

# Multiple Steady States in Ideal Two-Product Distillation

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*Simple distillation columns with ideal vapor-liquid equilibrium may display multiple steady-state solutions. Two fundamentally different sources for the multiplicity are presented. Both bring about the unexpected result that increasing reflux makes separation worse in the top part of the column. It corresponds to an unstable operating point.*

*The first type of multiplicity is found for columns with mass or volume inputs (e.g., mass reflux and molar boilup). Even for constant molar flows, the transformation from the actual input units to molar units may become singular (corresponding to a pitchfork bifurcation point), resulting in multiple steady-state solutions. The results are highly relevant in practice, as industrial columns usually have inputs on a mass or volume basis. The second type for specifications on a molar basis (e.g., molar reflux and molar boilup) depends on the presence of an energy balance in the model. The multiplicity is caused by interactions between flows and compositions in the column.*

## Introduction

Multiple steady states (multiplicity) in distillation columns have been studied extensively over the last 30 years. A review on homogeneous (liquid phase) distillation is given by Doherty and Perkins (1982). Rosenbrock (1960, 1962) was the first to prove, using a Krasovskii form of the Lyapunov function, that multiplicity is impossible for the binary case with constant relative volatility [ideal VLE (vapor-liquid equilibrium)] and constant molar flows (neglecting the energy balance). Doherty and Perkins (1982) considered the case with nonideal VLE and constant molar flows. They conclude that multiple steady states are impossible for single-staged "columns" and for any multistage column separating a binary mixture. Sridhar and Lucia (1989) include the energy balance in the model and conclude under certain assumptions that also in this case binary distillation columns will exhibit unique solutions. They do, however, study only two different sets of specifications ( $Q_D, Q_B$  and  $LB$ ).

In a simulation study on multiple solutions for a nonideal mixture of water-ethanol-benzene, Magnussen et al. (1979) do not explain why the multiplicity was predicted only by the NRTL and UNIQUAC activity coefficient models. Their results have been studied and reproduced in several other simulations (Prokopakis and Seider, 1983; Kovach and Seider, 1987; Venkataraman and Lucia, 1988). The main reason for

the multiplicity in this case is the nonideality in terms of potential liquid-liquid phase split in the mixture (Lucia et al., 1989). Widagdo et al. (1989) report multiplicity for another heterogeneous system.

Chavez et al. (1986) and Lin et al. (1987) find multiple steady-state solutions in interlinked distillation columns. The multiplicity they find, however, is due to the interlinking and is not found in single columns.

For the first time, we present examples of multiplicity in distillation columns with ideal thermodynamics. Two fundamentally different types of multiplicity presented are: I. multiplicity in input transformations and II. multiplicity for molar flows.

*I. Multiplicity in Input Transformations.* Common for all the works mentioned above is that the authors have assumed the independent flows (e.g., reflux  $L$  and boilup  $V$ ) to be given on a *molar* basis. In fact, this is not even mentioned as an assumption, but simply taken for granted. The main reason for using molar flows is that they enter directly into the tray material balances and thus determine the separation in the column. In addition, there must have been a belief that using other units for the flows would not alter the fundamental results. However, we believe that in real columns most streams,

in particular liquid streams, are *not* given on a molar basis but rather on a mass or volume basis. The transformation from mass or volume flows to molar flow rates depends on the compositions in the column and is nonlinear. As shown in this work, this transformation is singular in some cases, leading to multiplicity and instability even in ideal two-product distillation.

**II. Multiplicity for Molar Inputs.** We present results showing that also for specification of molar inputs we may get multiplicity in ideal distillation. The multiplicity is found for specification of molar reflux and boilup, and depends on the presence of an energy-balance in the model. The interaction between flows and compositions in the column may lead to multiple solutions, one of which is unstable. Also the multiplicity found here may be experienced in real columns as it is the size of the molar flows that determines separation in distillation. This type of multiplicity will add its importance for simulations since specifications usually are on a molar basis.

The term "multiplicity" refers to the case of *output multiplicity*: when there for a given value of the independent variables (inputs such as reflux and boilup) exists several possible sets of dependent variables (outputs such as product compositions). This is similar to the classical example of multiplicity in exothermic chemical reactors, in which two stable and one unstable steady states exist.

Another kind of multiplicity, in which for a given value of the output there exists several possible sets of inputs *input multiplicity*, is discussed only briefly here. It is quite common in chemical engineering, when there is an extremum in the relationship between the input and the output. For example, for multicomponent distillation columns the relationship between product flow and concentration of intermediate component generally has a maximum, as will be discussed later. In terms of control, output multiplicity is generally related to poles crossing the imaginary axis (unstable operating points), while input multiplicity is related to zeros crossing through the origin (changes in sign of gain and inverse response). A pole at the imaginary axis corresponds to a singularity in the transfer function from input to output, while a zero at the imaginary axis corresponds to a singularity in the transfer function from output to input.

In this article we consider output multiplicity in distillation columns from only a steady-state point of view. The implications for dynamics and control are discussed in another article (Jacobsen and Skogestad, 1990). We start the article by considering multiplicity for the case of input units other than molar (Part I). Here, we assume constant molar flows: we neglect the energy balance. In considering multiplicity for molar inputs (Part II), we include the energy balance in the model. This is a requirement for getting multiple steady states for molar inputs. Finally, we present results for the case when both types of output multiplicity may appear.

**Table 1. Data for Example Columns\***

Example	$z_F$	$F$	$\alpha$	$N$	$N_F$	$M_1$	$M_2$
Methanol-Propanol	0.50	1	3.55	8	4	32.04	60.10
One-Stage Column	0.50	1	4.0	1	1	20	40
Propanol-Acetic Acid	0.50	1	**	1	1		

\*Feed is saturated liquid; total condenser with saturated reflux

\*\* $\alpha$  varies from 1.85 to 2.25

## I. Multiple Steady States for Mass or Volume Inputs

We consider the simplest case with binary mixtures, constant relative volatility (ideal VLE), and constant molar flows. Similar results are obtained also in columns with more nonideal behavior.

Doherty and Perkins (1982) have shown that multiplicity is impossible in the binary, constant molar flow case; for a given  $L$  and  $V$  (molar basis), there exists only one possible steady state. For example, the top composition  $y_D = g(L, V)$  is a unique function of  $L$  and  $V$  in the constant molar flow case. This also applies if we select as independent variables any other two independent combinations of *molar* flows, for example,  $D$  and  $L$ . However, in real operating columns both flows are almost never specified on a molar basis. In the following we mainly consider the  $L_w V$  configuration, with reflux specified on mass basis and with boilup on molar basis. Also discussed is the effect of choosing other flows as independent inputs, for example, the  $D_w V$  and  $LQ_B$  configuration. In the latter case, the heat input  $Q_B$ , which indirectly sets  $V$ , is used as an independent variable.

### Introductory Example

**Example 1.** Data for a methanol-propanol column are given in Table 1. The assumption of the constant molar flows implies constant vapor and liquid molar flows through the column (except at the feed location). Boilup  $V$  is fixed at 2.0 kmol/min and we consider the steady-state solutions with reflux  $L_w$  in the range 47 to 55 kg/min. The results are summarized in Table 2 and in Figure 1. (The numerical results were actually obtained by varying  $y_D$  with fixed  $V$ .) For  $L_w$  between 48.8 and 52.2 kg/min, there exists three steady-state solutions. For example, with  $V=2.0$  kmol/min and  $L_w=50$  kg/min, we get the three steady states (II, III and IV) in Table 2. With fixed values of  $L_w$  and  $V$ , the solutions on the upper and lower branches on Figure 1 are stable, whereas the solutions on the intermediate branch (e.g., steady state III) are unstable. The reason for this multiplicity is the transformation  $L=L_w/M$  between mass and molar reflux. As seen from Figure 1, this transformation is not unique for  $L_w$  in the region 48.8 and 52.2 kg/min.

