Multistage Standard Specification

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There have been many articles in the last couple of decades demonstrating the existence of solution-multiplicities in distillation problems. Sridhar (1996) lists all these articles. In addition, there have been a few articles analyzing these problems to determine the cause for the existence of this solution multiplicity. Rosenbrock (1960), Doherty and Perkins (1982), Sridhar and Lucia (1989, 1990), Lucia and Li (1992), and Bekiaris et. al. (1993) have tried to provide reasons for the existence of this solution multiplicity.

Recently, Sridhar (1996) rigorously analyzed a two-stage separation process problem where the specification is the standard reflux-ratio and bottoms flow rate. The two-stage problem was solved by first establishing the one-to-one correspondence between the reflux-bottoms specification and the specification of the total vapor flow that exits each stage (VP specification). The VP problem was then analyzed to demonstrate that the existence of solution-multiplicity meant that one of the necessary conditions for the homogeneity of the mixture must be violated. Consequently, it was demonstrated that solution-multiplicities in two-stage separation process problems are a result of the mixture having a tendency to exhibit a second liquid phase. The objective of this article is to rigorously demonstrate that the same is true even in multistage separation process problems when the nonlinear energy balance equations come into play. The VP specification is analyzed to determine the cause for the existence of the solution multiplicities. A one-to-one correspondence between the standard specification and the VP specification is then proved thereby guaranteeing solution uniqueness for the standard specification. The analysis uses the *preliminary results* described in Sridhar (1996).

Multistage VP Problem

Consider a multistage separator where the specification on each stage is the total vapor flow exiting each stage and the pressure (Figure 1). The stages are numbered from top to bottom. Application of Eqs. 2 and 3 in Sridhar (1996) to each stage produces the equations

$$\Delta v_j = \bar{M}_j(\Delta v_{j+1} + \Delta l_{j-1}) \tag{1}$$

and

$$\Delta l_j = \left(I - \bar{M}_j\right)(\Delta v_{j+1} + \Delta l_{j-1}) \tag{2}$$

The matrices $\bar{M}$ and $I - \bar{M}$ are defined in Sridhar (1996); I is the identity matrix. $\bar{M}$, M and A are Jacobian matrices for the single-stage problem. Using Eqs. 1 and 2, we can formulate the multistage separation process problem where one needs to determine all the molar vapor component flows that exit each stage as a fixed point iteration as

$$v^{k+1} = v^k - [F']^{-1}F(v^k) \tag{3}$$

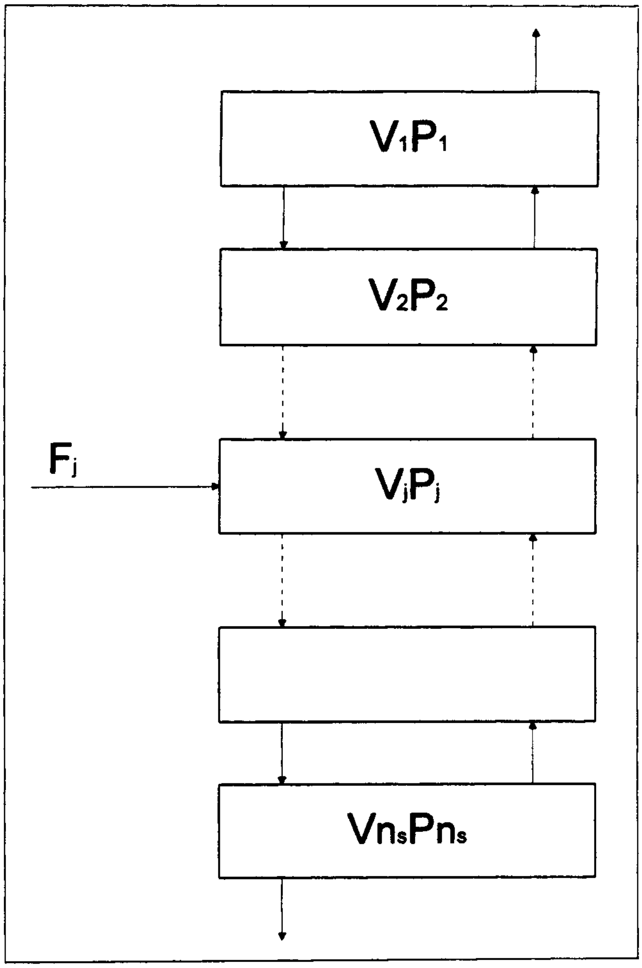

Figure 1. Multistage VP problem.

