakerveld et al., 2005; Ruiz et al., 2006). However, as indicated by Ung and Doherty (1995a,b), the numbers of moles are not proper variables to use in the modeling of reactive systems because they do not have the same dimensionality as the number of degrees of freedom (i.e., they are inconsistent with respect to the Gibbs phase rule).

To obtain a convenient description of reactive vapor–liquid equilibrium problem and to simplify the analysis of multiplicity in flash systems subject to chemical reactions, we have applied the reaction-invariant composition variables proposed by Ung and Doherty (1995a,b). These variables are based on transformation of the physical compositions and its principal benefit is that the chemical and physical equilibrium approach in the reactive mixture is identical to a strictly physical equilibrium model. The dimension of reaction-invariant composition space is equal to the number of degrees of freedom obtained from the Gibbs phase rule. Thus, these variables depend only on the initial composition of each independent chemical species, restrict the solution space to the compositions that satisfy stoichiometry requirements and also reduce the dimension of the composition space by the number of independent reactions (Ung and Doherty, 1995a,b). These features allow all of the procedures used to model non-reactive mixtures to be easily extended to systems subject to chemical equilibrium and, consequently, non-reactive algorithms can be modified to account for chemical reactions. Note that several approaches for modeling and designing reactive separation processes have been developed using these reaction-invariant composition variables and they include phase equilibrium calculations, phase stability analysis, azeotropy prediction, calculation of residues curves, among other calculations (e.g., Güttinger and Morari, 1999a,b; Bonilla-Petriciolet et al., 2006a,b, 2008a,b; Carrera-Rodriguez et al., 2011a,b).

For a reactive system of c components and r chemical reactions, transformed mole variables X are defined as

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

where x_i is the mole fraction of component i, x_{ref} is a column vector of mole fractions for r reference components, v_i is the row vector of stoichiometric coefficients of component i for each of the r reactions, N is an invertible and square matrix formed from the stoichiometric coefficients of the reference components in the r reactions, and v_{TOT} is a row vector where each element corresponds to the sum of stoichiometric coefficients for all components that participate in each of the r reactions, respectively. These transformed mole fractions (X) in reactive systems are similar to the mole fractions (x) in non-reactive mixtures, and the sum of all transformed mole fractions is equal to unity (i.e., $\sum_{i=1}^{c-r} X_i = 1$), but a transformed mole fraction can be negative or positive depending on the reference components, number and type of reactions. Therefore, for a reactive mixture, minimizing Gibbs free energy with respect to conventional compositions variables (i.e., mole numbers or fractions) is equivalent to minimizing the Gibbs free energy formulated with respect to the reaction-invariant composition variables (Ung and Doherty, 1995a,b). It is important to remark that X has the desirable property of taking the same numerical values before and after the reactions. This is in contrast to conventional mole variables (x and n), which have different values for the components in the unmixed and mixed (i.e., reacting) states (Ung and Doherty, 1995a,b).

Note that the transformed variables X are related to x via the reaction equilibrium constants $K_{eq,k}$:

$$K_{eq,k} = \prod_{i=1}^{c} a_i^{v_{ik}} \quad k = 1, \ldots, r \tag{2}$$

where v_{ik} is the stoichiometric coefficient of component i in reaction k, and a_i is the activity of component i. To evaluate thermodynamic properties in reactive systems using this approach, mole fractions are obtained from the transformation procedure $X \rightarrow x$ using Eqs. (1) and (2). This stage requires solution of one or more nonlinear equations depending on the number of chemical reactions. In particular, any solver such as the bisection method (for systems with only one reaction) or the Newton method (for multi-reaction systems) can be used for this variable transformation. The resulting mole fraction values (x) satisfy the stoichiometry requirements and are chemically equilibrated. It is important to remark that multiple solutions are not possible for x_{ref} during variable transformation $X \rightarrow x$ because only one solution set of x simultaneously satisfies the chemical equilibrium equations and corresponds to the specified values of the transformed composition variables (Ung and Doherty, 1995a). Therefore, the presence of multiple states in the modeling of reactive flash separation is not caused by the use of these variables.

The reactive vapor–liquid equilibrium problem for a multicomponent and multireactive system can be defined as (Bonilla-Petriciolet et al., 2006a,2008a):

$$X_i^L = \frac{(Z_i - \delta_i \hat{\phi}^V)}{(\hat{\phi}^V(K_i\theta - 1) + 1)} \quad i = 1, \ldots, c - r \tag{3}$$

$$X_i^V = X_i^L K_i\theta + \delta_i = \frac{(Z_i K_i \theta + \delta_i(1 - \hat{\phi}^V))}{(\hat{\phi}^V(K_i\theta - 1) + 1)} \quad i = 1, \ldots, c - r \tag{4}$$

where

$$\begin{aligned} \theta &= \frac{(1 - \upsilon_{TOT} N^{-1} x_{ref}^L)}{(1 - \upsilon_{TOT} N^{-1} x_{ref}^V)} \\ \delta_i &= \frac{(\upsilon_i N^{-1}(K_i x_{ref}^L - x_{ref}^V))}{(1 - \upsilon_{TOT} N^{-1} x_{ref}^V)} \end{aligned} \tag{5}$$

subject to the material balance given also in transformed composition space

$$Z_i - (1 - \hat{\phi}^V) X_i^L - X_i^V \hat{\phi}^V = 0 \quad i = 1, \ldots, c - r \tag{6}$$

$$\hat{\phi}^V = \frac{\phi^V (1 - \upsilon_{TOT} N^{-1} x_{ref}^V)}{(1 - \upsilon_{TOT} N^{-1} z_{ref})} \tag{7}$$

and equality constraints

$$\begin{aligned} &\sum_{i=1}^{c-r} X_i^L = 1 \\ &\sum_{i=1}^{c-r} X_i^V = 1 \\ &\hat{\phi}^V + \hat{\phi}^L = 1 \end{aligned} \tag{8}$$

where X_i^L and X_i^V are the transformed mole fraction of component i at liquid and vapor phase at equilibrium, Z_i is the global transformed composition of component i in the feed, K_i is the phase equilibrium constant of component i, $\hat{\phi}^V$ is the transformed amount fraction for vapor phase while ϕ^V is the conventional mole fraction of vapor phase whose feasible domain is (0, 1). Note that the feasible domain of $\hat{\phi}^V$ is not the same as that given for ϕ^V due to stoichiometric constraints of the reactive system, see Eq. (7). However, this fact is not a limitation to robustly solve the reactive phase equilibrium problem.

The implicit function to evaluate the transformed amount fraction for vapor phase is based on an alternative Rachford–Rice formulation using X (Bonilla-Petriciolet et al., 2006a,2008a). Thus, for the reactive flash problem we have to solve the following non-linear equation

$$f(\hat{\phi}^V) = \sum_{i=1}^{c-r} \left[\frac{(Z_i(K_i\theta - 1) + \delta_i)}{(\hat{\phi}^V(K_i\theta - 1) + 1)} \right] = 0 \tag{9}$$

Eq. (9) is employed to evaluate $\hat{\phi}^V$ (i.e., ϕ^V) and determine the vapor–liquid equilibrium compositions subject to chemical equilibrium. Herein, we restrict our analysis of reactive flash equations on the appearance of multiple solutions in the region of physical significance for flash separations, i.e. phase equilibrium calculations are bounded between reactive bubble and dew point conditions where $\phi^V \in (0, 1)$. Therefore, bubble and dew point calculations are performed using the next functions (Bonilla-Petriciolet et al., 2006a,2008a):

$$f_{bubble} = 1 - \sum_{i=1}^{c-r} (K_i\theta\, Z_i + \delta_i) = 0 \tag{10}$$

$$f_{dew} = 1 - \sum_{i=1}^{c-r} \left[\frac{Z_i - \delta_i}{K_i\theta} \right] = 0 \tag{11}$$

Note that the phase equilibrium constant K_i are calculated from

$$K_i\{X^L, X^V\} = \frac{\hat{\varphi}_i^L}{\hat{\varphi}_i^V} = \frac{\gamma_i^L}{\gamma_i^V} \quad i = 1, \ldots, c - r \tag{12}$$

where $\hat{\varphi}_i$ is the fugacity coefficient of component i in the mixture and γ_i is the activity coefficient of component i, respectively. These thermodynamic properties are determined using a proper model (e.g., equation of state or local composition model) and employing the results of the transformation procedure $X \rightarrow x$ (i.e., we use mole fractions that satisfy the chemical equilibrium to evaluate the system thermodynamic properties). Note that the general steps involved in the variable transformation between X and x are independent of both the type of reactive system and the model used in the calculation of thermodynamic properties for the different phases (e.g., equations of state or local composition models). In particular, the thermodynamic model only affects the approach used for calculating the fugacity or activity coefficients, which are involved in the evaluation of Eqs. (2) and (12); while the characteristics of the reactive system (i.e., the number of components and reactions) determine the dimensionality of the non-linear equation system to be solved during the transformation of composition variables. Therefore, in this study no restrictions are made with regard to these parameters. On the other hand, different numerical strategies can be used for performing flash calculations in reactive systems with reaction-invariant composition variables and they include, for example, simultaneous equation-solving methods, equation decoupling approaches and global optimization techniques (Bonilla-Petriciolet et al., 2006a,b, 2008a,b). In this study, proper numerical methods have been applied for reliably modeling the phase behavior of reactive systems used as cases of study and these calculations do not require a significant numerical effort and computer time.