### Specification of Flows in Distillation Columns

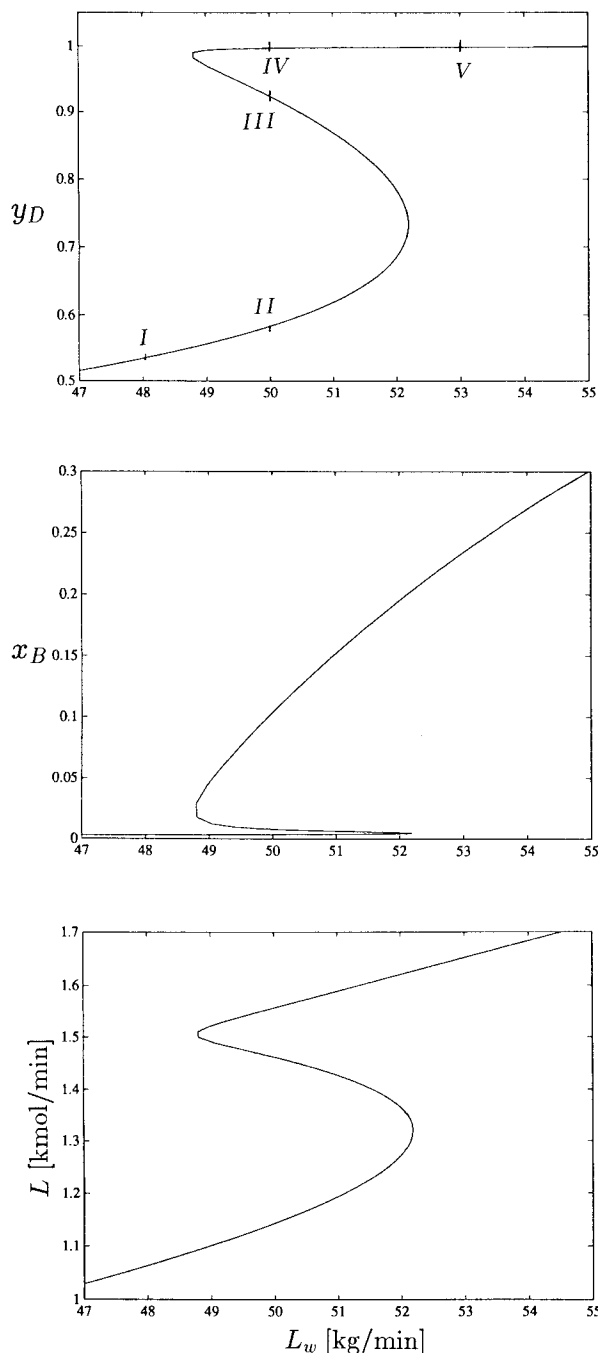
We discuss here which units are most often encountered for the flows in distillation columns during operation.

**Configurations.** Consider the two-product distillation column in Figure 2. If the feed to the column is given there are

**Table 2. Steady-State Solutions for Methanol-Propanol Column:  $V=2.0$  kmol/min and  $L_w$  48–53 kg/min\***

Steady State	$L$ kmol/min	$D$ kmol/min	$L_w$ kg/min	$y_D$	$x_B$
I	1.064	0.936	48.00	0.534	$3.10 \times 10^{-3}$
II	1.143	0.857	50.00	0.584	$3.50 \times 10^{-3}$
III	1.463	0.537	50.00	0.9237	$7.60 \times 10^{-3}$
IV	1.555	0.445	50.00	0.9969	0.104
V	1.650	0.350	53.00	0.9984	0.233

\*Assuming constant molar flows



**Figure 1. Multiple steady states for mass reflux  $L_w$  for the methanol-propanol column assuming constant molar flows.**

Boilup  $V = 2.0$  kmol/min

at least four flows that might be specified: reflux  $L$ , boilup  $V$ , distillate (top product) flow  $D$ , and bottoms flow  $B$ . However, for a given column there are only two degrees of freedom at steady state: only two of these flows may be specified independently. A specific choice of two independent flows is denoted as a "configuration." The term comes from process control and is the independent variables from a control point of view. Let,  $n$  (or no subscript) denote molar flow in kmol/min,  $w$  (or as subscript) mass flow in kg/min,  $q$  (or as subscript)

volumetric flow in  $\text{m}^3/\text{min}$ . For example,  $L$  is reflux in kmol/min,  $L_w$  in kg/min, and  $L_q$  in  $\text{m}^3/\text{min}$ . Furthermore,  $v$  (m/min) is the linear velocity,  $M$  (kg/kmol) is the molecular weight,  $\rho$  ( $\text{kg}/\text{m}^3$ ) is the density, and  $A$  ( $\text{m}^2$ ) is the cross-sectional area. We have

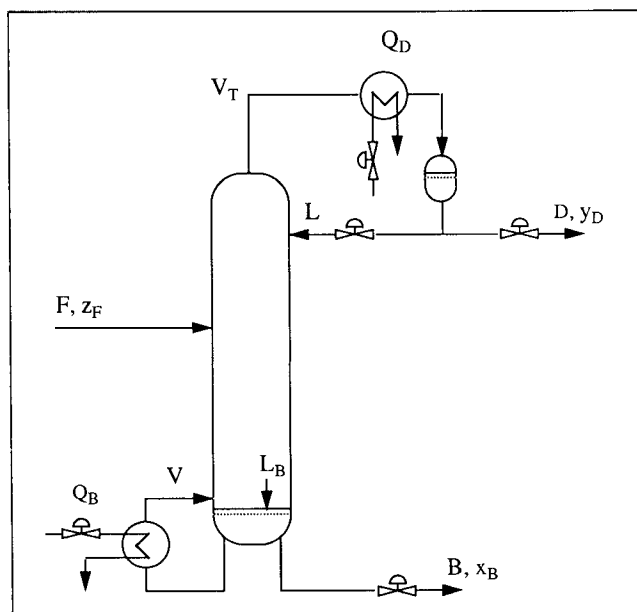
$$w = Mn = \rho q \quad (1)$$

$$q = Mn/\rho = Av \quad (2)$$

For example,  $L_w = \rho L_q = ML$ . The molecular weight  $M$  is often a strong function of composition (operating point). For liquids, the density  $\rho$  is usually a relatively weak function of composition, but the molar volume  $M/\rho$  is often a strong function of composition. For gases, the molar volume  $M/\rho$  is dependent weakly on composition.

**Liquid Flows without Measurements.** In this case, the liquid flow is usually changed either by adjusting a valve position or the power to a pump. In the first case, assume that the pressure drop  $\Delta p v$  across the valve is constant. Then, for turbulent flow  $\Delta p v = \hat{k}(z)\rho v^2 = k(z)q w$ , where  $k$  is a function of the valve position  $z$ . That is, fixing the valve position is the same as fixing the geometric average of mass and volumetric flow rate,  $\sqrt{q w}$ . In the second case, assume that the pressure drop across the pump  $\Delta p_p$  is fixed. The power is given by  $P = \Delta p_p q$ , and fixing the power is the same as fixing the volumetric flow rate  $q$ . In this case it is most natural to specify the flow on a volumetric or mass basis (as noted above these usually are not too different). In the special case, if a partial condenser is used, then the reflux may be given indirectly by the cooling duty and it may be reasonable to assume reflux to be given on a molar basis.

**Liquid Flows with Measurements.** In many cases, the valve position or pump power is adjusted to keep the *measured* value of the flow constant. Most liquid flow measurements are on a mass or volumetric basis (or mixed). For example, the flow is often inferred by measuring the pressure drop over a fixed



**Figure 2. Two product distillation column.**

restriction in a pipe, such as an orifice or venturi. As noted above, the pressure drop is proportional to the product  $q_w$ , and hence one gets a measure of the geometric average of the mass and volumetric flow rate. Other measuring devices give a direct measure of volumetric flow rate  $q$ , such as displacement meters, turbine meters, and magnetic meters. Direct measurements of mass flow rates also exist. However, for liquids no direct measurement of molar flow rate is in common use.

**Boilup  $V$ .** This is a vapor flow. However, usually the amount of boilup is given indirectly by the heat input  $Q_B$  to the reboiler. An energy balance around the reboiler gives:

$$Q_B = V(H_1^V - H_2^L) + B(H_1^L - H_2^L) \quad (3)$$

where  $H_i^V$  and  $H_i^L$  are the molar enthalpies on tray  $i$  of the vapor and liquid phases, respectively. Neglecting changes in the liquid enthalpy yields

$$Q_B \approx V(H_1^V - H^L) = V\Delta H_1^{\text{vap}} \quad (4)$$

where  $\Delta H_1^{\text{vap}}$  is the heat of vaporization in the reboiler. In many cases,  $\Delta H_1^{\text{vap}}$  depends only weakly on composition, and specifying  $Q_B$  is almost the same as fixing the molar boilup  $V$ . However, for widely different components or strongly nonideal systems, this may not be the case.

Therefore, it can be summarized that:

- For liquids, it is most natural to specify the flow rate on a volumetric or mass basis. In a distillation column,  $L$ ,  $D$ , and  $B$  are usually liquids.

- It seems reasonable in many cases to assume the boilup  $V$  to be given on a molar basis.

