

Prediction of Steady State Input Multiplicities for the Reactive Flash Separation using Reaction-Invariant Composition Variables

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Abstract

In this study, we report a new approach for predicting and analyzing steady state input multiplicities in reactive flash separation processes. Necessary conditions are suggested to detect these multiple steady states using reaction-invariant composition variables. Our results suggest that the conditions proposed for identifying the presence of input multiplicities of non-reactive systems are useful for the analysis of reactive systems if transformed composition variables are employed. Performance of our approach is illustrated using MTBE production as case of study.

Keywords: Reactive flash separation, multiple steady states, MTBE production

1. Introduction

Input multiplicity is an important feature of industrial processes and plays an important role in design, simulation and control of separation units [1]. In process system engineering, it is important to predict all multiple steady states within the practical domain of operating variables, to know whether they are desirable, and to understand how the separation scheme responds to changes in operation conditions. To date, theoretical and experimental studies have shown the existence of multiple steady-states (MSS) in both non-reactive and reactive separation processes. In particular, due to the interaction between chemical reaction and phase equilibrium, reactive separation processes exhibit high non-linear behavior and MSS solutions are often possible. The existence and possible explanation of multiplicity in reactive separation processes for specific systems (e.g., MTBE, ETBE or TAME production) have been investigated by several authors especially in reactive distillation columns [2]. However, only few studies have been conducted on multiplicity in reactive flash separations. Despite significant progress on design and modeling of reactive distillation columns have been achieved, more general results are needed concerning the steady state multiplicity in reactive flash operation. It is convenient to remark that the determination and analysis of the existence of MSS in reactive separation processes still appears to be a challenging task and it is more complex than those involved for conventional separation schemes. Based on this context, in this study we provide new conditions for the existence of MSS in reactive flash separations. These conditions are based on the application of reaction-invariant composition variables of Ung and Doherty [3]. The presence of the input multiplicity is studied for MTBE production as example of our approach. For this reactive system, we report the existence of MSS for different operating conditions and we show that necessary conditions for the existence of multiple solutions in non-reactive flash operation, previously reported by Monroy-Loperena [1] and Tiscareño et

al. [4], can be extended for reactive systems if reaction-invariant composition variables are used in multiplicity analysis.

2. Multiplicity analysis of flash separation in reactive systems

Given a temperature T and pressure P , consider a flash separation process for a system of c components that undergoes r independent chemical reactions. The thermodynamic problem for modeling the reactive vapor-liquid equilibrium is to solve the non-linear equation system that 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. However, as indicated by Ung and Doherty [3], the numbers of moles are not the natural composition 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 MSS in flash systems, we have applied the reaction-invariant composition variables proposed by Ung and Doherty [3]. 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. These features allow all of the procedures used to model non-reactive mixtures to be extended to systems subject to chemical equilibrium and, consequently, non-reactive algorithms can be easily modified to account for chemical reactions [3]. Therefore, transformed mole variables X for reactive systems are defined as

$$X_i = (x_i - v_i N^{-1} x_{ref}) / (1 - v_{TOT} N^{-1} x_{ref}) \quad \text{for } i = 1, \dots, c - r \quad (1)$$

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. Transformed mole fractions X are related to conventional mole fractions x using the reaction equilibrium constant K_{eq} . It is important to note that the set of 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 [3]. Based on this fact, the reactive vapor-liquid equilibrium problem is modeled using X as follows [5]

$$X_i^L = (Z_i - \delta_i \hat{\phi}^V) / (\hat{\phi}^V (K_i \theta - 1) + 1) \quad \text{for } i = 1, \dots, c - r \quad (2)$$

$$X_i^V = X_i^L K_i \theta + \delta_i = (Z_i K_i \theta + \delta_i (1 - \hat{\phi}^V)) / (\hat{\phi}^V (K_i \theta - 1) + 1) \quad \text{for } i = 1, \dots, c - r \quad (3)$$

where

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$$\begin{aligned}\theta &= (1 - v_{TOT} N^{-1} x_{ref}^L) / (1 - v_{TOT} N^{-1} x_{ref}^V) \\ \delta_i &= (v_i N^{-1} (K_i x_{ref}^L - x_{ref}^V)) / (1 - v_{TOT} N^{-1} x_{ref}^V)\end{aligned}\quad (4)$$

subject to the material balance

$$Z_i - (1 - \hat{\phi}^V) X_i^L - X_i^V \hat{\phi}^V = 0 \text{ for } i = 1, \dots, c - r \quad (5)$$

$$\hat{\phi}^V = \phi^V (1 - v_{TOT} N^{-1} x_{ref}^V) / (1 - v_{TOT} N^{-1} z_{ref}) \quad (6)$$

and equality constraints

$$\sum_{i=1}^{c-r} X_i^L = 1, \sum_{i=1}^{c-r} X_i^V, \sum_{i=1}^{c-r} Z_i = 1 \text{ and } \hat{\phi}^V + \hat{\phi}^L = 1 \quad (7)$$