2.2. *Input multiplicity analysis*

Using transformed variables, the reactive flash problem has $c-r+2$ degrees of freedom. For the analysis of input multiplicity, they are fixed by specifying $c-r$ transformed mole fractions Z_i of the feed, the pressure P of the reactive flash separation process and a product composition (X_i^L or X_i^V). In this study, we assume that the operating conditions of a nonazeotropic mixture are chosen below the critical state to avoid retrograde effects. If under these conditions the system shows multiple solutions (i.e., input multiplicity), more than one solution may exist for the reactive flash problem. It is important to note that our analysis also rests on the fact that the solution (i.e., phase equilibrium compositions) obtained for reactive flash separation problem is globally stable with respect to the formation of additional phases (Michelsen, 1982).

In particular, Tiscareño et al. (1998) and Monroy-Loperena (2001) have suggested that if input multiplicities exist in nonreactive mixtures, the corresponding flash equation for liquid or vapor mole fraction of component i must be a concave or convex function with respect to temperature or vapor phase fraction. Intuitively, we can expect the same performance for Eq. (3) or (4) in reactive systems using X. Therefore, analyzing the reactive flash problem of a nonazeotropic mixture in the temperature domain between the bubble-point temperature T_{bub} and the dew-point temperature T_{dew}, which implies a real vapor–liquid equilibrium solution, and assuming that a maximum or a minimum exists for $X_i^j - T$, the condition for a stationary point is given by

$$\frac{dX_i^j}{dT} = 0 \tag{13}$$

or, equivalently, for $X_i^j - \hat{\phi}^V$ we have

$$\frac{dX_i^j}{d\hat{\phi}^V} = 0 \tag{14}$$

where j is the liquid (L) or vapor phase (V), respectively. Note that the input multiplicity analysis can be performed in the vapor fraction domain or in the temperature domain because there is only one stable solution in flash calculations performed at operating conditions below the critical state of the mixture (Lucia, 1986; Monroy-Loperena, 2001).

However, based on the fact that the transformed composition variables are used only to simplify and facilitate the modeling of thermodynamic behavior of multicomponent and multireactive systems, the multiplicity analysis must be performed in the domain of mole fraction composition, which is the real operation variable. As stated, transformed composition variables (X) depend on both the molar composition (x) of the reactive system and T at the equilibrium conditions, if P is given. Therefore, we can state the mathematical functionality: $X=f(x)$ and $x=f(T)$ or $x = f(\hat{\phi}^V)$. Then, for reactive phase equilibrium, Eqs. (13) and (14) are the composition of two functions and can be written using Leibniz notation as follows

$$\frac{dX_i^j}{dT} = \frac{dX_i^j}{dx_k^j} \cdot \frac{dx_k^j}{dT} \quad i = 1, \ldots, c-r; \quad j = L, V; \quad k = 1, \ldots, c \tag{15}$$

or using the vapor phase fraction:

$$\frac{dX_i^j}{d\hat{\phi}^V} = \frac{dX_i^j}{dx_k^j} \cdot \frac{dx_k^j}{d\hat{\phi}^V} \quad i = 1, \ldots, c-r; \quad j = L, V; \quad k = 1, \ldots, c \tag{16}$$

where x_k^j is the mole fraction of component k in phase j at the equilibrium condition.

Rearranging these functions, we can define the stationary conditions for identifying input multiplicity in reactive flash separation using reaction-invariant composition variables

$$\frac{dx_k^j}{d\eta} = \frac{dX_i^j}{d\eta} \cdot \frac{dx_k^j}{dX_i^j} = 0 \tag{17}$$

where $\eta = T$ or $\hat{\phi}^V$ depending on the variable to be analyzed. Note that if Eq. (17) is to be satisfied, then we can have the following scenarios for finding a stationary point (i.e., a maximum or a minimum exists for $x_k^j - \eta$):

$$\text{Condition I}: \quad \frac{dx_k^j}{d\eta} = 0 \quad \text{if} \quad \frac{dX_i^j}{d\eta} = 0 \quad \text{and} \quad \frac{dx_k^j}{dX_i^j} \neq 0$$

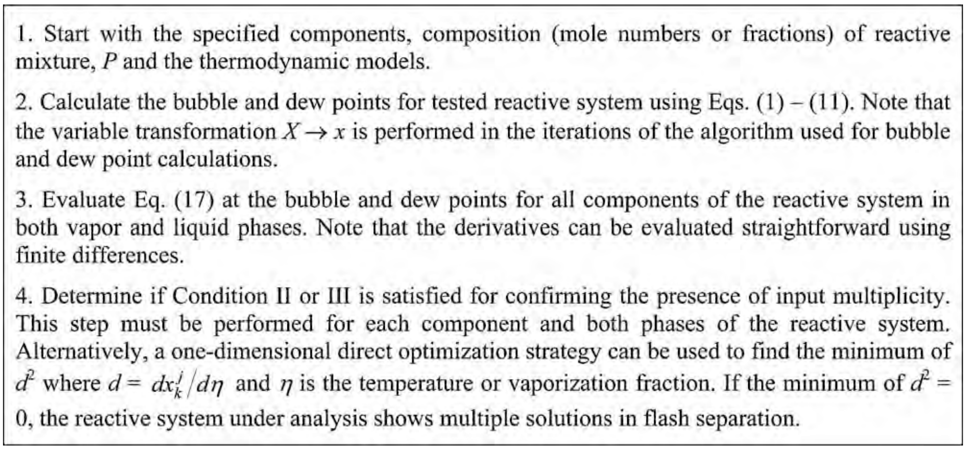
$$\text{Condition II}: \quad \frac{dx_k^j}{d\eta} = 0 \quad \text{if} \quad \frac{dX_i^j}{d\eta} \neq 0 \quad \text{and} \quad \frac{dx_k^j}{dX_i^j} = 0$$

$$\text{Condition III}: \quad \frac{dx_k^j}{d\eta} = 0 \quad \text{if} \quad \frac{dX_i^j}{d\eta} = 0 \quad \text{and} \quad \frac{dx_k^j}{dX_i^j} = 0$$

These conditions indicate that the derivative of X_i^j with respect to η equals zero or the derivative of x_k^j with respect to X_i^j equals zero, in an independent way or simultaneously. If the stationary point of Eq. (17) is bounded by $T \in [T_{bub}, T_{dew}]$ and $\phi^V \in [0,1]$, away from the retrograde region, we can confirm the presence of input multiplicities for the mole fraction of component i in phase j in a reactive flash separation. In particular, in the following section we provide numerical evidence to validate and support that Conditions II and III derived from Eq. (17) are necessary and sufficient conditions for detecting multiple solutions in reactive flash separations.

In summary, Eq. (17) is useful to predict the presence of multiple solutions in reactive flash separation and to easily recognize what component or set of components exhibits the multiplicity at the specified operating conditions. It is important to recall that the application of reaction-invariant composition variables allows the easy implementation of numerical strategies for modeling thermodynamic properties of reactive systems and they are used in this study to develop alternative conditions for predicting input multiplicity in the reactive flash separation problem. To explore the presence of input multiplicity in all the system, Eq. (17) must be tested for all components x_k^j for $k=1, \ldots, c$ in both vapor and liquid phases. However, this procedure is not time consuming because this criterion can be effectively tested at both the bubble and dew points where a change of sign in the derivatives will indicate the presence of a stationary point. Recall that these derivatives can be evaluated explicitly by considering

$$\left.\frac{dX_i^j}{dT}\right|_{T=T_{sat}} = \left.\frac{dX_i^j}{dx_k^j}\right|_{x=f(T_{sat})} \cdot \left.\frac{dx_k^j}{dT}\right|_{T=T_{sat}} \tag{18}$$



1. Start with the specified components, composition (mole numbers or fractions) of reactive mixture, P and the thermodynamic models.

2. Calculate the bubble and dew points for tested reactive system using Eqs. (1) – (11). Note that the variable transformation $X \rightarrow x$ is performed in the iterations of the algorithm used for bubble and dew point calculations.

3. Evaluate Eq. (17) at the bubble and dew points for all components of the reactive system in both vapor and liquid phases. Note that the derivatives can be evaluated straightforward using finite differences.

4. Determine if Condition II or III is satisfied for confirming the presence of input multiplicity. This step must be performed for each component and both phases of the reactive system. Alternatively, a one-dimensional direct optimization strategy can be used to find the minimum of d^2 where $d = dx_k^j / d\eta$ and η is the temperature or vaporization fraction. If the minimum of d^2 = 0, the reactive system under analysis shows multiple solutions in flash separation.

Fig. 3 – Flowchart of the proposed method for predicting input multiplicity in reactive flash separation.

where T_{sat} is the bubble-point temperature T_{bub} or the dew-point temperature T_{dew}. So, if the derivate $dx_k^j/d\eta|_T$ presents a change of signs at bubble and dew points, we can conclude the existence of multiple solutions for the reactive flash problem. This condition is equivalent to that reported by Tiscareño et al. (1998) and Monroy-Loperena (2001) for the non-reactive flash problem. It is convenient to remark that in the general case without any simplification of the model used for calculation of the thermodynamic properties; these derivatives are evaluated straightforward using finite differences. Alternatively, a one-dimensional direct optimization strategy can be used to find the minimum (i.e., stationary point for multiplicity analysis) of d^2 where d is given by $dx_k^j/d\eta$. If the minimum of $d^2 = 0$, we conclude that the reactive system shows multiple solutions in flash separation for the component and phase under analysis. Note that this optimization approach has also been used for input multiplicity analysis in non-reactive systems (Monroy-Loperena, 2001). Our numerical experience indicates that an optimization approach is more effective than root-finding methods for the location of the stationary point of these derivatives. In general, our approach is straightforward, easy to be implemented and does not require complex numerical calculations. With illustrative purposes, Fig. 3 shows the steps of our method for predicting input multiplicity. In the following section, we illustrate the application of this approach for predicting input multiple states in reactive flash separation problems using well-known reactive systems.