## $L_wV$ Configuration

This choice of independent variables is very common industrially, and the introductory example showed that it may display multiple steady states. Consider the simplest case with a binary separation, and let subscript 1 denote the most volatile ("light") component and 2 the least volatile component. The transformation between mass and molar reflux is given by:

$$L = L_w/M; \quad M = y_D M_1 + (1 - y_D) M_2 \quad (5)$$

where  $M_i$  is the mole weight of the individual components. We might expect  $L$  to increase uniformly with  $L_w$ :  $dL/dL_w > 0$  such that an increase in the mass reflux  $L_w$  will always increase the molar flow  $L$ . However, because  $M$  is a function of composition ( $y_D$ ) and thereby of  $L_w$  this may not be the case. Assume that the molar boilup  $V$  is fixed, and differentiate both sides of  $L_w = LM$  with respect to  $L$ :

$$\left(\frac{\partial L_w}{\partial L}\right)_V = M + L \left(\frac{\partial M}{\partial y_D}\right)_V \left(\frac{\partial y_D}{\partial L}\right)_V \quad (6)$$

A possible negative slope,  $(\partial L_w/\partial L)_V < 0$ , will correspond to an unstable operating point and is explained by two opposing effects. Since these effects have different time constant, it is most instructive to consider the dynamic response (although we are here interested in the steady-state effect). Consider an

increase in  $L$ . Initially,  $L_w = LM$  always increases, because  $M$  is unchanged. However, as a result of the increase in  $L$ , the fraction of light component will start increasing (see Appendix B) and hence  $M$  will change. If  $M_2 > M_1$  (which is usually the case),  $M$  will decrease and the resulting decrease in  $L_w$  may eventually offset the initial increase. Note that multiple steady states and instability will not occur for the  $L_wV$  configuration when  $M_2 < M_1$ .

The instability may be explained physically as follows: Assume  $M_2 > M_1$  and that  $L_w$  and  $V$  are constant. The column is perturbed slightly such that  $y_D$  increases by  $\Delta y_{D1}$ . This reduces  $M$  and thus increases  $L$  by  $\Delta L_1 = (\partial L/\partial y_D)_{L_w} \Delta y_{D1}$ . The increased  $L$  will subsequently increase  $y_D$  even more. If this second increase  $\Delta y_{D2} = (\partial y_D/\partial L)_V \Delta L_1$  is larger than the initial perturbation  $\Delta y_{D1}$ , then the column will start drifting away and we have instability. The condition for instability then becomes  $\Delta y_{D2} > \Delta y_{D1}$  or

$$\left(\frac{\partial y_D}{\partial L}\right)_V \left(\frac{\partial L}{\partial y_D}\right)_{L_w} > 1 \quad (7)$$

which may be shown to be equivalent to having a negative slope in Eq. 6. Note that this derivation is not rigorous as it is based on steady-state arguments only. A more detailed analysis using dynamics is given in Jacobsen and Skogestad (1990).

The fact that an operating point is unstable does not necessarily imply that there exists another stable operating point for the same values of  $L_w$  and  $V$  (see Figure 3c). For example, if  $L$  starts increasing as discussed above, it may reach a point where the specified value of  $L_w$  corresponds to a  $L > V_T$ . This is impossible as it would drain the condenser or require a negative distillate flow  $D$ . In practice, the operator would then have to increase  $V$  or reduce  $L_w$ . However, as shown in example 1, there does exist cases where multiple steady states exist for a given  $L_w$  and  $V$ . This happens when there for the given  $V$  exist points (values of  $L_w$ ), where the transformation from  $L_w$  to  $L$  is singular ( $\partial L/\partial L_w = \infty$  or  $\partial L_w/\partial L = 0$  in Eq. 6).

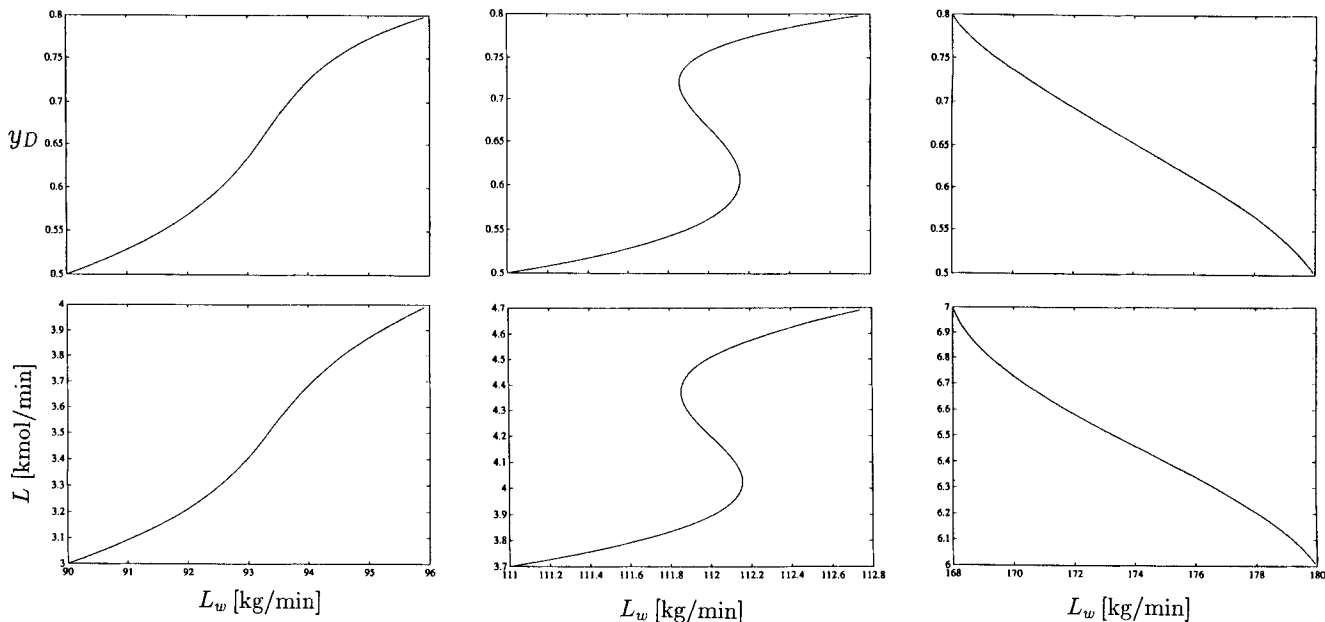
## Analytical treatment

To understand the characteristics of columns, in which multiplicity and instability are most likely to occur, the ideal case with constant molar flows and constant relative volatility is considered. From Eq. 6 we know that for binary separations instability occurs at operating points where

$$y_D + L \left(\frac{\partial y_D}{\partial L}\right)_V > \frac{M_2}{M_2 - M_1} \quad (8)$$

Here it was assumed that  $M_2 > M_1$  which is a necessary condition for instability for this configuration. To understand the implications of condition 8, we need an analytical expression for the gain  $(\partial y_D/\partial L)_V$ . We shall consider a one-stage column where exact expressions are easily derived, and subsequently a multistage column where good approximations exist.

**Example 2.** Consider the simple column in Figure 4 with one theoretical stage (the reboiler) and a total condenser. This is the simplest column for which the instability and multiplicity may be observed. Of course, such a column will never be operated in practice because the reflux is simply wasting energy



**Figure 3. Steady-state solutions as a function of mass reflux  $L_w$  for one-stage column with  $\alpha = 4$ .**

a.  $V = 4.0$  kmol/min: unique stable solution; b.  $V = 4.7$  kmol/min: multiple solutions; c.  $V = 7.0$  kmol/min: unique unstable solution

and has no effect on separation. The following equations apply:

$$Fz_F = Dy_D + Bx_B \quad (9)$$

$$D = V - L; \quad B = L + F - V \quad (10)$$

$$\alpha = \frac{y_D(1-x_B)}{(1-y_D)x_B} \quad (11)$$

$$L_w = LM; \quad M = y_D M_1 + (1-y_D)M_2 \quad (12)$$

Let  $\alpha = 4.0$ ,  $z_F = 0.5$ ,  $M_1 = 20$  kg/kmol and  $M_2 = 40$  kg/kmol. Consider a nominal operating point with  $V = 4.7$  kmol/min and  $L = 4.2$  kmol/min. From Eqs. 9-12 we get  $D = B = 0.5$  kmol/min,  $x_B = 0.33$ ,  $y_D = 0.67$ , and  $L_w = 112$  kg/min. However, this is not the only possible steady state with  $V = 4.7$

kmol/min and  $L_w = 112$  kg/min. Table 3 shows that there exist two other solutions with  $y_D = 0.56$  and  $y_D = 0.76$ , respectively. The results are shown in Figure 3b. Note that the nominal steady state with  $y_D = 0.67$  is in the region where the relationship between  $L_w$  and  $L$  has a negative slope and thus is unstable with  $V$  and  $L_w$  as independent variables.