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). In this study, the algorithm used for phase equilibrium calculations is based on an alternative Rachford-Rice formulation for reactive systems using also transformed variables [5]. Thus, for the reactive flash problem we have

$$f(\hat{\phi}^V) = \sum_{i=1}^{c-r} [(Z_i (K_i \theta - 1) + \delta_i) / (\hat{\phi}^V (K_i \theta - 1) + 1)] = 0 \quad (8)$$

Equation (8) is an implicit function used to evaluate $\hat{\phi}^V$ and determine the vapor-liquid equilibrium compositions subject to chemical equilibrium. 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. Using transformed variables, the reactive flash problem has $c - r + 2$ degrees of freedom. For our analysis, 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). If under these conditions the system shows MSS, more than one solution may exist for the reactive flash problem. Monroy-Loperena [1] and Tiscareño et al. [4] have suggested that if steady-state input multiplicities exist in non-reactive 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. (2) or (3) in reactive systems using X . Therefore, analyzing the reactive flash problem 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 corresponding stationary point is given by

$$dX_i^j / dT = 0 \quad (9)$$

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

$$dX_i^j / d\hat{\phi}^V = 0 \quad (10)$$

where j is the liquid (L) or vapor phase (V). Using the same analogy reported for non-reactive systems, if the stationary point is bounded by $T \in [T_{bub}, T_{dew}]$ and $\hat{\phi}^V \in [0, 1]$, Eqs. (9) and (10) are necessary conditions to identify steady-state input multiplicities for the transformed composition variable i in either phase. Note that these conditions are useful to predict the presence of MSS in reactive systems but not for identifying the component that shows the multiplicity behavior. However, due to the transformation procedure $X \rightarrow x$, we can easily recognize what component or set of components exhibits steady-state input multiplicity at the specified operating conditions. To explore the presence of input multiplicity, the derivative dX_i^j / dT or $dX_i^j / d\hat{\phi}^V$ must be evaluated at both the bubble and dew points; a change of sign will indicate the existence of multiple solutions for reactive flash problem. These conditions are equivalent to that reported by Monroy-Loperena [1] and Tiscareño et al. [4] for 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 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_i^2 where d_i is given by Eq. (9) or (10). If the minimum of $d_i^2 = 0$, the reactive system under analysis shows MSS. Our numerical experience indicates that an optimization approach is more effective than root-finding methods for the location of the stationary point of $X_i^j - T$ and $X_i^j - \hat{\phi}^V$.

3. Numerical example: MSS in methyl tert-butyl ether (MTBE) production

We have performed several numerical calculations on a variety of reactive systems to validate and verify the conditions proposed in this paper for MSS analysis. For illustration, the MTBE production is selected as case of study. MTBE is considered an important industrial chemical because large quantities of MTBE have been used as an octane booster in gasoline. Several simulation and experimental researches have been performed to study the multiplicity of MTBE reactive distillation process. For the single reaction of MTBE production, we have three reactive components: isobutene (1) + methanol (2) \leftrightarrow methyl tert-butyl ether (3), and one inert component: n-butane (4). In our analysis transformed variables are defined using MTBE as reference component and are given by: $X_1 = (x_1 + x_3)/(1 + x_3)$, $X_2 = (x_2 + x_3)/(1 + x_3)$ and $X_4 = x_4/(1 + x_3)$ where all $X_i \in (0, 1)$. The reaction takes place in both liquid and vapor phases and thermodynamic properties are calculated using Wilson solution model and Antoine equation with model parameters reported by Bonilla-Petriciolet et al. [5]. The steady state solutions are found by solving Eqs. (2) - (8) for an arbitrary transformed feed of Z (0.2257, 0.0796, 0.6947) at different conditions of P . Figures 1a and 1b show the dependence of MSS for X_1^V and X_4^V with respect to the transformed vaporization fraction and the temperature. The phase equilibrium behavior of X_1 and X_4 indicates the presence of MSS in only the vapor phase for the tested range of 1.0 to 22.0 atm. As expected, Eqs. (9) and (10) have changes of sign when $T = T_{bub}$ and $T = T_{dew}$; X_1 shows a change of sign for the stationary condition from 1.0 to 22.0 atm, while the criterion of input MSS for X_4 is satisfied from 1.0 to 12.0 atm.