3. Results and discussion

We use two reactive systems as cases of study to illustrate the application of our approach for predicting input multiplicity in reactive flash separation. These systems are well-known in the literature for the production of fuel ethers (Mohl et al., 1999) and include the synthesis of methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME). Details of reactive systems are reported in Table 1 and all model parameters are reported by Maier et al. (2000), Bonilla-Petriciolet et al. (2008a,b) and Carrera-Rodriguez et al. (2011a,b). We assume that all reactions are reversible and in thermodynamic equilibrium. Phase equilibrium calculations, including the determination of bubble and dew points, have been performed according to the numerical strategies reported by Bonilla-Petriciolet et al. (2006a,b) and Bonilla-Petriciolet et al. (2008a,b). Phase stability of all reactive phase equilibrium calculations, including bubble and dew points, has been

Table 1 – Examples selected for input multiplicity analysis in a reactive flash separation.

No.	System	Thermodynamic models
1	$A_1 + A_2 \leftrightarrow A_3$, and A_4 as an inert component (1) Isobutene (2) Methanol (3) Methyl-*tert*-butyl ether (4) n-Butane	Wilson model and ideal gas: $\Delta G^o_{rxs}/R =$ $-4205.05 + 10.0982T \quad - 0.2667T \ln T$ $lnK_{eq,1} = \frac{-\Delta G^0_{rxs}}{RT}$ where T is in K
2	$A_1 + A_2 + 2A_3 \leftrightarrow 2A_4$ (1) 2-Methyl-1-butene (2) 2-Methyl-2-butene (3) Methanol (4) *Tert*-amyl methyl ether	Wilson model and ideal gas: $K_{eq,1} = 1.057 \cdot 10^{-04} e^{4273.5/T}$ where T is in K
3	$A_1 + A_2 + 2A_3 \leftrightarrow 2A_4$ with A_5 as inert component (1) 2-Methyl-1-butene (2) 2-Methyl-2-butene (3) Methanol (4) *Tert*-amyl methyl ether (5) n-pentane	Wilson model and ideal gas: $K_{eq,1} = 1.057 \cdot 10^{-04} e^{4273.5/T}$ where T is in K

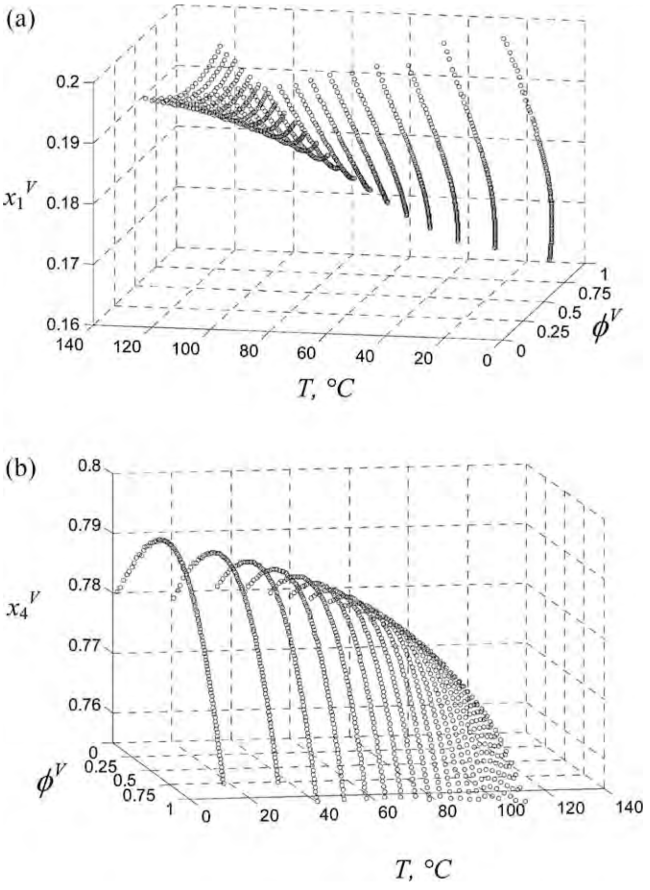


Fig. 4 – Vapor phase composition behavior of (a) isobutene and (b) butane as a function of temperature and vaporization fraction for MTBE production.

performed by minimizing the tangent plane distance function for reactive mixtures (Bonilla-Petriciolet et al., 2006a,b). In this study, all calculated reactive phase equilibrium compositions are stable. In summary, the conditions used in this study meet the requirement for a unique stable solution for the reactive phase equilibrium calculations. Finally, in this study bisection method is used to reliably perform the composition transformation $X \rightarrow x$ during reactive flash calculations.

3.1. *Reactive system for MTBE synthesis*

We have analyzed the presence of input multiplicity in the reactive system involved in the synthesis of MTBE (x_3) from Isobutene (x_1), Methanol (x_2) and with n-butane (x_4) as inert:

$$\text{Isobutene}\,(x_1) + \text{Methanol}\,(x_2) \Leftrightarrow \text{MTBE}\,(x_3) \tag{19}$$

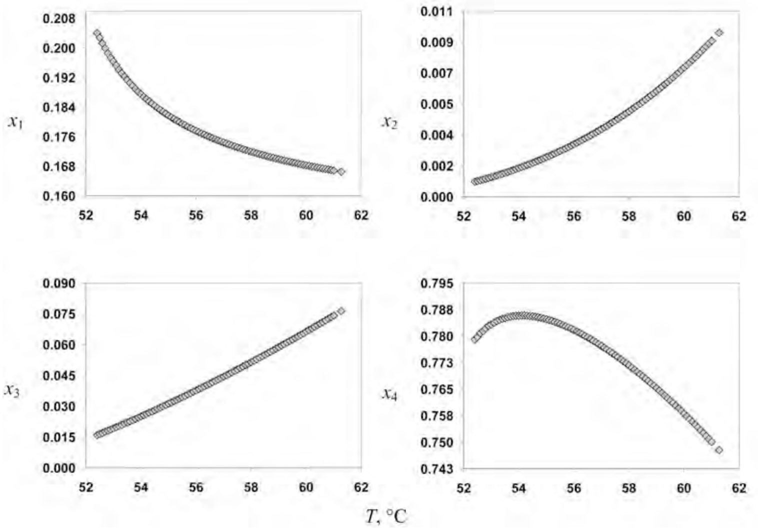
Wilson and Antoine models were used for the calculation of thermodynamic properties employing the parameters reported by Maier et al. (2000). This reactive system is a benchmark problem used in reactive process design and has been studied extensively by Ung and Doherty (1995a), Bonilla-Petriciolet et al. (2006a,b), Ruiz et al. (2006), and Carrera-Rodriguez et al. (2011a,b), among other authors. In particular, Ruiz et al. (2006) showed the presence of Hopf bifurcations and multiple solutions in the isothermal reactive flash processes involving MTBE mixture. In our study, MTBE is selected as the reference component (x_3) and transformed mole fractions for this mixture are given by

$$X_1 = \frac{x_1 + x_3}{1 + x_3} \tag{20}$$

$$X_2 = \frac{x_2 + x_3}{1 + x_3} \tag{21}$$

$$X_4 = \frac{x_4}{1 + x_3} = 1 - X_1 - X_2 \tag{22}$$

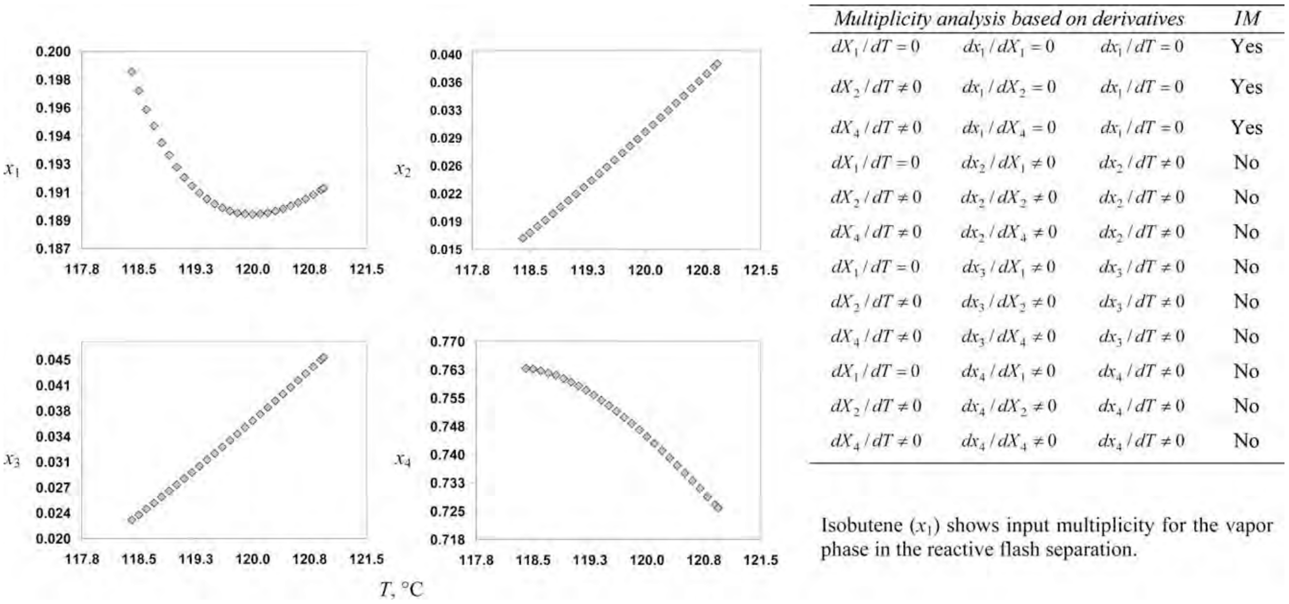
Multiplicity analysis has been performed for a feed composition $n_0 = (0.163, 0.005, 0.081, 0.751)$, or in transformed variables $Z = (0.2257, 0.0796, 0.6947)$, using different conditions of pressure (P). Note that Ruiz et al. (2006) have analyzed the same feed for obtaining the Hopf bifurcation diagrams. The multiple solutions of reactive flash problem are found by solving Eqs. (3)–(9) for this feed composition and different operating conditions (i.e., T and P). Fig. 4 shows the results of reactive flash calculations for x_1^V and x_4^V with respect to the vaporization fraction and the temperature at different pressures from 1 to 20 atm. Phase equilibrium behavior of isobutene (x_1) and butane (x_4) indicates the presence of multiplicity in the vapor phase at some operating conditions and, as a consequence, Eq. (17) is satisfied for these components where this derivative has changes of sign when $T = T_{bub}$ and



