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,b; 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;
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).

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; Rodriguez 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
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 $n_0 = (n_{0,1}, \ldots, n_{0,c})$ 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

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

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 $K_{eq,k}$:

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

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
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

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

(9)

Eq. (9) is employed to evaluate \( \hat{\phi}^V \) (i.e., \( \phi^V \)) 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):

\[
f_{\text{bubble}} = 1 - \sum_{i=1}^{c-r} (K_i\theta Z_i + \hat{\delta}_i) = 0
\]  

(10)

\[
f_{\text{dew}} = 1 - \sum_{i=1}^{c-r} \left( \frac{Z_i - \hat{\delta}_i}{K_i\theta} \right) = 0
\]  

(11)

Note that the phase equilibrium constant \( K_i \) are calculated from

\[
K_i(X^L, X^V) = \frac{\hat{\phi}_i^V}{\phi_i^V} = \frac{\phi_i^V}{\phi_i^L}
\]  

(12)

where \( \hat{\phi}_i \) is the fugacity coefficient of component \( i \) in the mixture and \( \gamma_i \) 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 \((X_i^r, X_i^V)\). 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 \( k \) must be a concave or convex function with respect to temperature or vapor phase fraction. Intuitively, we can expect the same performance for vapor 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

\[
\frac{dX_i^j}{d\phi^V} = \frac{dX_i^j}{d\phi^L} \cdot \frac{d\phi^L}{d\phi^V} = 0
\]  

(16)

where \( X_i^j \) is the mole fraction of component \( k \) in phase \( j \) at the equilibrium condition.

or using the vapor phase fraction:

\[
\frac{dX_i^j}{d\eta} = \frac{dX_i}{d\phi^V} \cdot \frac{d\phi^V}{d\eta} = 0
\]  

(17)

where \( \eta \) is \( T \) or \( \phi^V \) 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 \( X_i^j \)):

Condition I: \( \frac{dX_i^j}{d\eta} = 0 \) if \( \frac{dX_i}{d\phi^V} = 0 \) and \( \frac{d\phi^V}{d\eta} \neq 0 \)

Condition II: \( \frac{dX_i}{d\eta} = 0 \) if \( \frac{dX_i}{d\phi^V} \neq 0 \) and \( \frac{d\phi^V}{d\eta} = 0 \)

Condition III: \( \frac{dX_i}{d\eta} = 0 \) if \( \frac{dX_i}{d\phi^V} = 0 \) and \( \frac{d\phi^V}{d\eta} = 0 \)

These conditions indicate that the derivative of \( X_i^j \) with respect to \( \eta \) equals zero or the derivative of \( X_i^j \) 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 \( X_i^j \) 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

\[
\frac{dX_i^j}{dT} \bigg|_{T=T_{Sat}} = \frac{dX_i}{dT} \bigg|_{T=T_{Sat}} \cdot \frac{dx_j}{dx_i^j} \cdot \frac{dx_i}{dx_k^j} \cdot \frac{dx_k}{dT} \bigg|_{T=T_{Sat}}
\]  

(18)
where $T_{sat}$ is the bubble-point temperature $T_{bub}$ or the dew-point temperature $T_{dew}$. So, if the derivates \( \frac{dx_j}{d\eta} \bigg|_{T_0} \) 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 derivates are evaluated straightforward using finite differences. Alternatively, a one-dimensional direct optimization strategy can be used to find the minimum of \( d^2 \) where \( d = \frac{dx_j}{d\eta} \) and \( \eta \) 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.

