Analysis of Two-Stage Heterogeneous Separation Processes

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In this article, rigorous mathematical analysis is used to prove that the necessary condition for multiple steady-state solutions to exist in two-stage separation process problems involving ternary mixtures is the tendency of the mixture to exhibit a second liquid phase. The unrealistic solution multiplicity that exists in these problems, when phase splitting is not included in the model equations used to solve them, vanishes when phase splitting is included. The standard specification of reflux ratio and bottoms flow rate has been investigated.

Introduction

Recent interest in the existence of solution multiplicities in multistage separation processes has led to a large number of articles that try to provide various explanations for the cause of this solution multiplicity. Magnussen et al. (1979); Kovach and Seider (1987), Venkataraman and Lucia (1988), Rovaglio and Doherty (1990), and Bekiaris et al. (1993) have confirmed the existence of multiple steady states for the ethanol, benzene, water dehydration column. Moreover all the steady-states lie in the homogeneous region. However, all this work involved large columns and have consequently failed to reduce the problem to its simplest possible form. The first step to understand the cause(s) for the solution-multiplicity is to reduce the problem to its simplest possible form (i.e., to the smallest number of stages that will yield solution multiplicity).

Bekiaris et al. (1993) conclude that solution multiplicity tends to vanish for small columns and/or for low-reflux flows in *homogeneous* azeotropic distillation problems. The aim of this article is to prove rigorously that the necessary condition for solution multiplicity to exist in two-stage separation processes is the tendency of the mixture to exhibit a second liquid phase. Sridhar and Lucia (1989) and Lucia and Li (1992) investigated binary mixtures involving a variety of specifications and conclude solution uniqueness for certain sets of specifications. Sridhar and Lucia (1990) show that a unique steady state exists for multicomponent homogeneous separation processes for fixed temperature and pressure profiles. They suggest that mapping from the temperature-profile specification to the standard specification will resolve the issue as to what causes the solution multiplicity that was observed by Magnussen et al. (1979). However, as there has not been any successful attempt to resolve this problem, it is our belief that the suggested approach is difficult, particularly for problems where solution multiplicities occur. A more direct approach used here has revealed a strategy to prove that the necessary condition for solution multiplicity to exist in two-stage separation processes involving the standard specification of reflux ratio and bottoms flow rate, is the ability of the mixture to exhibit a second liquid phase.

Single-Stage Vapor-Pressure Problem

A single-stage vapor-pressure (VP) problem (where the specification is the total vapor flow and the pressure; see Figure 1) is completely described by the mass-balance and phase equilibrium relationships in addition to the specification equation

$$V - \sum_i v_i = 0. \tag{1}$$

Consider first a single-stage VP problem where the feed is being perturbed. The change in vapor component flows, Δv, for a change in the feed vector, Δf, is given by

$$\Delta v = M\Delta f - \frac{(\nabla^2 G^V + \nabla^2 G^L)^{-1} \dfrac{(\bar{H}^v - \bar{H}^l)}{T} J^T}{J^T (\nabla^2 G^V + \nabla^2 G^L)^{-1} \dfrac{(\bar{H}^v - \bar{H}^l)}{T}} M\Delta f = \bar{M}\Delta f, \tag{2}$$

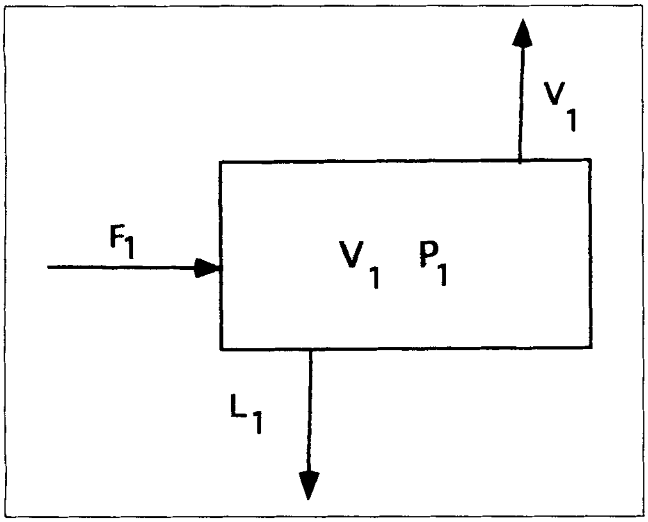

Figure 1. Single-stage VP problem.

where $M = (\nabla^2 G^V + \nabla^2 G^L)^{-1} \nabla^2 G^L$. Details of this derivation are in Sridhar (1990). $\nabla^2 G^V$ and $\nabla^2 G^L$ are the Hessian matrices of the Gibbs free energy function for the vapor and liquid phases. $\overline{H}^v$ and $\overline{H}^l$ are the partial molar enthalpies of the vapor and liquid phases, T is the temperature, and $J^T = [1, 1, 1, \ldots, 1]$.