where $v^T = (v_2^T, v_3^T, \ldots, v_{n_s}^T)^T$, represents the vector of molar component flows that exit each stage, ($\overline{T}$ is temperature), $F' = I - G'$ and

$$G' = \begin{bmatrix} \overline{M}_2(I-\overline{M}_1) & \overline{M}_2 & 0 & \cdot & \vdots \\ \overline{M}_3(I-\overline{M}_2)(I-\overline{M}_1) & \overline{M}_3(I-\overline{M}_2)(I-\overline{M}_1) & \overline{M}_3 & \cdot & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \overline{M}_{n_s} \\ \overline{M}_{n_s}\left(I-\overline{M}_{n_s}-1\right)\ldots(I-\overline{M}_1) & \cdot & \cdot & & \overline{M}_{n_s}\left(I-\overline{M}_{n_s}-1\right) \end{bmatrix}. \quad (4)$$

v_1 is not a fixed point variable as it is fixed when v_2 is fixed. k is the iteration number. $F(v)$ represents the set of equations for the multistage separation process problem. Again, as in the two-stage case discussed by Sridhar (1996), the solution multiplicity is a result of the singularity of the Jacobian matrix F'. In the next section, it is shown that a singularity in the matrix F' will lead to a violation of homogeneity, and, therefore, any solution multiplicity in the multistage problem is a direct consequence of the mixture having a tendency to exhibit a second liquid phase.

Analysis of Multistage VP Problem

In this section, we rigorously analyze the multistage VP problem to determine the cause(s) for the existence of solution-multiplicities in these problems. We start by using Gaussian elimination on the matrix $(I - G')$. Following the approach of Sridhar and Lucia (1990) and Sridhar (1990), we reduce the matrix $(I - G')$ to the form

$$F_{VP} = \begin{bmatrix} A_{11} & 0 & \cdot & \cdot & \cdot & \vdots & \vdots \\ A_{21} & I & 0 & \cdot & \cdot & \vdots & \vdots \\ A_{31} & A_{32} & I & \cdot & \cdot & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ A_{n_s-1,1} & A_{n_s-1,2} & \cdot & \cdot & \cdot & A_{n_s-1,n_s-2} & I \end{bmatrix}. \quad (5)$$

where

$$A_{11} = (I - \overline{M}_2) + \overline{M}_2(\overline{M}_1 + C) \quad (6)$$

the $n_c \times n_c$ matrix C is given by

$$C = -I_{n_s,2}^{-1}\overline{M}_3 I_{n_s,3}^{-1}(I - \overline{M}_2)(I - \overline{M}_1) \quad (7)$$

and

$$I_{n_s,j}^{-1} = \left[I - \overline{M}_{j+1} I_{n_s,j+1}^{-1}\left(I - \overline{M}_j\right)\right]^{-1}, j = n_s - 1, \ldots, 2. \quad (8)$$

I_{n_s,n_s}^{-1} is equal to the Identity matrix I. n_c is the number of components in the mixture. n_s is the maximum number of stages. Note the similarity between this equation and the corresponding equation for the two-stage problem discussed by Sridhar (1996) where the value of C is 0. All block matrices in Eq. 5 are well defined since the condition of induction guarantees that all the inverses are well defined. Since all the diagonal blocks except A_{11} are identity matrices, the singularity of the entire matrix $(I - G')$ can be guaranteed by the singularity of the matrix A_{11}. In order to determine the cause for this singularity, one must try to find a $z \neq 0$ such that

$$A_{11}z = (I - \overline{M}_2)z + \overline{M}_2(\overline{M}_1 + C)z = 0 \quad (9)$$