Multiplicity analysis based on derivatives			*IM*
$dX_1/dT = 0$	$dx_1/dX_1 \neq 0$	$dx_1/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_1/dX_2 \neq 0$	$dx_1/dT \neq 0$	No
$dX_4/dT = 0$	$dx_1/dX_4 \neq 0$	$dx_1/dT \neq 0$	No
$dX_1/dT = 0$	$dx_2/dX_1 \neq 0$	$dx_2/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_2/dX_2 \neq 0$	$dx_2/dT \neq 0$	No
$dX_4/dT = 0$	$dx_2/dX_4 \neq 0$	$dx_2/dT \neq 0$	No
$dX_1/dT = 0$	$dx_3/dX_1 \neq 0$	$dx_3/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_3/dX_2 \neq 0$	$dx_3/dT \neq 0$	No
$dX_4/dT = 0$	$dx_3/dX_4 \neq 0$	$dx_3/dT \neq 0$	No
$dX_1/dT = 0$	$dx_4/dX_1 = 0$	$dx_4/dT = 0$	Yes
$dX_2/dT \neq 0$	$dx_4/dX_2 = 0$	$dx_4/dT = 0$	Yes
$dX_4/dT = 0$	$dx_4/dX_4 = 0$	$dx_4/dT = 0$	Yes

MTBE (x_4) shows input multiplicity for the vapor phase in the reactive flash separation.

Fig. 5 – Input multiplicity (IM) analysis of the vapor phase for the MTBE production in a flash separation at 5 atm.



Multiplicity analysis based on derivatives			IM
$dX_1/dT=0$	$dx_1/dX_1=0$	$dx_1/dT=0$	Yes
$dX_2/dT\neq0$	$dx_1/dX_2=0$	$dx_1/dT=0$	Yes
$dX_4/dT\neq0$	$dx_1/dX_4=0$	$dx_1/dT=0$	Yes
$dX_1/dT=0$	$dx_2/dX_1\neq0$	$dx_2/dT\neq0$	No
$dX_2/dT\neq0$	$dx_2/dX_2\neq0$	$dx_2/dT\neq0$	No
$dX_4/dT\neq0$	$dx_2/dX_4\neq0$	$dx_2/dT\neq0$	No
$dX_1/dT=0$	$dx_3/dX_1\neq0$	$dx_3/dT\neq0$	No
$dX_2/dT\neq0$	$dx_3/dX_2\neq0$	$dx_3/dT\neq0$	No
$dX_4/dT\neq0$	$dx_3/dX_4\neq0$	$dx_3/dT\neq0$	No
$dX_1/dT=0$	$dx_4/dX_1\neq0$	$dx_4/dT\neq0$	No
$dX_2/dT\neq0$	$dx_4/dX_2\neq0$	$dx_4/dT\neq0$	No
$dX_4/dT\neq0$	$dx_4/dX_4\neq0$	$dx_4/dT\neq0$	No

Isobutene (x_1) shows input multiplicity for the vapor phase in the reactive flash separation.

Fig. 6 – Input multiplicity (IM) analysis of the vapor phase for the MTBE production in a flash separation at 20 atm.

$T=T_{dew}$. Note that we can easily establish that both components have multiple solutions in the vapor phase but at different conditions of P (see Fig. 4). As example, Figs. 5 and 6 show the multiplicity analysis for the vapor phase at 5 and 20 atm. In particular, these figures show the dependence of x_k with T and the evaluation of the derivatives dX_i/dT, dx_k/dX_i and dx_k/dT for all components of this reactive mixture. It is observed that the reactive flash problem shows multiple solutions for the vapor mole fraction of n-butane at 5 atm, while isobutene shows multiplicity at 20 atm. As stated, the mole fractions of these components are concave or convex functions with respect to T when multiple solutions are present for reactive flash separation. It is interesting to note that Eq. (17) is satisfied if only if: $dX_i/dT\neq0$ and $dx_k/dX_i=0$ or $dX_i/dT=0$ and $dX_i/dx_k=0$ (i.e., Conditions II and III given below). Similar results have been obtained for the remaining operating conditions where input multiplicity occurs. In fact, if $dX_i/dT=0$ and $dX_i/dx_k\neq0$, this condition indicates that x_k does not have multiplicity of solutions in tested phase. These results are illustrated in Figs. 7 and 8 for this reactive system at

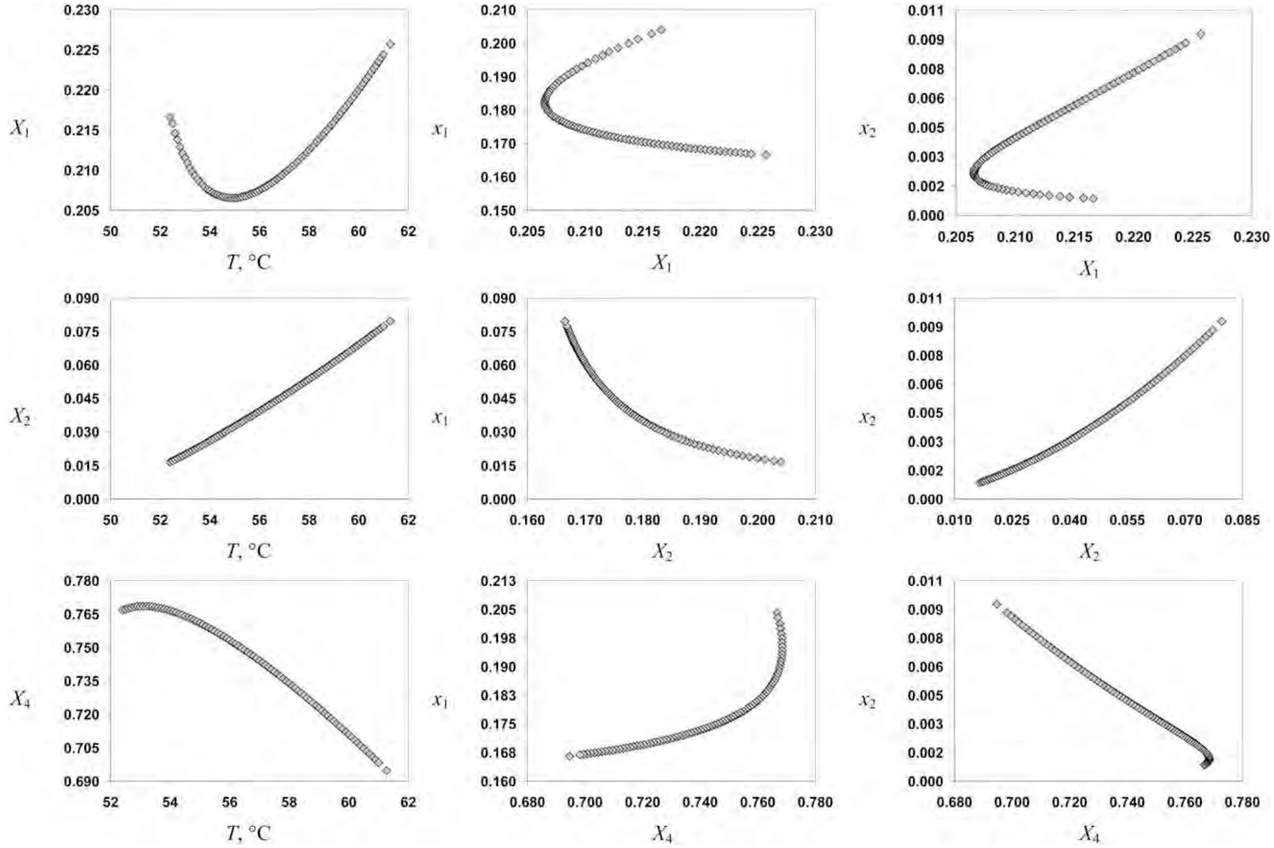


Fig. 7 – X_i versus T and x_k versus X_i for the vapor phase of MTBE production in a reactive flash separation at 5 atm.