The effect of increasing the internal flows is illustrated by Figure 3c where  $V$  has been increased from 4.7 to 7.0 kmol/min. Here, the relationship between  $L$  and  $L_w$  has a negative slope over the entire region. The two stable branches have disappeared and we have only one *unstable* solution for any given  $L_w$ . On the other hand, for low values of the internal flows there exists only one *stable* solution. This is illustrated by Figure 3a where  $V = 4.0$  kmol/min.

Differentiating Eqs. 9-11 yields the following exact expression for the gain:

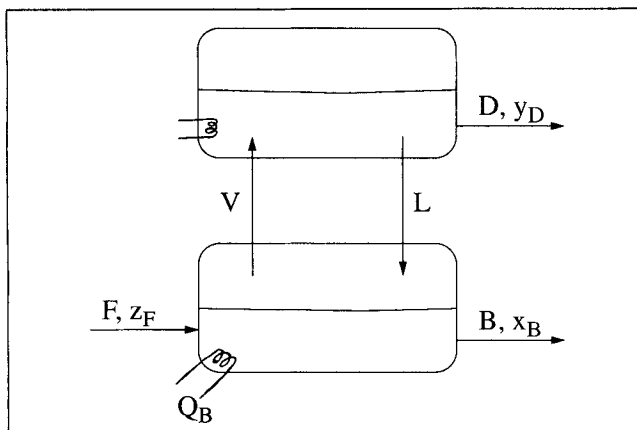
$$\left(\frac{\partial y_D}{\partial L}\right)_V = \frac{(1-y_D)y_D(y_D-x_B)}{Bx_B(1-x_B) + Dy_D(1-y_D)} \quad (13)$$

Condition 8 for instability then becomes:

$$y_D + L \frac{(1-y_D)y_D(y_D-x_B)}{Bx_B(1-x_B) + Dy_D(1-y_D)} > \frac{M_2}{M_2 - M_1} \quad (14)$$

**Table 3. Steady-State Solutions for One-Stage Column:  $V = 4.7$  kmol/min and  $L$  3.7-4.7 kmol/min**

$L$ kmol/min	$D$ kmol/min	$L_w$ kg/min	$y_D$
3.7	1.0	111.00	0.500
3.9	0.8	112.01	0.564
4.2	0.5	112.00	0.667
4.5	0.2	111.99	0.756
4.7	0.0	112.80	0.800



**Figure 4. One-stage column with total condenser.**

The gain (Eq. 13) varies only moderately with operating conditions for a single-stage column. Thus, we conclude from (Eq. 14) that any operating point may be unstable with the  $L_wV$  configuration, provided the internal flows ( $L$ ) are sufficiently large.

To test stability of the nominal operating point in example 2, let  $D=B=0.5$ ,  $x_B=0.33$ ,  $y_D=0.67$ ,  $M_2/(M_2-M_1)=2$  and derive from Eq. 14 the instability condition  $L>4.0$ . Since we have  $L=4.2$ , the operating point is unstable.

**Multistage Column.** Somewhat surprisingly, the analytical results for the one-stage column carry over almost directly to the multistage case. For example, expression 13 for the gain  $(\partial y_D/\partial L)_V$  is a good approximation for multistage columns with constant relative volatility and constant molar flows (e.g., Skogestad and Morari, 1987b). The reason is that the overall separation factor

$$S = \frac{y_D(1-x_B)}{(1-y_D)x_B} \quad (15)$$

usually does not change very much with operating conditions and may be assumed constant when estimating the gain (for a one-stage column the separation factor is equal to the relative volatility  $\alpha$ ). Equation 15 then takes the place of Eq. 11, and assuming  $S$  constant yields the same expression for the gain as for the one-stage column. [The exact expression when  $S$  is not constant is

$$\left(\frac{\partial y_D}{\partial L}\right)_V = \frac{(1-y_D)y_D(y_D-x_B)}{Bx_B(1-x_B)+Dy_D(1-y_D)} \times \left[ 1 + \frac{Bx_B(1-x_B)}{y_D-x_B} \left(\frac{\partial \ln S}{\partial L}\right)_V \right] \quad (16)$$

The only assumption made here is the one of constant molar flows such that Eq. 10 applies. Equation 16 shows that the effect of changes in  $S$  on the gain is always negligible when the bottom product is pure,  $x_B \approx 0$ .]

The main difference from the single-stage case is that in a multistage column the compositions and the gain (Eq. 13) may change drastically with operating conditions. To study this effect consider the following three cases:

I. Top impure, bottom pure [ $x_B \ll (1-y_D)$ ]. Equation 13 is simplified to:

$$\left(\frac{\partial y_D}{\partial L}\right)_V \approx \frac{y_D-x_B}{D} \approx \frac{y_D}{D} \quad (17)$$

II. Equal purity in top and bottom [ $x_B \approx (1-y_D)$ ]. Equation 13 is simplified to:

$$\left(\frac{\partial y_D}{\partial L}\right)_V \approx \frac{y_D-x_B}{F} \approx \frac{1}{F} \quad (18)$$

III. Top pure, bottom impure [ $x_B > (1-y_D)$ ]. Equation 13 is simplified to:

$$\left(\frac{\partial y_D}{\partial L}\right)_V \approx \frac{1-y_D}{Bx_B} \approx 0 \quad (19)$$

Recall the instability condition (Eq. 8). We conclude that instability is unlikely in case III, when the top product is pure relative to the bottom product. The approximate condition for instability in case I when the bottom product is pure ( $x_B \approx 0$ ) becomes:

$$y_D(1+L/D) > \frac{M_2}{M_2-M_1} \quad (20)$$

From this derivation, we conclude that instability with the  $L_wV$  configuration is most likely to be observed in the following cases: 1. bottom product relatively pure [ $x_B \ll (1-y_D)$ ]; 2. mole weight of light component much smaller than of heavy component; and 3.  $L/D$  large. We note that any column with  $M_1 < M_2$  may become unstable with sufficiently large  $L/D$ .

In practice, conditions 2 and 3 often are not satisfied at the same time. First, large values of  $L/D$  should be used only for difficult separations ( $\alpha$  close to one) which usually involve components with similar mole weights. Second, columns with large values of  $L/D$  (greater than five according to Luyben, 1979) usually are not operated with the  $L_wV$  configuration at all. The reason usually given for this is that controlling the condenser level with a small stream is difficult, and reflux  $L$  should be used for level control whenever  $L/D$  is large. While this argument certainly is true, it is also possible that open-loop instability of the  $L_wV$  configuration may have caused the poor observed behavior.

## Other Configurations

### $D_wV$ configuration

We have

$$D = D_w/M \quad (21)$$

where  $M$  is defined by Eq. 5. Differentiating yields the following condition for instability:

$$\left(\frac{\partial D_w}{\partial D}\right)_V = M + D(M_1 - M_2) \left(\frac{\partial y_D}{\partial D}\right)_V < 0 \quad (22)$$

Note that the condition for instability is almost independent of the size of the internal flows. Since  $(\partial y_D/\partial D)_V$  is essentially always negative (Appendix A), we see from Eq. 22 that a necessary condition for instability or singularity is that  $M_1 > M_2$ : the most volatile component must have the largest mole weight. This implies that we have the opposite case as compared to the  $L_wV$  configuration. Thus, instability and multiple steady states in a given operating point with the  $L_wV$  configuration is avoided by using the  $D_wV$  configuration instead. During operation, this is accomplished by changing condenser level control from using distillate to using reflux.

In fact, it seems very unlikely that multiple steady states or instability may ever occur for this configuration: consider the case  $M_1 > M_2$ . As we have no multiplicity for the molar  $DV$  configuration (Doherty and Perkins, 1982) the gains  $(\partial y_D/\partial D)_V$  and  $(\partial x_B/\partial D)_V$  are negative (see Appendix 1). An analysis of the differentiated component material balance (Eq. 9), then gives  $(\partial y_D/\partial D)_V > -y_D/D$ . For the worst case with  $(\partial y_D/\partial D)_V = -y_D/D$  the condition for instability (Eq. 22) becomes  $M_2 < 0$  which of course is impossible.