Since $\overline{M} = (I - A)M$, where the matrices A and M are defined in Sridhar (1996), this equation reduces to

$$A_{11}z = [I - (I - A_2)M_2]z \\ + (I - A_2)M_2[(I - A_1)M_1 + C]z = 0 \quad (10)$$

Further simplification yields

$$A_{11}z = (I - M_2)z + A_2M_2z + M_2(M_1 + C)z - M_2A_1M_1z \\ - A_2M_2(\overline{M}_1 + C)z = 0 \quad (11)$$

From result 2 and Eq. 12 in Sridhar (1996), it can be seen that the range space of the operator A is the vapor composition y and the $R(M) = [y, p]$ and $R(I - M) = [x, p]$. As discussed in Sridhar (1996), the vector x is the liquid phase composition, y is the vapor phase composition, and p is the third eigenvector of the matrix M which we refer to as the "noncomposition" eigenvector. Furthermore, in the absence of an azeotropic or a phase-boundary condition the matrix A_{11} can be singular only if the matrices $(I - M_2)$ and $M_2(M_1 + C)$ have equal and opposite images along the noncomposition vector p_2 as shown by Sridhar and Lucia (1990). The matrices involving A can be ignored as A does not have an image along the noncomposition direction p. The matrix C also has combinations involving the matrix A, and these combinations involving the matrix A can also be ignored as the matrix A does not have an image along the direction p. This will leave us with the Jacobian matrix for the temperature profile specification problem derived and analyzed by Sridhar and Lucia (1990). Imposition of the singularity condition on this Jacobian matrix will lead to a violation of homogeneity as it will result in one of the eigenvalues of the matrix M_1 having a negative value as shown by Sridhar and Lucia (1990). Consequently, the solution-multiplicity in the multistage VP problem is a consequence of the tendency of the mixture to exhibit a second liquid phase.

Standard Specification

The standard specification in the multistage case is the specification of the reflux-ratio, bottoms flow rate, and the input heat duties of the intermediate stages. This is also equivalent to specifying V_2, V_1 and the intermediate heat duties. In the multistage case, there is a one-to-one correspondence between the standard specification and the specification of the total vapor flow that exits each stage. This is because the transformation from the VP specification to the standard specification is a nonsingular one. A simple proof for this is presented in the next few paragraphs.

The energy-balance equation around stage j can be expressed as

$$Q_j = V_j H^{V_j} + L_j H^{L_j} - F_j H^{F_j} - V_{j+1} H^{V_{j+1}} - L_{j-1} H^{L_{j-1}} \quad (12)$$

where Q_j is the input heat-duty to any given stage j. H^L and H^V are the molar enthalpies of the liquid and vapor phases. The liquid flows can be eliminated using the mass balance relationships as

$$L_j = V_{j+1} - V_1 + \sum_{k=1}^{j} F_k \quad (13)$$

Consequently, we can write the energy balance equation around stage j as

$$Q_j = V_j H^{V_j} + \left(V_{j+1} - V_1 + \sum_{k=1}^{j} F_k \right) H^{L_j} - F_j H^{F_j} - \left(V_j - V_1 + \sum_{k=1}^{j-1} F_k \right) H^{L_{j-1}} - V_{j+1} H^{V_{j+1}} \quad (14)$$

Q_j is a function of V_j and V_{j+1}.