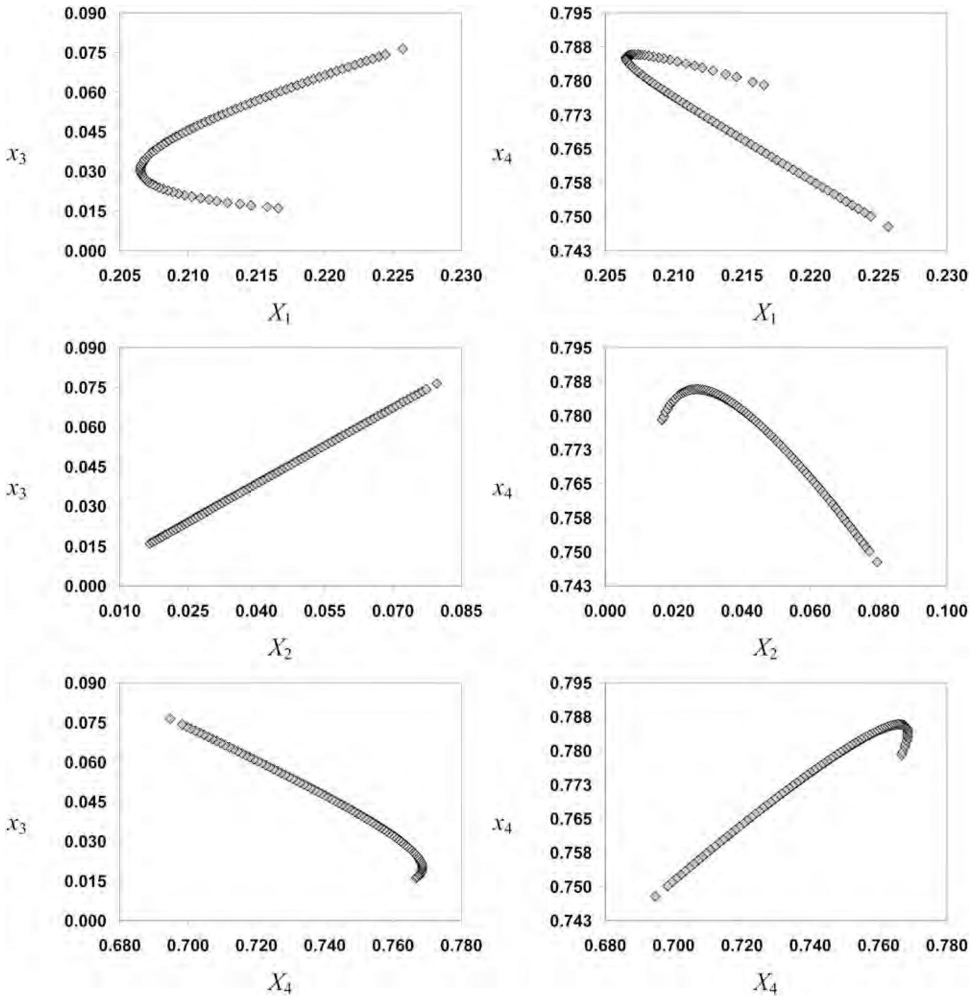


Fig. 8 – x_k versus X_i for the vapor phase of MTBE production in a reactive flash separation at 5 atm.

5 atm, where the dependence of X_i with T and the dependence of x_k with X_i are shown. For example, the derivatives of the isobutene (x_1) are $dx_1/dX_i \neq 0$ (for $i = 1$, 2 and 4), while $dX_1/dT = 0$, $dX_2/dT \neq 0$ and $dX_4/dT = 0$; therefore, based on previous analysis, we can conclude that this component does not show multiple solutions in the vapor phase at tested conditions. Similar analysis has been performed for determining the presence of multiple states in the remaining components of this mixture.

In this context, it is convenient to recall that Tiscareño et al. (1998) proposed a set of conditions to predict input multiplicity in non-reactive flash systems. These conditions are based in the values of phase equilibrium constants K_i. In particular, these authors have suggested that the vapor mole fraction of component i can show a stationary point only if $K_i > 1$, which is considered a necessary but not sufficient condition for the presence of multiple solutions in non-reactive flash separation. By analyzing the values of K_i for both isobutene and n-butane, our results indicate that this condition is satisfied for all operating conditions where the multiplicity is present. With illustrative purposes, Fig. 9 shows the temperature dependence of K_i in the range of T_{bub} and T_{dew} for this reactive system at 5 and 20 atm. Both K_1 and K_4 are higher than 1 within the tested temperature interval. On the other hand, the less volatile component cannot have multiplicity in the vapor phase (Tiscareño et al., 1998). In this reactive system, MTBE is the less volatile component and also meets this condition. In general, this agreement may suggest that the necessary K-based conditions for multiple solutions proposed for non-reactive systems could be useful to explain the presence of input multiplicities in a reactive flash separation.

3.2. Reactive system for TAME synthesis with and without inert

TAME is commonly produced by liquid-phase etherification between methanol and iso-amylenes, in the presence of an acidic catalyst. Among the three iso-amylenes, only 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) are reactive, whereas 3-methyl-1-butene (3M1B) is non-reactive. In this study, we have considered the lumped single reaction with and without n-pentane (x_5) as inert, which can be written as:

$$2\text{M1B}(x_1) + 2\text{M2B}(x_2) + 2\,\text{Methanol}\,(x_3) \Leftrightarrow 2\,\text{TAME}\,(x_4) \tag{23}$$

Wilson and ideal gas models have been also used to calculate thermodynamic properties of this mixture. Model parameters are taken from Chen et al. (2002) and Bonilla-Petriciolet et al. (2008a,b). This reactive system has been also analyzed by Ruiz et al. (2006) using Hopf bifurcations and shows multiple solutions for the isothermal reactive flash process. Reaction-invariant mole fractions, considering TAME as reference component (x_4) and without inert, are defined as

$$X_1 = \frac{x_1 + 0.5x_4}{1 + x_4} \tag{24}$$

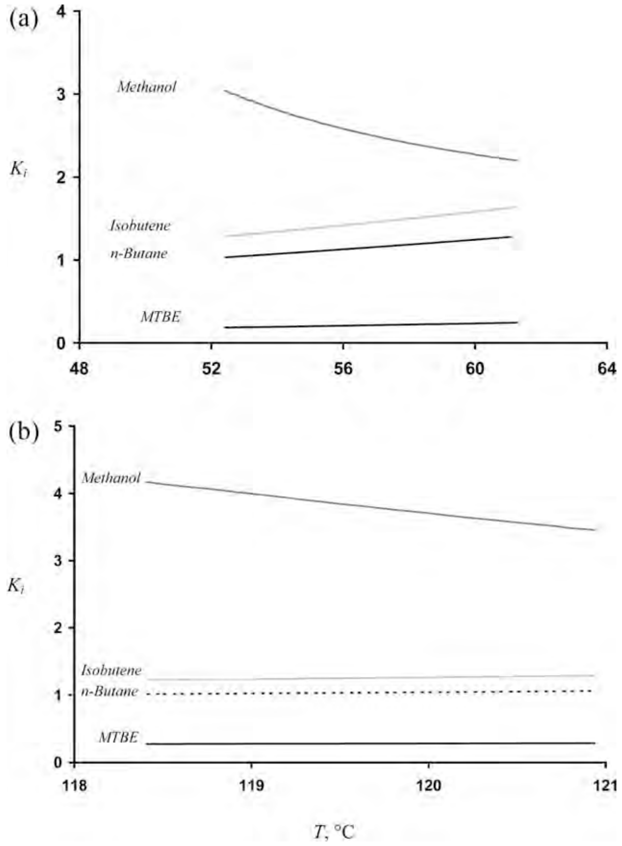


Fig. 9 – Temperature dependence of K_i for the MTBE production in a reactive flash separation at (a) 5 and (b) 20 atm.

$$X_2 = \frac{x_2 + 0.5x_4}{1 + x_4} \tag{25}$$

$$X_3 = \frac{x_3 + x_4}{1 + x_4} = 1 - X_1 - X_2 \tag{26}$$

For this reactive system without inert, we have selected a feed transformed composition: $Z = (0.1382, 0.3646, 0.4972)$ and multiplicity analysis has been performed at different pressures. Fig. 10 shows the response surfaces of vapor–liquid equilibrium for that component with multiple solutions, which corresponds to TAME (x_4). In particular, we have analyzed the reactive flash separation of this system at 2 atm. At these operating conditions, derivatives for this component present change of sign only in the liquid phase. None of all components presents a change of the derivative signs between the bubble and dew points in the vapor phase and, as a consequence, the multiplicity does not occur in this phase. The multiplicity analysis for the liquid phase is given in Fig. 11 where the derivatives of all components are reported. Again, the Conditions II and III are satisfied if multiple solutions are present for the reactive flash separation (see Figs. 12 and 13). In this reactive, the liquid mole fraction of TAME satisfies the necessary and sufficient conditions for detecting the presence of input multiplicity in the flash separation. Note that the evaluation of Eq. (17) is an easy and straightforward approach for predicting the presence of multiple solutions in a reactive flash separation.