Also, since $\Delta l = \Delta f - \Delta v$,

$$\Delta l = (I - \overline{M})\Delta f, \tag{3}$$

where I is the identity matrix.

Equations 2 and 3 will be used to construct a Newton-like algorithm to solve the two-stage VP problem (where the specification is the total vapor-flow profile and pressure on each stage).

Two-stage VP Problem

The two-stage VP problem (Figure 2) can be posed as a fixed-point iteration in the following way. Since

$$\Delta v_2 = \overline{M}_2 \Delta l_1 \tag{4}$$

and

$$\Delta l_1 = (I - \overline{M}_1)\Delta v_2, \tag{5}$$

we can pose the two-stage problem as a Newton fixed-point iteration of the form

$$v_2^{k+1} = v_2^k - [F']^{-1}[F(v_2^k)], \tag{6}$$

where the Jacobian matrix $F' = I - \overline{M}_2(I - \overline{M}_1)$.

The solution corresponds to $F(v_2) = 0$. The singular point of the Jacobian matrix F' is the one from where the multiple solutions of the two-stage VP problem emanate. Furthermore, in the two-stage case, the standard specification is equivalent to specifying the total vapor flow that exits each stage because once the reflux ratio and bottoms flow rate are fixed, all the flows in the column are fixed. Consequently, the transformation from the VP specification to the standard specification is a nonsingular one. Hence, it is enough to analyze the VP specification in the two-stage case. Analysis of the Jacobian matrix $[I - \overline{M}_2(I - \overline{M}_1)]$ at the point of singularity will reveal the necessary condition for the existence of the solution multiplicity.

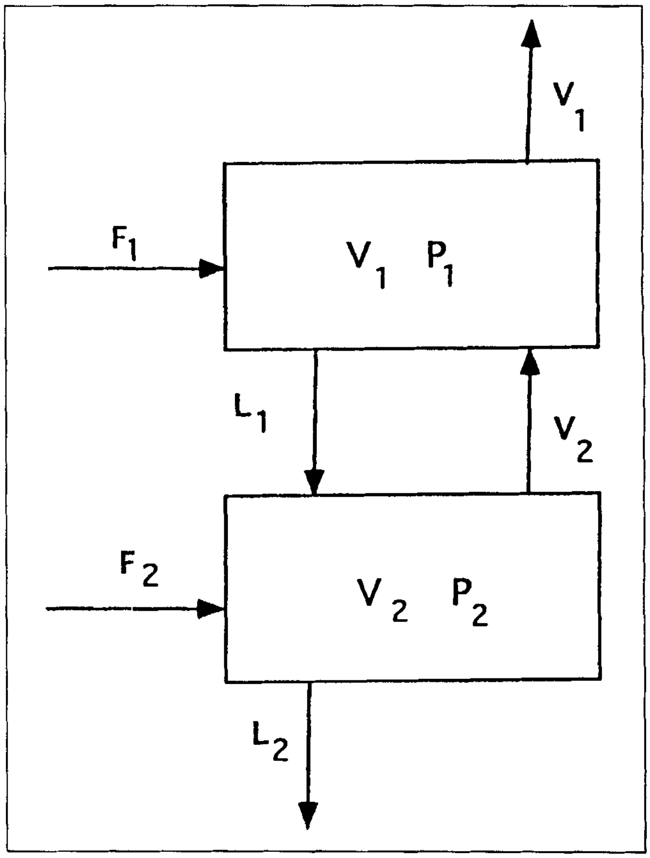

Figure 2. Two-stage VP problem.

False multiple solutions for two-stage problems

In this section we present an example involving a two-stage separator and the mixture ethanol, benzene and water (see Table 1). The solution multiplicity that exists in this problem when phase splitting is not included is found to disappear when the models include liquid–liquid phase splitting. The vapor and liquid phases are nonideal solutions modeled by the B-truncated virial equation and UNIQUAC equation, respectively, using the procedures and data given by Prausnitz et al. (1980). The external feed is 10, 65, 37.6 kmol/h to the first stage while the pressure is 0.1 MPa on both stages. The reflux ratio is denoted by the symbol R and the bottoms flow rate is represented by B (kmol/h).