### $LQ_B$ configuration

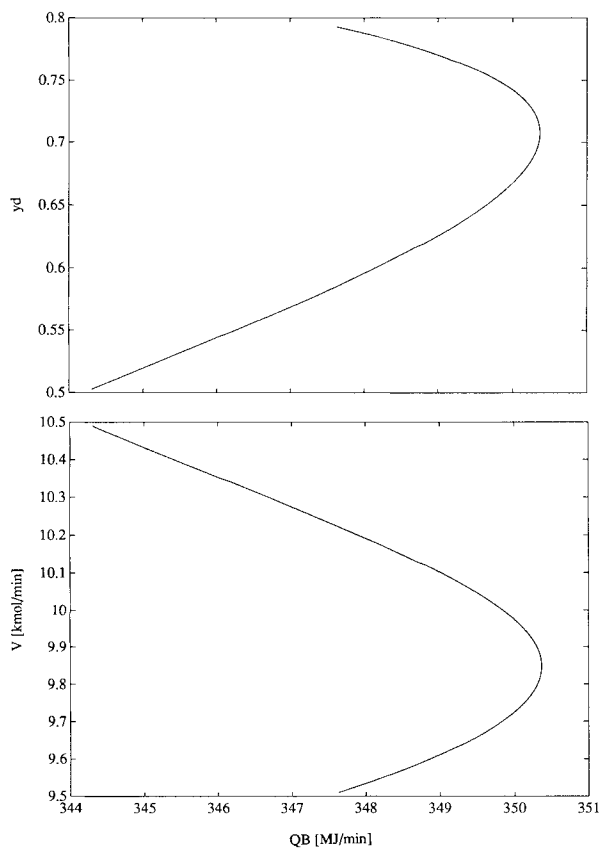
We have assumed the boilup to be measured on a molar basis. However, as discussed previously, the boilup will often be set indirectly by the amount of heat input,  $Q_B$ , to the reboiler. The energy balance for the reboiler when liquid enthalpy changes are neglected yields (Eq. 4):

$$V \approx Q_B / \Delta H^{\text{vap}}(x_B) \quad (23)$$

Here we have indicated that the heat of vaporization,  $\Delta H^{\text{vap}}$ , in general depends on the composition in the reboiler,  $x_B$ . Note the similarity between this transformation and the transformation  $L = L_w/M(y_D)$  studied above. For simplicity, assume reflux to be kept constant on a molar basis, and consider a binary mixture where  $x_B$  is the mole fraction of light component. The differential of  $Q_B$  with respect to  $V$  becomes:

$$\left(\frac{\partial Q_B}{\partial V}\right)_L = \Delta H^{\text{vap}} + V \frac{d\Delta H^{\text{vap}}}{dx_B} \left(\frac{\partial x_B}{\partial V}\right)_L \quad (24)$$

and we have instability if this slope is negative. For constant molar flows  $(\partial x_B / \partial V)_L$  is always negative (Appendix B), and we see from Eq. 24 that a necessary condition for instability or singularity is that  $d\Delta H^{\text{vap}}/dx_B > 0$  for the actual value of  $x_B$ . This is not too common in practice. It will be the case when the lightest component has the largest heat of vaporization,



**Figure 5. Multiple steady states for heat input  $Q_B$  for one-stage propanol-acetic acid column.**  
Reflux  $L = 9.5$  kmol/min

but may also happen for nonideal systems where this is not the case.

A similar analysis as for the  $L_wV$  configuration shows that instability is most likely for the  $LQ_B$  configuration when the internal streams are large and when the bottom product is relatively unpure.

**Example 3: One-Stage Propanol-Acetic Acid Column.** Propanol is the more volatile component and the relative volatility,  $\alpha$ , is in the range 1.85 to 2.25. The heat of vaporizations is 41.2 kJ/mol for propanol and 23.7 kJ/mol for acetic acid, implying that multiplicity is possible. In this example, we use the exact energy balance (Eq. 3) and the Van Laar activity coefficient model the vapor-liquid equilibrium. Consider a nominal operating point with reflux  $L = 9.5$  kmol/min and boilup  $Q_B = 349$  MJ/min. We obtain two steady-state solutions for these specifications: 1)  $y_D = 0.596$  and 2)  $y_D = 0.787$ . If we could allow for negative product flows, we would get three solutions. Solution 1 is unstable while solution 2 is stable. The multiplicity is illustrated graphically in Figure 5.

### Other cases

As seen from the above, possible singularities in the transformation of streams vary depending on the choice of configuration, or in terms of steady-state simulation, the specifications of flows. Singularity occurs when  $\partial w / \partial n$  is zero. For liquid flows, we conclude that singularity may occur for reflux  $L_w$  and bottoms product  $B_w$  when  $M_2 > M_1$ , while distillate  $D_w$  and boilup  $V_w$  require the opposite, i.e.,  $M_1 > M_2$ . This is easily seen from the sign of the respective gains (Appendixes 1 and 2). However, as noted above, singularity seems unlikely to occur for  $D_w$  or  $B_w$ . For ratio inputs, singularities are also unlikely in most cases. For example,  $(L/D)$  is independent of composition provided that the column has a total condenser and  $L$  and  $D$  are measured in the same units.

## II. Multiple Steady States for Molar Inputs

We have discussed the multiplicity resulted from the use of input units other than molar. In Part II, we consider the multiplicity when molar reflux and boilup are used as specifications (i.e.,  $LV$  configuration). This type of multiplicity does not occur for the case of constant molar flows, and thus depends on the energy balance.

### LV Configuration

**Example 1.** We will continue to study the methanol-propanol column in Table 1. We now include an energy balance on each tray where we previously assumed constant molar flows (see Table 4):

$$Q_i + V_{i-1}H_{i-1}^V + L_{i+1}H_{i+1}^L - V_iH_i^V - L_iH_i^L + F_iH_i^F = 0 \quad (25)$$

Here, subscript  $i$  denotes tray number (trays are numbered from the bottom). We assume constant relative volatility as before, while enthalpies are computed from the equations given in Table 4. Molar boilup  $V$  is kept constant at 4.5 kmol/min and we consider solutions for molar reflux between 4.6 and

**Table 4. Saturated Molar Enthalpies (kJ/mol) for Methanol-Propanol System at a Pressure of 1 atm\***

$$H_i^L = 16.67 \times e^{-1.087x_i}$$

$$H_i^V = 13.49 \times e^{-3.98x_i} + 43.97 \times e^{-0.088x_i}$$

\*Reference state: pure components as liquid at 0°C, where  $x_i$  denotes mole-fraction methanol in liquid phase.

4.75 kmol/min. Some solutions in Table 5 show that for  $L = 4.70$  kmol/min we get the three solutions, II, III, and IV. Solution III is found to be unstable. The multiplicity is illustrated in Figure 6.

Similar results were obtained with commercial simulators using consistent thermodynamic data for VLE and enthalpy (e.g., SRK equation of state) which satisfy the Gibbs-Duhem equation.

**Analytical Treatment.** The example above shows that we may have multiplicity for the  $LV$  configuration even in ideal binary distillation. To understand the source of the multiplicity, the transformation between the  $DV$  configuration, which yields unique solutions in terms of compositions in all examples studied, and the  $LV$  configuration is examined.

Consider the gain  $(\partial y_D / \partial L)_V$ . This gain is usually positive, but as seen above (Figure 6) it may be negative in some cases and the operating point will then be unstable. We have:

$$\left(\frac{\partial y_D}{\partial L}\right)_V = \left(\frac{\partial y_D}{\partial D}\right)_V \left(\frac{\partial D}{\partial L}\right)_V \quad (26)$$

where the gain  $(\partial y_D / \partial D)_V$  is essentially always negative (Appendix A). For constant molar flows  $(\partial D / \partial L)_V = -1$  and  $(\partial y_D / \partial L)_V$  is positive. However, due to the energy balance, the flows *inside* the column depend on the compositions and instability occurs if

$$\left(\frac{\partial D}{\partial L}\right)_V > 0 \quad (27)$$

Using the material balances around the condenser ( $V_T = L + D$ ) and around the column interior ( $L + V = L_B + V_T$ ) yields:

$$\left(\frac{\partial D}{\partial L}\right)_V = -1 + \left(\frac{\partial V_T}{\partial L}\right)_V = -\left(\frac{\partial L_B}{\partial L}\right)_V \quad (28)$$