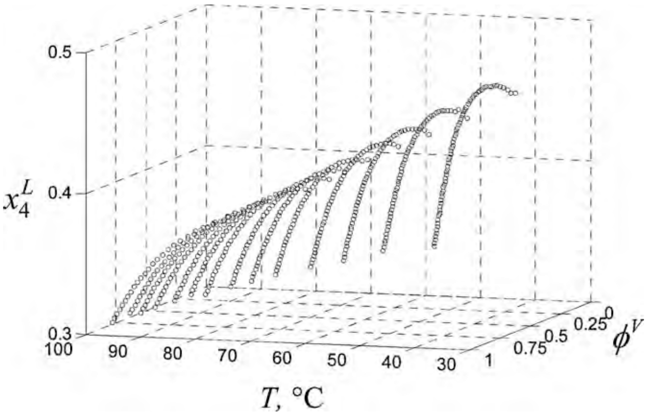
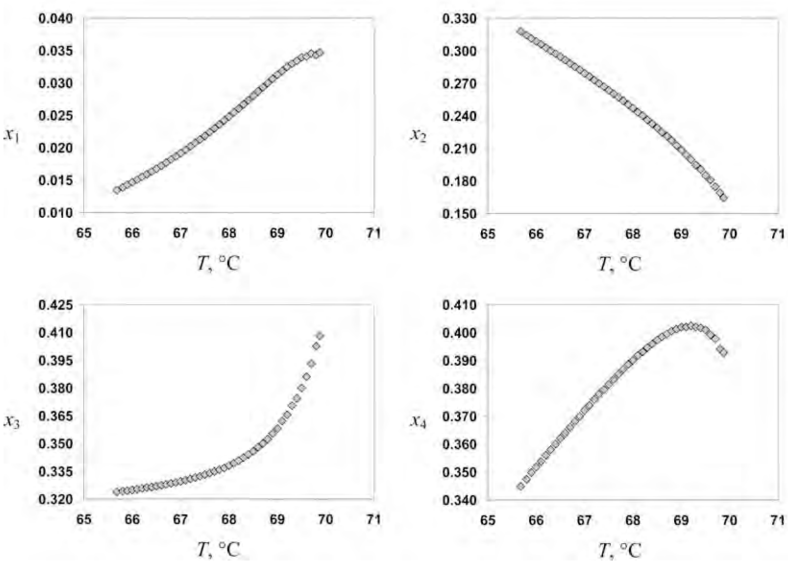


Fig. 10 – Liquid phase composition behavior of TAME as a function of temperature and vaporization fraction for TAME production without inert.

Fig. 14 shows the temperature dependence of K_i for each component that participates in this reactive system at 2 atm. As stated, TAME showed input multiplicity in liquid phase and its $K_i < 1$ for the interval $T_{bub} \le T \le T_{dew}$ where the multiplicity is



Multiplicity analysis based on derivatives			*IM*
$dX_1/dT = 0$	$dx_1/dX_1 \ne 0$	$dx_1/dT \ne 0$	No
$dX_2/dT \ne 0$	$dx_1/dX_2 \ne 0$	$dx_1/dT \ne 0$	No
$dX_3/dT \ne 0$	$dx_1/dX_3 \ne 0$	$dx_1/dT \ne 0$	No
$dX_1/dT = 0$	$dx_2/dX_1 \ne 0$	$dx_2/dT \ne 0$	No
$dX_2/dT \ne 0$	$dx_2/dX_2 \ne 0$	$dx_2/dT \ne 0$	No
$dX_3/dT \ne 0$	$dx_2/dX_3 \ne 0$	$dx_2/dT \ne 0$	No
$dX_1/dT = 0$	$dx_3/dX_1 \ne 0$	$dx_3/dT \ne 0$	No
$dX_2/dT \ne 0$	$dx_3/dX_2 \ne 0$	$dx_3/dT \ne 0$	No
$dX_3/dT \ne 0$	$dx_3/dX_3 \ne 0$	$dx_3/dT \ne 0$	No
$dX_1/dT = 0$	$dx_4/dX_1 = 0$	$dx_4/dT = 0$	Yes
$dX_2/dT \ne 0$	$dx_4/dX_2 = 0$	$dx_4/dT = 0$	Yes
$dX_3/dT \ne 0$	$dx_4/dX_3 = 0$	$dx_4/dT = 0$	Yes

TAME (x_4) shows input multiplicity for the liquid phase in the reactive flash separation.

Fig. 11 – Input multiplicity (IM) analysis of the liquid phase for the TAME production without inert in a flash separation at 2 atm.

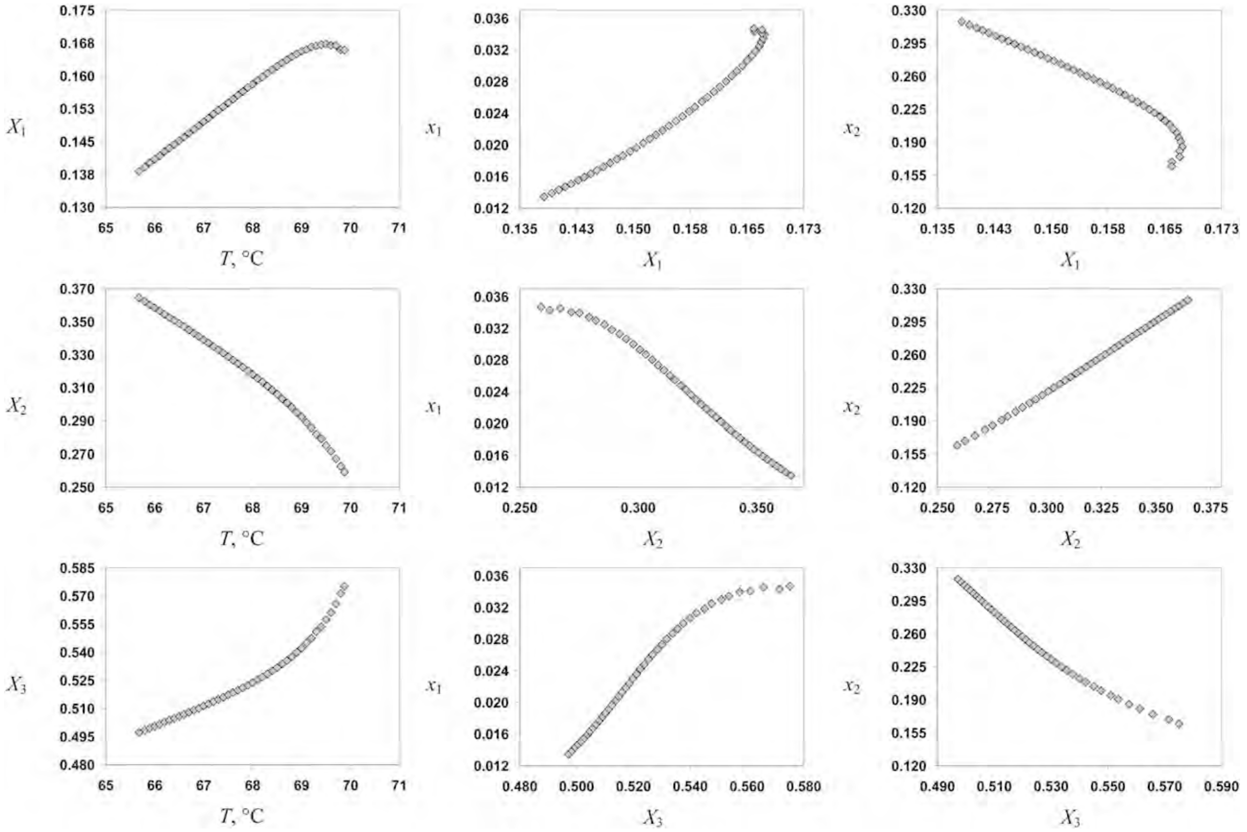


Fig. 12 – X_i versus T and x_k versus X_i for the liquid phase of TAME production without inert in a reactive flash separation at 2 atm.

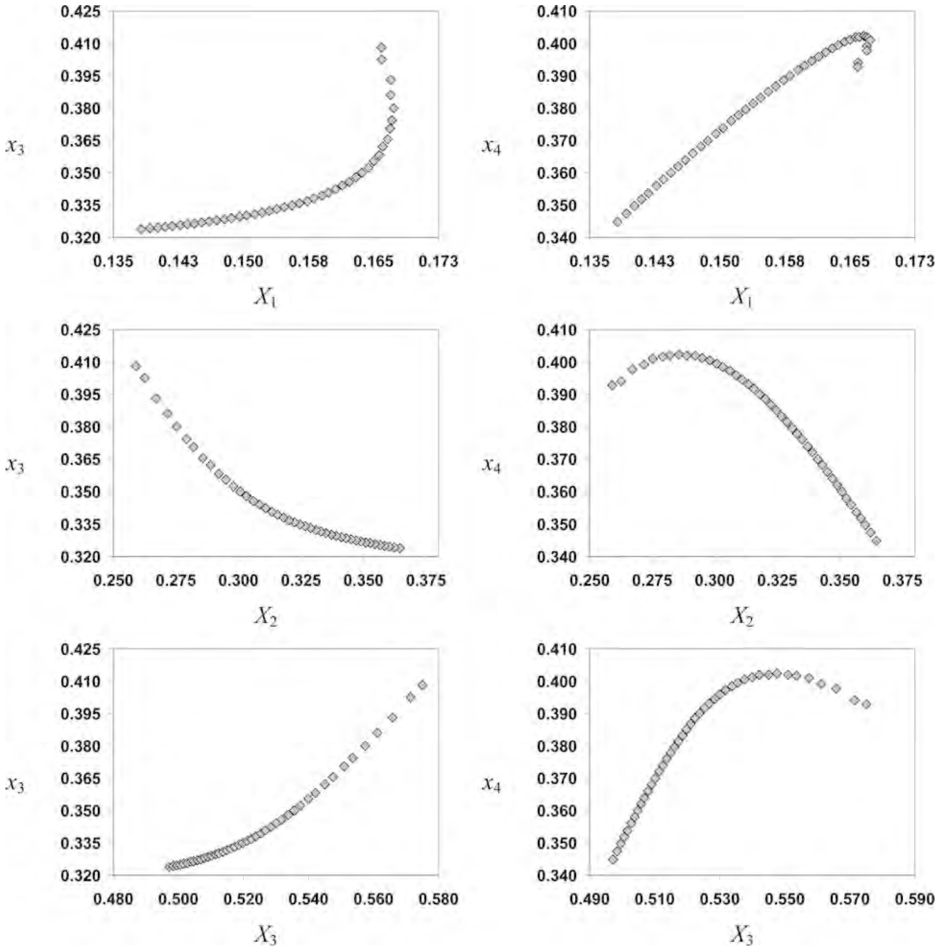


Fig. 13 – x_k versus X_i for the liquid phase of TAME production without inert in a reactive flash separation at 2 atm.