Hence, the Jacobian matrix that maps from the VP specification to the standard specification is a bi-diagonal matrix of the form

$$J_{vs} = \begin{bmatrix} \frac{\partial Q_2}{\partial V_3} & \cdot & \cdot & \cdot & \cdot \\ \frac{\partial Q_3}{\partial V_3} & \frac{\partial Q_3}{\partial V_4} & 0 & \cdot & \cdot \\ 0 & \frac{\partial Q_4}{\partial V_4} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \frac{\partial Q_{n_s-2}}{\partial V_{n_s-1}} & \cdot \\ \cdot & \cdot & \cdot & \frac{\partial Q_{n_s-1}}{\partial V_{n_s-1}} & \frac{\partial Q_{n_s-1}}{\partial V_{n_s}} \end{bmatrix}. \quad (15)$$

The expression for the diagonal terms is given by the equation

$$\frac{\partial Q_j}{\partial V_{j+1}} = H^{L_j} - H^{V_{j+1}} + V_j \left(\frac{\partial H^{V_j}}{\partial V_{j+1}} \right) - V_{j+1} \left(\frac{\partial H^{V_{j+1}}}{\partial V_{j+1}} \right) + L_j \left(\frac{\partial H^{L_j}}{\partial V_{j+1}} \right) - L_{j-1} \left(\frac{\partial H^{L_j-1}}{\partial V_{j+1}} \right). \quad (16)$$

For nonideal problems (which are not very wide boiling), the dominant terms are the enthalpy terms and consequently the approximation $(\partial Q_j / \partial V_{j+1}) \approx H^{L_j} - H^{V_{j+1}}$ is valid. Furthermore, for a reference state such that

$$H^L < 0; \quad H^V > 0 \quad (17)$$

it can be seen that the diagonal terms are all negative. The eigenvalues of the Jacobian matrix are the diagonal terms, and since all the terms are nonzero, the Jacobian matrix is a nonsingular one. Furthermore, since vapor and liquid enthalpies are never equal, the nonsingularity is independent of the choice of reference. There is, therefore, a one-to-one correspondence between the VP specification and the standard specification. Hence, even in the multistage case, any solution-multiplicity in the standard specification problem is a result of the solution-multiplicity in the VP problem. Since it has been demonstrated that the solution-multiplicity in the VP problem is a direct consequence of the mixture having a tendency to exhibit a second liquid phase, it can be concluded that in a multistage separation process where the specification is the standard one of reflux-ratio, bottoms flow rate, and the input heat-duties to the intermediate stages, solution-multiplicities can occur only because of the tendency of the mixture to exhibit a second liquid phase.

Conclusions

Rigorous analysis is used to demonstrate that the cause for the existence of the solution multiplicities in multistage separation process problems involving the standard specification is the tendency of the mixture to exhibit a second liquid phase.

Literature Cited

Bekiaris, N., G. A. Meski, C. M. Radu, and M. Morari, "Multiple Steady-States in Homogeneous Azeotropic Distillation," *Ind. Eng. Chem. Res.*, 32, 2023 (1993).

Doherty, M. F., and J. D. Perkins, "On the Dynamics of Distillation Processes: IV. Uniqueness and Stability of the Steady-State in Homogeneous Continuous Distillations," *Chem. Eng. Sci.*, **37**, 381 (1982).

Lucia, A., and H. Li, "Constrained Separations and the Analysis of Binary Homogeneous Separators," *Ind. Eng. Chem. Res.*, **31**, 2579 (1992).

Rosenbrock, H. H., "A Theorem for Dynamic Conservation for Distillation," *Trans. Instn. Chem. Engrs.*, **38**, 279 (1960).

Sridhar, L. N., and A. Lucia, "Analysis and Algorithms for Multistage Separation Processes," *Ind. Eng. Chem. Res.*, **28**, 793 (1989).

Sridhar, L. N., and A. Lucia, "Analysis of Multicomponent Multistage Separation Processes: Fixed Temperature and Pressure Profiles," *Ind. Eng. Chem. Res.*, **29**, 1668 (1990).

Sridhar, L. N., "Analysis of Homogeneous Separation Processes," PhD Thesis, Clarkson Univ., Potsdam, NY (1990).

Sridhar, L. N., "Analysis of Two-Stage Heterogeneous Separation Processes," *AIChE J.*, **42**, 2761 (Oct. 1996).

Manuscript received Mar. 11, 1996, and revision received Nov. 12, 1996.