In this table, where there is vapor–liquid solution multiplicity, there is at least one unstable liquid phase. A unique vapor–liquid–liquid solution is found when we include phase splitting in the calculations. The superscript I refers to the first liquid phase, while the superscript II refers to the second liquid phase. The relationship between the liquid phase instability and the solution multiplicity is shown in the next few sections.

Table 1. Two-stage Multiple Unstable Vapor–Liquid Solutions*

Vapor–Liquid Solution 1			
l_1	4.5231	1.7153	29.581
l_2	4.332	0.66203	29.342
v_1	5.6680	64.3380	8.2580
v_2	0.19117	1.05330	0.23851
$T_1 = 321.6$; $T_2 = 330.32$			
Vapor–Liquid Solution 2			
l_1	3.8934	20.4110	11.5140
l_2	3.7743	19.550	11.011
v_1	6.2257	45.4500	26.5890
v_2	0.1191	0.8609	0.50299
$T_1 = 334.55$; $T_2 = 334.56$			
Vapor–Liquid–Liquid Solution			
l_1^I	0.5396	16.5936	0 2332
l_1^{II}	0.8201	0.0211	17.6060
l_2^I	0.4687	15.6578	0.2163
l_2^{II}	0.7347	0.0195	17.2391
v_1	8.7964	49.3202	20.1433
v_2	0.1566	0.9389	0.3844
$T_1 = 339.7$; $T_2 = 339.8$			

*$R = 0.4576$; $B = 34.336$.

Analysis of Solution Multiplicity

In the next few sections we analyze the singularity condition of the Jacobian matrix $[I - \bar{M}_2(I - \bar{M}_1)]$ and show that the cause for the existence of solution multiplicity is the ability of the mixture to exhibit a second liquid phase. We first present some preliminary results, and use some of these results in analyzing the single-stage and the two-stage VP problems.

Preliminary results

For three-component mixtures, we present some preliminary results already described in detail in Sridhar and Lucia (1990).

Result 1. For a three-component homogeneous mixture, the matrices M and $I - M$ have real eigenvalues that lie in the closed interval [0, 1], and share the same set of linearly independent eigenvectors. These eigenvectors are the liquid-phase composition x, the vapor-phase composition y, and a third eigenvector $[p]$ that corresponds to the intermediate eigenvalue. We will refer to this eigenvector as the "noncomposition" eigenvector. Consequently, we have the equations, $Mx = 0$, $My = y$, and $Mp = \lambda p$, where $\lambda \in (0, 1)$. It is also obvious that $(I - M)x = x$; $(I - M)y = 0$; and $(I - M)p = (1 - \lambda)p$. If M has eigenvalues that lie outside the interval [0, 1], it can be concluded that the mixture is heterogeneous.

Result 2. In order to have a two-stage, two-phase solution, the two-phase regions of both the stages must intersect. As a result of the intersection of the two-phase regions of the adjacent stages, we can approximately express y_2 as a linear combination of x_1 and y_1, and x_1 as a linear combination of y_2 and x_2. Arguments justifying these approximations can be found in Sridhar and Lucia (1990). These results can be expressed concisely as

$$y_2 \in [x_1, y_1] \tag{7}$$

and

$$x_1 \in [x_2, y_2]. \tag{8}$$

Analysis of the single-stage VP problem

In this section we present some properties of the matrix $\bar{M}$, which has the form given by Eq. 2 and can be simply expressed as

$$\bar{M} = (I - A)M, \tag{9}$$

where

$$A = \frac{(\nabla^2 G^V + \nabla^2 G^L)^{-1} \dfrac{(\bar{H}^v - \bar{H}^l)}{T} J^T}{J^T (\nabla^2 G^V + \nabla^2 G^L)^{-1} \dfrac{(\bar{H}^v - \bar{H}^l)}{T}}. \tag{10}$$

The matrix A consists of positive terms (Lucia, 1986) and has the form

$$A = \frac{1}{a + b + c} \begin{bmatrix} a & a & a \\ b & b & b \\ c & c & c \end{bmatrix}, \tag{11}$$

where a, b, and c are all greater than zero. The matrix A has two zero eigenvalues and one unit eigenvalue. The eigenvector corresponding to the zero eigenvalues are [0, 1, −1] and [1, −1, 0], while the eigenvector corresponding to the unit eigenvalue, $\hat{y}$, is one of the columns of the matrix A. The vector $\hat{y}$ can be approximated by the vapor-phase composition y (Sridhar and Lucia (1989), Appendix A, p. 801). Since this is the eigenvector corresponding to the only nonzero eigenvalue of A, the matrix A must take all vectors approximately to y. In mathematical terms, the range space of the operator A is the vector y, resulting in the equation.