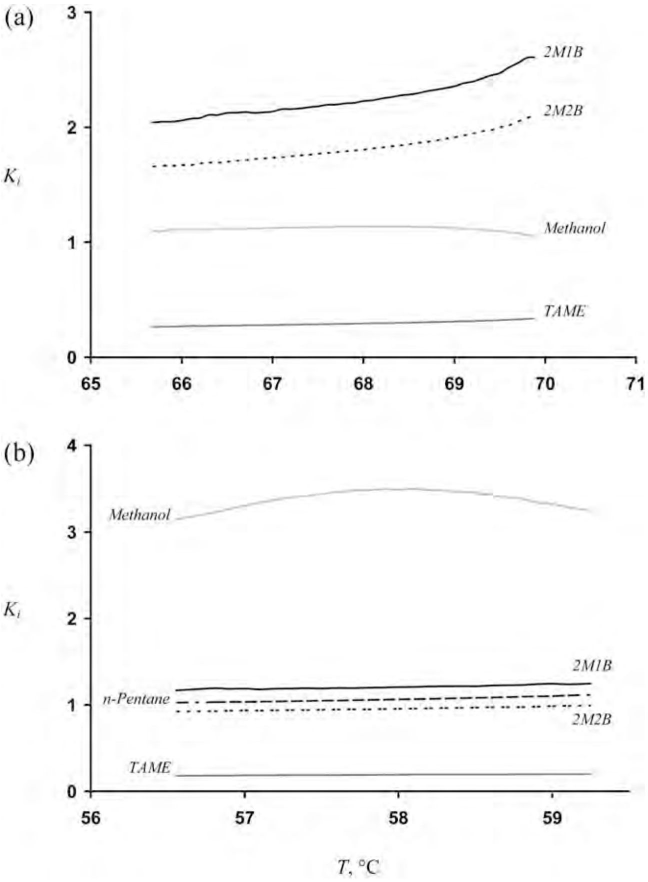


Fig. 14 – Temperature dependence of K_i for the TAME production in a reactive flash separation at 2 atm (a) without and (b) with the presence of an inert.

present. These results also agree with the necessary condition proposed by Tiscareño et al. (1998) for input multiplicity in the liquid phase, which indicates that the liquid mole fraction of a component in a flash separation can show multiplicity if $K_i < 1$. This condition also implies that the more volatile component cannot present input multiplicity in the liquid phase. In this reactive system, 2M1B is the lightest component and does not show multiple solutions in liquid phase.

Finally, we have studied this reactive system but considering the presence of n-pentane (x_5) as inert using the same thermodynamic models. Transformed mole fractions of this quinary system are given by Eqs. (24)–(26) and

$$X_5 = \frac{x_5}{1 + x_4} = 1 - X_1 - X_2 - X_3 \qquad (27)$$

We have analyzed a feed composition Z = (0.0907, 0.1512, 0.190, 0.5681) and results of reactive flash calculations from 1 to 4 atm are reported in Fig. 15. In particular, our results indicate that methanol (x_3) shows input multiplicity in both the liquid and the vapor phases at 2 atm, see Figs. 16 and 17. As expected, there are convex functions (i.e., x_3 versus T) for the composition of this component in both phases. Therefore, its derivatives show a change of slope sign at bubble and dew points and satisfy Eq. (17) if Conditions II and III are met, indicating the presence of multiple solutions in a reactive flash separation problem (see Fig. 16). Particularly, this component shows $K_3 > 1$ in all operating conditions where the multiplicity is present. For example, we report the K_i values for this reactive system at 2 atm in Fig. 14b. Note that both the lightest and the heaviest components (i.e., 2M1B and TAME) do not have input multiplicity for the reactive flash separation in the liquid phase and in the vapor phase, respectively. In fact, these components meet the necessary conditions established by Tiscareño et al. (1998) for input multiplicity in non-reactive systems. In summary, our results indicate that the necessary conditions proposed by Tiscareño et al. (1998) to determine the input multiplicity in non-reactive systems, which are based in the analysis of the equilibrium constants values (K_i), may be applicable for studying multiple solutions in reactive systems. However, it is convenient to remark that the interaction of simultaneous chemical and physical equilibrium may cause a complex phase behavior in systems subject to chemical reactions. Therefore, we could expect that, for some reactive mixtures with complex phase behavior, the based-K_i conditions may not apply.

Finally, based on our numerical calculations and analysis, we conclude that the necessary conditions for a stationary point of x_k (i.e., multiple solutions) to occur in the feasible domain of η in a reactive flash separation are:

(1) The mole fraction of component k in phase j shows a stationary point with respect to η in a reactive flash separation if $dX_i^j/d\eta \neq 0$ and $dx_k^j/dX_i^j = 0$ for at least one X_i^j where $i = 1,\ldots,c-r$.

(2) The mole fraction of component k in phase j shows a stationary point with respect to η in a reactive flash

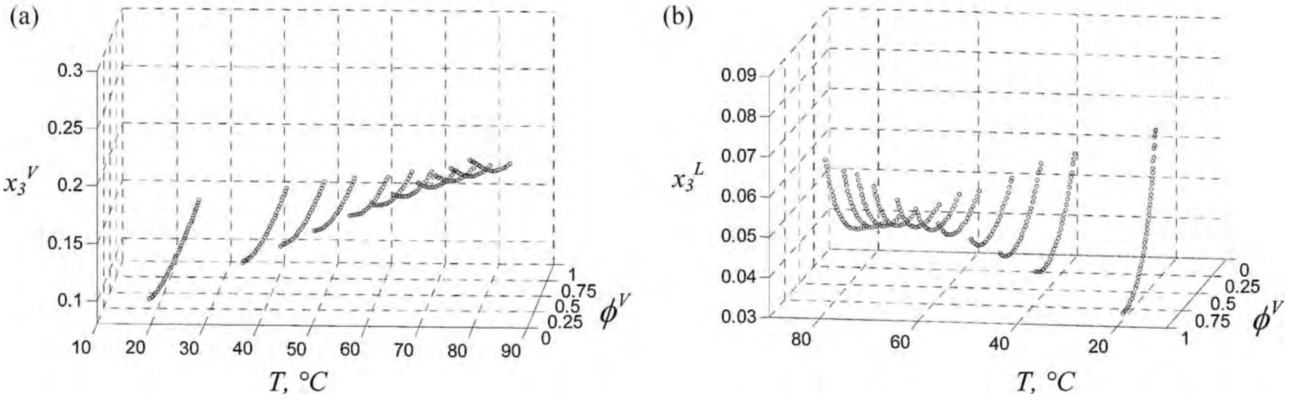
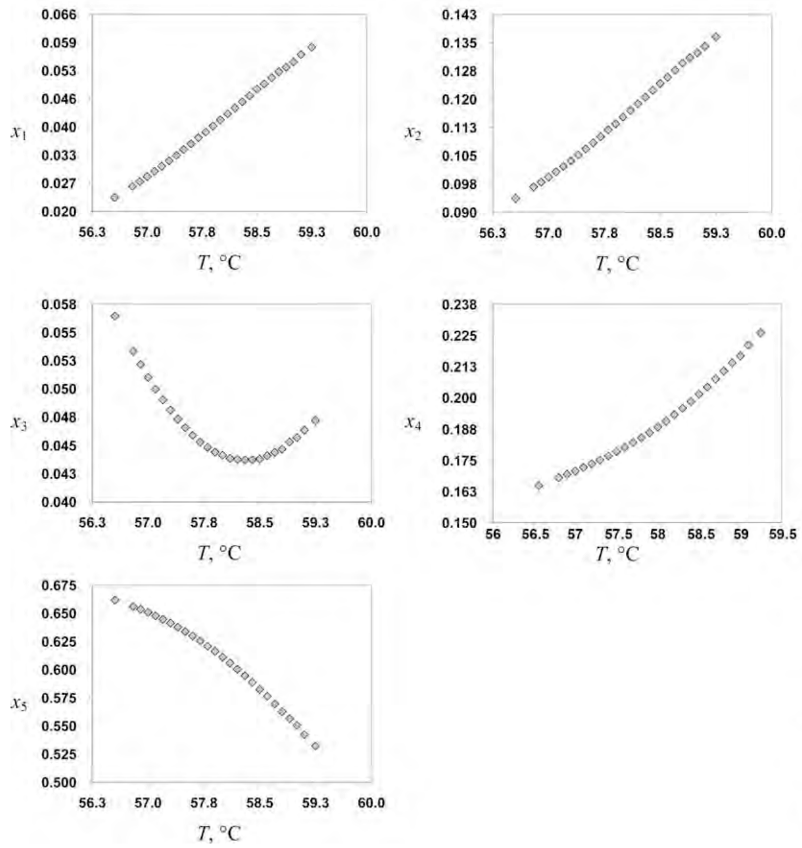