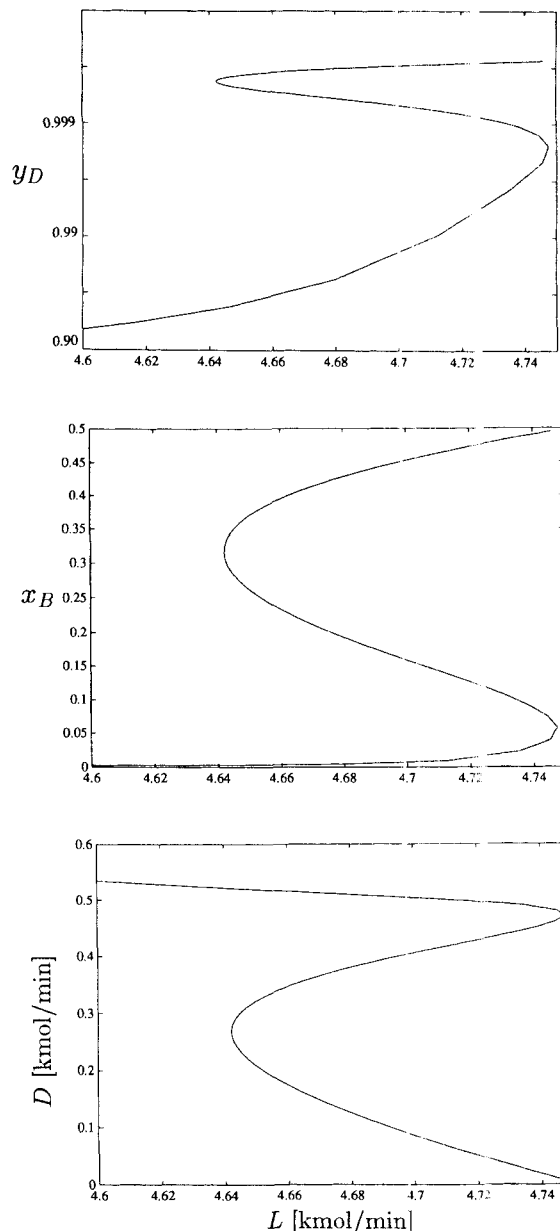
and Eq. 27 is equivalent to:

$$\left(\frac{\partial L_B}{\partial L}\right)_V < 0 \quad (29)$$

**Table 5. Steady-State Solutions for Methanol-Propanol Column with Boilup  $V = 4.5$  kmol/min\***

	$L$ kmol/min	$D$ kmol/min	$y_D$	$x_B$
I	4.60	0.535	0.9324	$2.474 \times 10^{-3}$
II	4.70	0.505	0.9845	$6.344 \times 10^{-3}$
III	4.70	0.406	0.9993	0.1587
IV	4.70	0.0866	0.9997	0.4526

\*The energy balances are included in the model.



**Figure 6. Multiple steady states for molar reflux  $L$  for methanol-propanol column.**

Boilup  $V = 4.5$  kmol/min  
Energy balance included

Here  $V_T$  denotes vapor flow from top tray to the condenser, and  $L_B$  is liquid flow from bottom tray to the reboiler. This means that in the unstable region an increase in reflux will result in a decrease in liquid flows in the lower parts of the column. Figure 7 shows two liquid flow profiles in the unstable region for the methanol-propanol column.

Neglecting changes in liquid enthalpy with composition yields the following relationship between boilup  $V$  and vapor flow from top tray  $V_T$  (liquid feed):

$$V_T = \frac{\Delta H_1^{\text{vap}}}{\Delta H_T^{\text{vap}}} V \quad (30)$$

The instability condition (Eq. 27) is equivalent to:



$$\left(\frac{\partial L}{\partial D}\right)_V = -1 + \left(\frac{\partial V_T}{\partial D}\right)_V > 0 \quad (31)$$

and we get

$$\left(\frac{\partial L}{\partial D}\right)_V = -1 + \frac{\left(\frac{d\Delta H^{\text{vap}}}{dx}\right)_{x=x_B} \left(\frac{\partial x_B}{\partial D}\right)_V \Delta H_T^{\text{vap}} - \left(\frac{d\Delta H^{\text{vap}}}{dx}\right)_{x=x_T} \left(\frac{\partial x_T}{\partial D}\right)_V \Delta H_1^{\text{vap}}}{(\Delta H_T^{\text{vap}})^2} V \quad (32)$$

Assuming no multiplicity for the  $DV$  configuration implies that  $(\partial x_i/\partial D)_V$  always will be negative (Appendix 1). Furthermore, in most systems  $(d\Delta H^{\text{vap}}/dx)$  will be negative, i.e., the heat of vaporization decreases with fraction of most volatile component. From Eq. 32 we see that in this case instability will be most likely when the magnitude of  $(\partial x_B/\partial D)_V$  is large and the magnitude of  $(\partial x_T/\partial D)_V$  is small. This will happen when there are high purity in the top and a relatively unpure bottom product. This agrees with the results found for the methanol-propanol column (Table 5 and Figure 6), where instability was found for top composition between 0.9984 and 0.9996, and bottom composition between 0.3152 and 0.0580. In the case where  $(d\Delta H^{\text{vap}}/dx)$  is positive, instability will be most likely when the bottom product is pure while the top product is relatively unpure. We also see from Eq. 32 that instability is favored by high internal flows (i.e., large  $V$ ).

Similar relations are obtained when considering changes in molar boilup. In this case, transformation between the  $LB$  and  $LV$  configuration is considered. Instability is equivalent to:

$$\left(\frac{\partial V_T}{\partial V}\right)_L < 0 \quad (33)$$

We conclude that the multiplicity found for the  $LV$  configuration is due to the interactions between flows and compositions in the column. The flows affect compositions through the material balances, while compositions will affect the flows through the energy balances. In some regions, this interaction leads to an inversed response in compositions compared to that for constant molar flows [e.g.,  $(\partial y_D/\partial L)_V < 0$ ] and we get multiple steady-state solutions, one of which is unstable. Rademakar et al. (1975) claim that the influence of compositions on flow rates usually will be negligible. Our results show that the influence in many cases will be crucial, leading even to inversed gains and instability in some cases.

### Combination of Mass Inputs and Energy Balance

The two types of multiplicity discussed may occur in the same region of operation for a column. Consider the  $L_wV$  configuration. We have:

$$\left(\frac{\partial y_D}{\partial L_w}\right)_V = \left(\frac{\partial y_D}{\partial L}\right)_V \left(\frac{\partial L}{\partial L_w}\right)_V \quad (34)$$

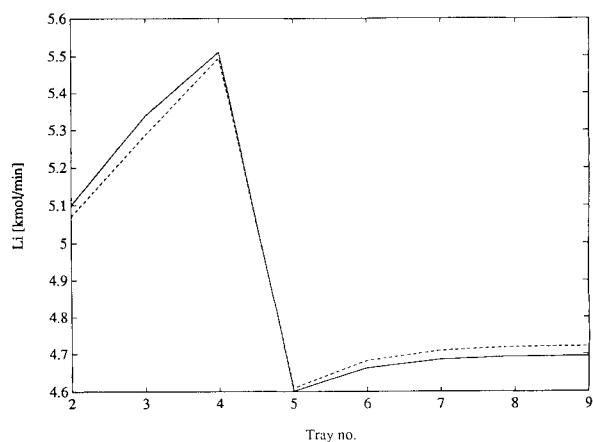
Instability (negative slope between  $L_w$  and  $y_D$ ) occurs when one of the elements on the righthand side of Eq. 34 is negative: I) there is a negative slope between molar reflux and mass reflux, or II) there is a negative slope between molar reflux

and top composition. Equation 34 indicates that there may be a positive slope between mass reflux  $L_w$  and top composition  $y_D$  if both I and II occur at the same time. However, Eq. 6 for the case  $M_2 > M_1$  shows that when  $(\partial y_D/\partial L)_V$  is negative

neither singularity nor negative slope exists between mass and molar reflux. This implies that the instability for the molar reflux usually is preserved when using mass reflux.