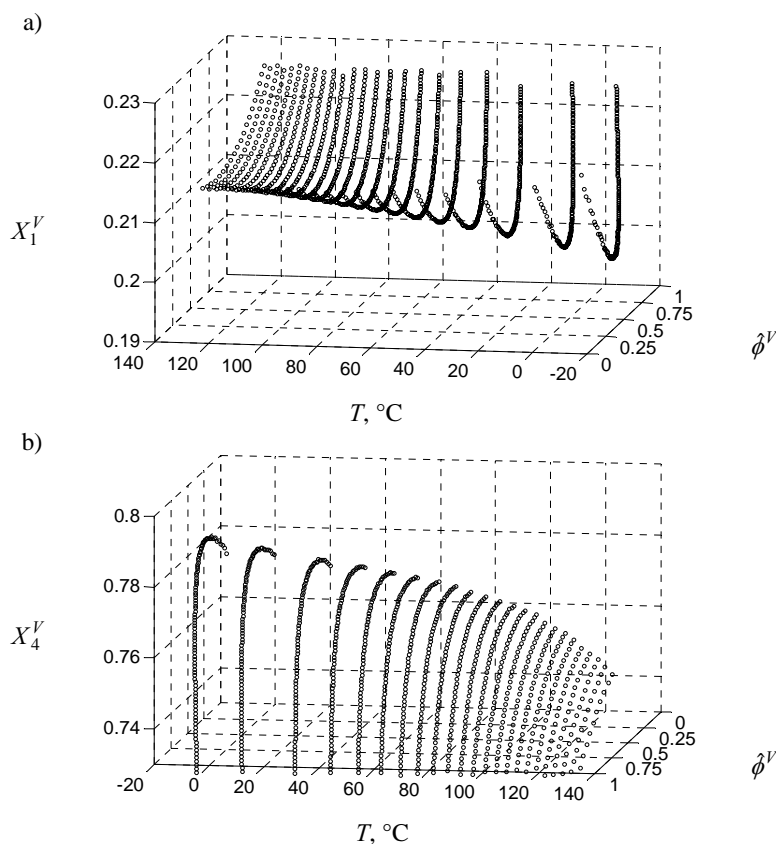


Figure 1. Vapor phase composition behavior of (a) X_1 and (b) X_4 as a function of temperature and vaporization ratio for MTBE production.

By performing the transformation $X \rightarrow x$, we can easily establish that isobutene and n-butane have MSS in the vapor phase but at different conditions of P (see Figure 2). Specifically, it is observed that the vapor mole fraction of n-butane reaches a maximum within the range of 1.0 to 16.0 atm, while isobutene shows MSS from 11.0 to 22.0 atm. Tiscareño et al. [4] 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 condition for MSS in non-reactive systems. By analyzing the values of K_i for both isobutene and n-butane (not reported in this paper), our results indicate that this condition is satisfied for the tested range of pressure. This agreement suggests that the necessary conditions for MSS proposed for non-reactive systems could be useful to explain the presence of input multiplicities in reactive flash separation.

4. Conclusions

This study introduces new conditions to identify steady-states input multiplicities in reactive flash separation process, which are based on the application of reaction-invariant composition variables. Our results indicate that proposed multiplicity analysis

is easy to use and effective for determining the presence of steady-state input multiplicities in reactive flash operation. Besides, our strategy can be applied with any thermodynamic model and seems suitable for the analysis of multi-reactive and multi-component systems. Further work will be focused on the study of MSS in kinetically controlled reactive systems.

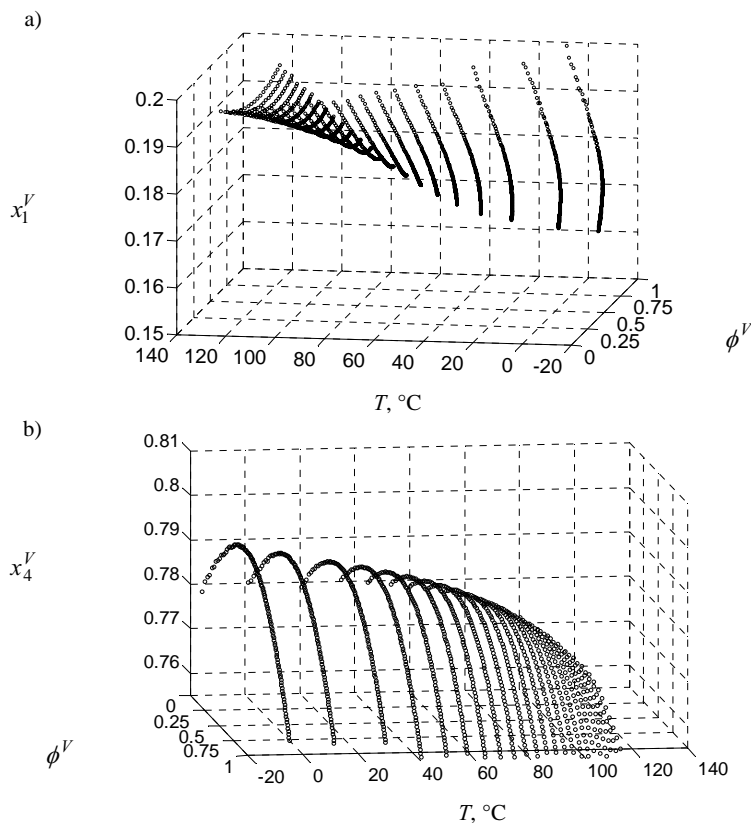


Figure 2. Vapor phase composition behavior of (a) x_1 and (b) x_4 as a function of temperature and vaporization ratio for MTBE production.

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