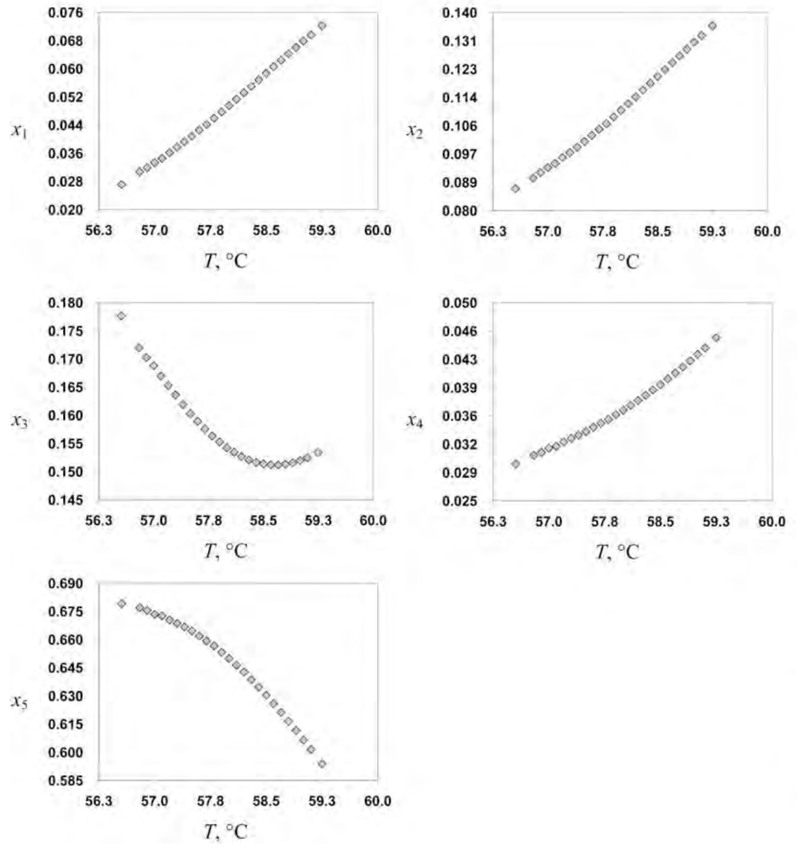
Fig. 15 – (a) Vapor and (b) Liquid phase composition behavior of TAME as a function of temperature and vaporization fraction for TAME production with n-pentane as inert.



Multiplicity analysis based on derivatives			IM
$dX_1/dT \neq 0$	$dx_1/dX_1 \neq 0$	$dx_1/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_1/dX_2 \neq 0$	$dx_1/dT \neq 0$	No
$dX_3/dT = 0$	$dx_1/dX_3 \neq 0$	$dx_1/dT \neq 0$	No
$dX_5/dT \neq 0$	$dx_1/dX_5 \neq 0$	$dx_1/dT \neq 0$	No
$dX_1/dT \neq 0$	$dx_2/dX_1 \neq 0$	$dx_2/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_2/dX_2 \neq 0$	$dx_2/dT \neq 0$	No
$dX_3/dT = 0$	$dx_2/dX_3 \neq 0$	$dx_2/dT \neq 0$	No
$dX_5/dT \neq 0$	$dx_2/dX_5 \neq 0$	$dx_2/dT \neq 0$	No
$dX_1/dT \neq 0$	$dx_3/dX_1 = 0$	$dx_3/dT = 0$	Yes
$dX_2/dT \neq 0$	$dx_3/dX_2 = 0$	$dx_3/dT = 0$	Yes
$dX_3/dT = 0$	$dx_3/dX_3 = 0$	$dx_3/dT = 0$	Yes
$dX_5/dT \neq 0$	$dx_3/dX_5 = 0$	$dx_3/dT = 0$	Yes
$dX_1/dT \neq 0$	$dx_4/dX_1 \neq 0$	$dx_4/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_4/dX_2 \neq 0$	$dx_4/dT \neq 0$	No
$dX_3/dT = 0$	$dx_4/dX_3 \neq 0$	$dx_4/dT \neq 0$	No
$dX_5/dT \neq 0$	$dx_4/dX_5 \neq 0$	$dx_4/dT \neq 0$	No
$dX_1/dT \neq 0$	$dx_5/dX_1 \neq 0$	$dx_5/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_5/dX_2 \neq 0$	$dx_5/dT \neq 0$	No
$dX_3/dT = 0$	$dx_5/dX_3 \neq 0$	$dx_5/dT \neq 0$	No
$dX_5/dT \neq 0$	$dx_5/dX_5 \neq 0$	$dx_5/dT \neq 0$	No

Methanol (x_3) shows input multiplicity for the liquid phase in the reactive flash separation.

Fig. 16 – Input multiplicity (IM) analysis of the liquid phase for the TAME production with inert in a flash separation at 2 atm.



Multiplicity analysis based on derivatives			IM
$dX_1/dT \neq 0$	$dx_1/dX_1 \neq 0$	$dx_1/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_1/dX_2 \neq 0$	$dx_1/dT \neq 0$	No
$dX_3/dT = 0$	$dx_1/dX_3 \neq 0$	$dx_1/dT \neq 0$	No
$dX_5/dT \neq 0$	$dx_1/dX_5 \neq 0$	$dx_1/dT \neq 0$	No
$dX_1/dT \neq 0$	$dx_2/dX_1 \neq 0$	$dx_2/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_2/dX_2 \neq 0$	$dx_2/dT \neq 0$	No
$dX_3/dT = 0$	$dx_2/dX_3 \neq 0$	$dx_2/dT \neq 0$	No
$dX_5/dT \neq 0$	$dx_2/dX_5 \neq 0$	$dx_2/dT \neq 0$	No
$dX_1/dT \neq 0$	$dx_3/dX_1 = 0$	$dx_3/dT = 0$	Yes
$dX_2/dT \neq 0$	$dx_3/dX_2 = 0$	$dx_3/dT = 0$	Yes
$dX_3/dT = 0$	$dx_3/dX_3 = 0$	$dx_3/dT = 0$	Yes
$dX_5/dT \neq 0$	$dx_3/dX_5 = 0$	$dx_3/dT = 0$	Yes
$dX_1/dT \neq 0$	$dx_4/dX_1 \neq 0$	$dx_4/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_4/dX_2 \neq 0$	$dx_4/dT \neq 0$	No
$dX_3/dT = 0$	$dx_4/dX_3 \neq 0$	$dx_4/dT \neq 0$	No
$dX_5/dT \neq 0$	$dx_4/dX_5 \neq 0$	$dx_4/dT \neq 0$	No
$dX_1/dT \neq 0$	$dx_5/dX_1 \neq 0$	$dx_5/dT \neq 0$	No
$dX_2/dT \neq 0$	$dx_5/dX_2 \neq 0$	$dx_5/dT \neq 0$	No
$dX_3/dT = 0$	$dx_5/dX_3 \neq 0$	$dx_5/dT \neq 0$	No
$dX_5/dT \neq 0$	$dx_5/dX_5 \neq 0$	$dx_5/dT \neq 0$	No

Methanol (x_3) shows input multiplicity for the vapor phase in the reactive flash separation.

Fig. 17 – Input multiplicity (IM) analysis of the vapor phase for the TAME production with inert in a flash separation at 2 atm.

separation if $dX_i^j/d\eta = 0$ and $dx_k^j/dX_i^j = 0$ for at least one X_i^j where $i = 1,\ldots,c-r$.

Our numerical experience indicates that if the derivatives $dX_i^j/d\eta = 0$ and $dx_k^j/dX_i^j \neq 0$, this result is a reliable indicator of the absence of multiple solutions of component k in phase j for a reactive flash separation at tested operating conditions.

Finally, it is important to remark that any thermodynamic model and reactive system, assuming that all reactions are reversible and in thermodynamic equilibrium, can be used in our approach because these parameters do not affect the structure and assumptions of the proposed algorithm for predicting input multiplicity. In general, our strategy is based on straightforward phase equilibrium calculations and the evaluation of simple mathematical conditions for predicting the presence of multiple states in reactive flash separation and, as a consequence, it appears to be competitive with respect to other methods reported in the literature. As stated, several methods for predicting input multiplicities mainly relies on the application of homotopy continuation methods due to their capabilities for finding multiple solutions. In general, these methods imply the resolution of non-linear equation systems using an initial value problem to define the solution's path. Even though these numerical methods are generally robust, some authors have recognized that the homotopy methods may be time-consuming and require considerable computational effort (Malinen and Tanskanen, 2010). Based on this fact, we consider that our approach is an alternative strategy, relatively flexible an easy to use, for predicting input multiplicity in flash separation of systems subject to chemical reactions.

4. Conclusions

This study introduces a new approach and conditions to identify input multiplicities in reactive flash separation process, which are based on the application of reaction-invariant composition variables. This approach has been tested and applied for predicting and analyzing input multiplicity in two reactive systems of industrial relevance. Numerical results support and validate the proposed conditions and they can be regarded as necessary conditions to predict the presence or absence of input multiplicity in reactive flash separation. Our calculations indicate that the proposed approach is easy to use and effective for determining the presence of multiple solutions in reactive flash calculations. In fact, our strategy can be applied with any reactive system and model for determining thermodynamic properties, assuming that all reactions are reversible and in thermodynamic equilibrium and the operating conditions are away from the retrograde region. In fact, our method seems suitable and robust to perform the multiplicity analysis of multi-reactive and multi-component systems. Finally, it appears that the necessary conditions proposed to determine the input multiplicity in non-reactive systems, which are based in the analysis of the equilibrium constants values (K_i), may be applicable for studying multiple solutions in reactive systems. Further work will be focused on the study of multiple solutions in reactive flash separations for kinetically controlled reactive systems.

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