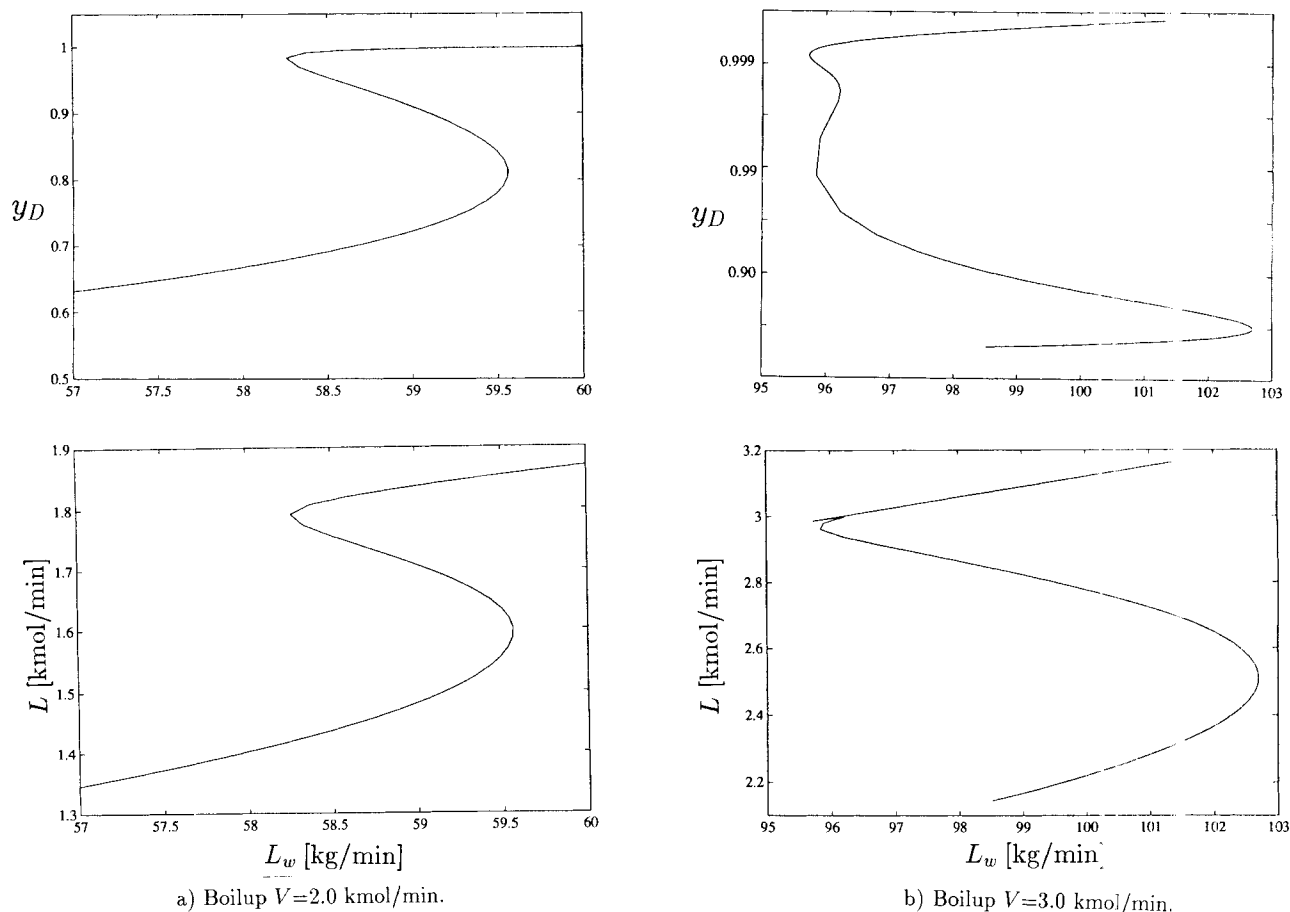
*Example 1 continued.* Figure 8a shows solutions for the methanol-propanol column using the  $L_wV$  configuration with the energy balance included. Mass reflux is in the range 57 to 60 kg/min while keeping molar boilup at 2.0 kmol/min. Compared to Figure 1 which shows the corresponding results for the case of constant molar flows, the range of multiplicity in terms of mass reflux becomes narrower. The reason for this is that with the energy balance included we get a larger value of  $(\partial y_D/\partial L)_V$  in the region of interest. Note that for this value of boilup there is no multiplicity between molar reflux  $L$  and top composition  $y_D$ :  $(\partial y_D/\partial L)_V > 0$ .

Figure 8b shows solutions with mass reflux in the range 95 kg/min to 103 kg/min while keeping boilup at 3.0 kmol/min. We now have two regions of multiplicity, and due to a partial overlap we get four solutions for mass reflux in the range 95.75 to 96.2 kg/min. If we allow for negative product flows, we would get five solutions as the lower branch would also overlap. The two lower singular points are caused by a multiplicity between mass reflux  $L_w$  and molar reflux  $L$ , while the two upper singular points (high purity in top) are caused by a multiplicity between molar reflux  $L$  and top composition  $y_D$ . This may be seen from the plot of mass reflux vs. molar reflux in Figure 8b. The analysis presented earlier showed that mass-flow instability (type I) is most likely with relatively low purity



**Figure 7. Liquid flow profiles for two molar refluxes in the unstable region of the methanol-propanol column.**

Boilup  $V = 4.5$  kmol/min  
 —, original; - - -, after increase in  $L$   
 Energy balance included



a) Boilup  $V=2.0$  kmol/min.

b) Boilup  $V=3.0$  kmol/min.

**Figure 8. Multiple steady states for mass reflux  $L_w$  for methanol-propanol column with energy-balances included in model.**

a. Boilup  $V = 2.0$  kmol/min; b. Boilup  $V = 3.0$  kmol/min

in the top, while molar flow instability (type II) is most likely with relatively high purity in the top. The results in this example support this analysis.

## Discussion

**Global Stability.** We have derived such conditions as Eq. 8 to check the local stability of a certain operating point. However, it is not easy to tell if it is globally stable, that is, if it is at a point where we have uniqueness. For Example 1 (Table 2), it is easily shown with the use of Eq. 8 that operating point III is unstable and operating points I, II, IV, and V are (locally) stable. It is clear from Figure 1 that operating points I and V are globally stable (with  $L_w$  and  $V$ ), whereas II and IV are not. However, there exists no simple method to check this directly. To do this analytically one would have to apply some kind of Lyapunov function to the dynamic model, which is not at all straightforward due to the high order and complexity of a dynamic model of a distillation column. In fact, the easiest way to check for global stability is to obtain solutions in the whole range of operation specifying one input and one composition (e.g., boilup  $V$  and top composition  $y_D$ ) in a steady-state simulator and then generate a figure similar to Figure 1.

**Subcooling.** We have not discussed all issues that may be important for multiplicity and instability in distillation. For instance, subcooling of the reflux may be important as the degree of subcooling may depend on the temperature and thereby on the composition. The separation in the column is determined by the effective reflux  $L_{\text{eff}} > L$ , which takes into account the additional internal reflux caused by subcooling. The degree of subcooling will usually decrease as  $y_D$  increases because the top part of the column cools down. With subcooling the second term in Eq. 7 is therefore reduced in magnitude, and we conclude that subcooling makes instability somewhat less likely for the  $L_w V$  configuration.

**Multicomponent Mixtures.** Introducing additional nonkey components will generally make multiplicity and instability less probable. The reason is that the "dead weight" of the nonkey components generally will reduce the effect of changes in the compositions of the key components on mole weight,  $M$ , and heat of vaporization,  $\Delta H^{\text{vap}}$ .

**Volume Basis.** We have not discussed volume inputs in particular, but the results obtained for mass inputs will in general apply to the volume case. For the case with ideal mixing we need substitute only the molecular weights with the molar volumes in the equations presented. For example, consider the  $L_q V$  configuration. Similar to the mass case,  $V_2 > V_1$  is nec-

essary for instability, and in this case the instability condition becomes:

$$y_D + L \left( \frac{\partial y_D}{\partial L} \right)_V > \frac{V_2}{V_2 - V_1} \quad (35)$$

For most mixtures, the difference in densities between the components are small, and very similar results will be obtained for volume inputs as those found for mass inputs. For the methanol-propanol example, we have a density of methanol of 795 kg/m<sup>3</sup> and a density of propanol of 806 kg/m<sup>3</sup> at normal conditions, and the results for volume inputs would be almost identical to what is found for mass inputs. For nonideal mixtures, the volume of mixing must also be accounted for.

**Instability during Industrial Operation.** As we have discussed above, instability for the  $L_wV$  configuration is likely to occur during operation if the reflux is large. Since the  $L_wV$  configuration is commonly used in the industry, it is surprising that there have been no previous experimental reports of instability. One possible reason is that multiplicity and instability always have been believed to be impossible in distillation, and consequently observations of instability during operation have been explained in other ways.

During the operation, the presence of instability and multiple steady states with the  $L_wV$  configuration may be observed as follows:

- A column may easily be operated at an unstable operating point by use of feedback, for example, by adjusting  $L_w$  such that a tray temperature is kept constant. The operating point is (open-loop) unstable if one observes that the steady-state effect of an increase in purity in the top is to decrease  $L_w$ . If this column is switched to a manual mode, instability will occur.

- Multiple steady states may be observed when a column is operated with constant  $L_w$  and  $V$  (manual control) close to a singular point. A small upset to the column may bring the column past the singular point, and one will observe catastrophic behavior as the entire column profile is changed when the column moves to its new steady state on another branch (Figure 9). Hysteresis may also be experienced during operation: if one takes an input (e.g.,  $L_w$ ) through a singular point, the outputs of the column will jump to totally different values.

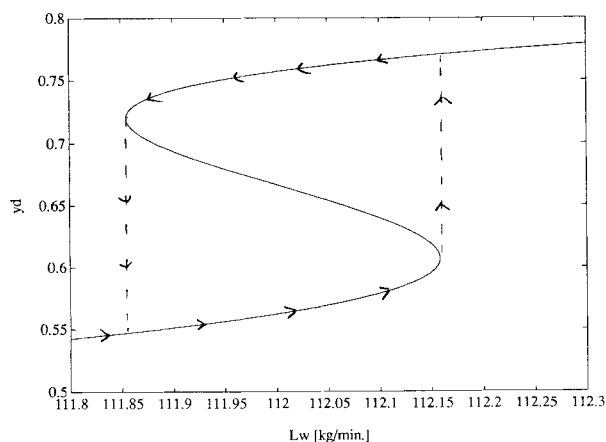


Figure 9. Hysteresis with jump phenomena in distillation.