$$R(A) \approx y. \tag{12}$$

Two-Stage Analysis

Now let us consider the two-stage VP Problem. The matrix whose singularity condition we wish to analyze is $[I - \bar{M}_2(I - \bar{M}_1)]$. We start by assuming that there is a nonzero vector z such that

$$[I - \bar{M}_2(I - \bar{M}_1)]z = 0. \tag{13}$$

Since $\bar{M} = (I - A)M$, Eq. 13 can be written as

$$[I - (I - A_2)M_2(I - (I - A_1)M_1)]z = 0 \tag{14}$$

or

$$[I - M_2]z + [M_2 M_1]z - [M_2 A_1 M_1]z + [A_2(M_2 - M_2 M_1 + M_2 A_1 M_1)]z = 0. \tag{15}$$

There are four bracketed terms that need to be analyzed. The sum of the first two, result in the Jacobian matrix for the two-stage problem, where the specification is the temperature and pressure on each stage (see Sridhar and Lucia (1990)). In the third term, A_1 takes all vectors to y_1, which approximately lies in the space spanned by $[x_2, y_2]$. Since $M_2 x_2 = 0$ and $M_2 y_2 = y_2$, the range space of $M_2 A_1 M_1$ is y_2. Furthermore, since $R(A_2) = y_2$, the range space of $[A_2(M_2 - M_2 M_1 + M_2 A_1 M_1)]$ is y_2. The range space of $(I - M_2)$ is the linear span of x_2 and p_2 denoted by $[x_2, p_2]$, while the range space of $M_2 M_1$ is $[y_2, p_2]$.

Consequently, we have the equations,

$$R(I - M_2) = [x_2, p_2] \tag{16}$$

$$R(M_2 M_1) = [y_2, p_2] \tag{17}$$

$$R(M_2 A_1 M_1) = [y_2] \tag{18}$$

and

$$R[A_2(M_2 - M_2 M_1 + M_2 A_1 M_1)] = y_2. \tag{19}$$

The analysis now follows the same pattern as in Sridhar and Lucia (1990). In the absence of an azeotropic condition, $(x_2 = y_2)$, or when an iterate does not lie on a phase boundary, $(y_2 = x_1)$, the matrix $[I - \overline{M}_2(I - \overline{M}_1)]$ can be singular only if the matrices $(I - M_2)$ and $M_2 M_1$ have images that are equal and opposite and lie along the noncomposition eigendirection p_2. The matrices $M_2 A_1 M_1$ and $[A_2(M_2 - M_2 M_1 + M_2 A_1 M_1)]$ do not have images along p_2, since the matrix A has only one nonzero eigenvalue and takes all vectors to y. Therefore, these matrices do not cause a singularity in the Jacobian matrix $[I - \overline{M}_2(I - \overline{M}_1)]$ without violation of the phase-boundary or the nonazeotropic condition. Hence the matrix $[I - \overline{M}_2(I - \overline{M}_1)]$ is singular if and only if the matrix $[I - M_2(I - M_1)]$ is singular, and this will result in a violation of homogeneity, as one of the eigenvalues of M_1 must be negative as shown by Sridhar and Lucia (1990).

The example presented illustrates the correctness of the analysis. The solutions in both problems, the vector v_2, has the values (0.19117, 1.0533, 0.23851) and (0.1191, 0.8609, 0.5209). Both solutions are close to each other and are therefore close to the singular point. The eigenvalue of M_1 is negative (-0.2478 and -4.0607) at both solutions, as the analysis predicts.

Conclusions

Rigorous mathematical analysis is used to prove that the necessary condition for solution multiplicity to exist in a two-stage separation process problem, involving a mixture that has the potential for phase-splitting, is the tendency of the mixture to exhibit a second liquid phase. The false solution multiplicity that is observed in these problems when liquid-liquid phase splitting is not included in the model, is found to vanish when one includes the liquid–liquid phase splitting.

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Notation

V = total vapor flow
R = reflux-ratio
B = bottoms flow rate

Superscript and Subscript

k = iteration number
n_s = maximum number of stages

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