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>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Therodynamic models</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( A_1 + A_2 \leftrightarrow A_3, ) and ( A_4 ) as an inert component</td>
<td>Wilson model and ideal gas: ( \Delta G_{r_1s}^{\text{mix}}/R = -4205.05 + 10.092T - 0.2667T \ln T ) where ( T ) is in K</td>
</tr>
<tr>
<td></td>
<td>(1) Isobutene</td>
<td>( \ln K_{eq,1} = -0.255 )</td>
</tr>
<tr>
<td></td>
<td>(2) Methanol</td>
<td>( \ln K_{eq,1} = -0.255 )</td>
</tr>
<tr>
<td></td>
<td>(3) Methyl-tert-butyl ether</td>
<td>( \ln K_{eq,1} = -0.255 )</td>
</tr>
<tr>
<td></td>
<td>(4) n-Butane</td>
<td>( \ln K_{eq,1} = -0.255 )</td>
</tr>
<tr>
<td>2</td>
<td>( A_1 + 2A_2 \leftrightarrow 2A_4 )</td>
<td>Wilson model and ideal gas: ( K_{eq,1} = 1.057 \times 10^{-6} \times e^{-4273.5/T} ) where ( T ) is in K</td>
</tr>
<tr>
<td></td>
<td>(1) 2-Methyl-1-butene</td>
<td>( K_{eq,1} = 1.057 \times 10^{-6} \times e^{-4273.5/T} )</td>
</tr>
<tr>
<td></td>
<td>(2) 2-Methyl-2-butene</td>
<td>( K_{eq,1} = 1.057 \times 10^{-6} \times e^{-4273.5/T} )</td>
</tr>
<tr>
<td></td>
<td>(3) Methanol</td>
<td>( K_{eq,1} = 1.057 \times 10^{-6} \times e^{-4273.5/T} )</td>
</tr>
<tr>
<td></td>
<td>(4) Tert-amyl methyl ether</td>
<td>( K_{eq,1} = 1.057 \times 10^{-6} \times e^{-4273.5/T} )</td>
</tr>
<tr>
<td>3</td>
<td>( A_1 + 2A_2 \leftrightarrow 2A_4 ) with ( A_5 ) as inert component</td>
<td>Wilson model and ideal gas: ( K_{eq,1} = 1.057 \times 10^{-6} \times e^{-4273.5/T} ) where ( T ) is in K</td>
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</tr>
<tr>
<td></td>
<td>(5) n-pentane</td>
<td>( K_{eq,1} = 1.057 \times 10^{-6} \times e^{-4273.5/T} )</td>
</tr>
</tbody>
</table>
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:

\[
\text{Isobutene} \ (x_1) + \text{Methanol} \ (x_2) \rightleftharpoons \text{MTBE} \ (x_3)
\]  

(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

\[
X_1 = \frac{x_1 + x_3}{1 + x_3}
\]  

(20)

\[
X_2 = \frac{x_2 + x_3}{1 + x_3}
\]  

(21)

\[
X_4 = \frac{x_4}{1 + x_3} = 1 - X_1 - X_2
\]  

(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 \( T = T_{\text{bub}} \) and

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

**Fig. 5** – Input multiplicity (IM) analysis of the vapor phase for the MTBE production in a flash separation at 5 atm.
Fig. 6 – Input multiplicity (IM) analysis of the vapor phase for the MTBE production in a flash separation at 20 atm.

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: $dX_i/dT=0$ and $dx_k/dX_i=0$ or $dX_i/dT=0$ and $dx_k/dX_i=0$ (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 $dx_k/dX_i \neq 0$, 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 $dx_1/dX_i 
eq 0$ (for $i = 1, 2$ and 4), while $dX_1/dT = 0$, $dX_2/dT = 0$ 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 Tiscareno 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 $T_{sub}$ 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:

$$2M1B(x_1) + 2M2B(x_2) + 2\text{Methanol}(x_3) \leftrightarrow 2\text{TAME}(x_4) \quad (23)$$

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

$$x_1 = \frac{x_1 + 0.5x_4}{1 + x_4} \quad (24)$$
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 \( T_{\text{bub}} \leq T \leq T_{\text{dew}} \) where the multiplicity is
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

$$X_5 = \frac{x_5}{1 + x_4} = 1 - X_1 - X_2 - X_3$$

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 $\eta$ in a reactive flash separation are:

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

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

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

Methanol ($x_3$) shows input multiplicity for the liquid 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.

Methanol ($x_3$) shows input multiplicity for the vapor phase in the reactive flash separation.
phase analysis of the equilibrium constants values (multiplicity in non-reactive systems, which are based on the necessary conditions proposed to determine the input multiplicity in the retrograde region. In fact, our method seems suitable and our strategy can be applied with any reactive system and is easy to use and effective for determining the presence or absence of input multiplicity in reactive flash separations. Our calculations indicate that the proposed approach can be regarded as necessary conditions to predict 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 rely 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 and 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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References