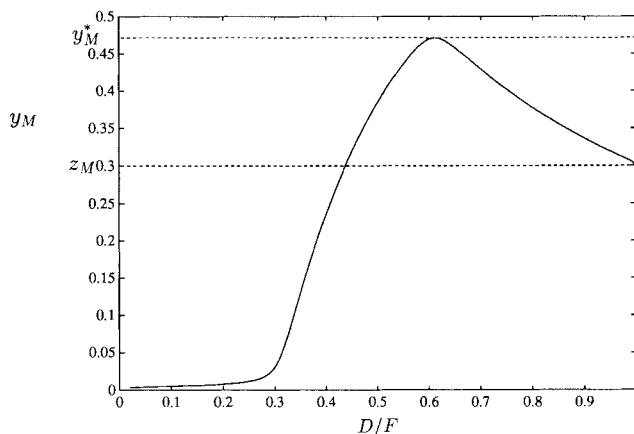


Figure 10. Input multiplicity in distillation.

Mole fraction of intermediate component in distillate,  $y_M$ , as a function of distillate flow rate,  $D$ .  
Column data:  $N=11$ ,  $N_F=6$ ,  $z_L=0.3$ ,  $z_M=0.3$ ,  $z_H=0.4$ ,  $\alpha_{LM}=\alpha_{MH}=2.0$ ,  $V=2.5$  kmol/min

However, resetting the input to its original value will not force the outputs back to their original values. This closed-loop hysteresis phenomenon with jumps at the singular points is well known from catastrophe theory (Poston and Stewart, 1978), and is illustrated in Figure 9.

**Input Multiplicity.** All results above are for the case of output multiplicity. As mentioned in the introduction, we may also have input multiplicity in distillation columns, at least for multicomponent separations. As an example, consider a separation of components  $L$  (light),  $M$  (intermediate), and  $H$  (heavy). Let  $z$  and  $y$  represent mole fractions in the feed and top product, respectively. Let  $V/F$  be fixed and consider the effect on  $y_M$  of varying the top product rate,  $D$ . For large values of  $D$  ( $D \approx F$ ), there is no separation in the top and we have  $y_M \approx z_M$ . As  $D$  is reduced,  $y_M$  increases because component  $H$  is taken out in the bottom rather than in the top. For  $D \approx F(1 - z_H)$  we have the best separation between components  $M$  and  $H$ , and we have  $y_M^* \approx z_M / (1 - z_H) > z_M$ . However, as  $D$  is reduced beyond this value, the column starts separating between components  $L$  and  $M$ , and  $y_M$  decreases, and for small values of  $D$  we have  $y_M \approx 0$ . Consequently, the relationship between  $D$  and  $y_M$  has a maximum (see Figure 10). If  $y_M$  is specified between  $z_M$  and  $y_M^*$ , there exists two possible values for  $D$ : we have input multiplicity. To avoid this problem in a practical situation, one should redefine the outputs, for example, by specifying compositions in terms of ratios of key components.

## Conclusions

Two-product distillation columns may have multiple steady-state solutions as well as unstable operating points. These results are independent of complex thermodynamics and are found even for single-staged, ideal binary distillation columns.

The behavior may have been caused by two different effects:

- Possible singularities in the transformation from the actual independent flows to the molar flows  $L$  and  $V$  which determine separation in the column. The relationship between mass and molar reflux is  $L_w = LM$ . An increase in  $L$  will in most systems reduce the mole weight  $M$  of the top product. If this reduction

is sufficiently large, the overall effect may be a decrease in  $L_w$ , and the operating point is unstable. This is most likely to happen when: the mole weight of the light component is much smaller than that of the heavy component, but relative volatility is still reasonably close to 1; the bottom product is relatively pure [ $x_B \ll (1 - y_D)$ ]; and  $L/D$  ratio is large.

- Possible singularities between molar reflux  $L$  and top composition  $y_D$  due to interactions between flows and compositions in the column. The flows will affect compositions through the material balances while compositions will affect flows through the energy-balances. The total effect may result in a negative slope between molar reflux  $L$  and top composition  $y_D$ , which corresponds to an unstable operating point.

For both types of multiplicities, the following three operating regimes exist:

- Internal flows low: no multiplicity and no instability
- Internal flows intermediate: multiple steady states, one of which is unstable (in some cases there may be two unstable states for the  $L_wV$  configuration due to both molar- and mass-input multiplicity in the same area of operation)
- Internal flows high: no multiple steady states with all the operating points unstable.

## Notation

- $B$  = bottoms flow, kmol/min  
 $D$  = distillate flow, kmol/min  
 $F$  = feed rate, kmol/min  
 $H^L$  = liquid phase enthalpy, kJ/kmol  
 $H^V$  = vapor phase enthalpy, kJ/kmol  
 $\Delta H^{\text{vap}}$  = heat of vaporization, kJ/kmol  
 $L$  = reflux flow rate, kmol/min  
 $L_B$  = liquid flow from bottom tray, kmol/min  
 $M$  = mole weight, usually of top product, kg/kmol  
 $M_1$  = pure component mole weight of most volatile component, kg/kmol  
 $M_2$  = pure component mole weight of least volatile component, kg/kmol  
 $N$  = no. of theoretical stages in column  
 $N_F$  = feed stage location, 1-reboiler  
 $\Delta p$  = pressure drop, atm  
 $Q_B$  = heat input to reboiler, kJ/min  
 $Q_D$  = heat removal in condenser, kJ/min  
 $S$  =  $y_D(1 - x_B)/(1 - y_D)x_B$  separation factor (binary mixture)  
 $V$  = boilup from reboiler (determined indirectly by heating  $Q_B$ ), kmol/min  
 $V_T$  = vapor flow rate from top tray (determined indirectly by cooling  $Q_D$ ), kmol/min  
 $V_1$  = pure component molar volume of most volatile component,  $\text{m}^3/\text{kmol}$   
 $V_2$  = pure component molar volume of least volatile component,  $\text{m}^3/\text{kmol}$   
 $x_B$  = mole fraction of most volatile component in bottom product  
 $x_i$  = mole fraction of most volatile component on tray  $i$   
 $y_D$  = mole fraction of most volatile component in distillate (top product)  
 $z_F$  = mole fraction of most volatile component in feed

## Greek letters

- $\alpha$  =  $(y_i/x_i)/[(1 - y_i)/(1 - x_i)]$  = relative volatility (binary mixture)  
 $\rho$  = density,  $\text{kg}/\text{m}^3$

## Subscripts

- $q$  = flow rate,  $\text{m}^3/\text{min}$   
 $w$  = flow rate,  $\text{kg}/\text{min}$

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## Appendix A: Sign of Gains $(\partial y_D/\partial D)_V$ and $(\partial x_B/\partial B)_L$

1. Assume no multiplicity for the  $DV$  configuration, i.e., neither output nor input multiplicity. No output multiplicity (i.e., specifying  $D$  and  $V$  uniquely determines  $x_i$ ) seems to apply generally. No input multiplicity (e.g., specifying  $V$  and  $x_i$  uniquely determines  $D$ ) seems to always apply to binary mixtures and multicomponent mixtures if we consider the components that distribute to one product, i.e., not for intermediate components (see Figure 10).

2. Let  $y_D$  denote the mole fraction in the distillate of the most volatile component. Then,

$$\lim_{D \rightarrow 0} y_D > z_F; \quad \lim_{D \rightarrow F} y_D = z_F \quad (\text{A1})$$

As  $y_D$  decreases when  $D$  goes from 0 to  $F$ , the gain  $(\partial y_D/\partial D)_V$  must be negative for some  $D$ . Assumption 1 then implies that the gain is negative for all  $D$ ,

$$\left(\frac{\partial y_D}{\partial D}\right)_V < 0. \quad (\text{A2})$$

Similar reasoning for compositions on other trays gives:

$$\left(\frac{\partial x_i}{\partial D}\right)_V < 0. \quad (\text{A3})$$

for all  $i$ .

3. Assuming  $(\partial V_T/\partial V)_D$  and  $(\partial L_B/\partial L)_D$ , nonzero implies that the transformations between the  $DV$  and the  $LB$  configuration are nonsingular. Uniqueness for the  $DV$  configuration is then conserved with the  $LB$  configuration.

4. A similar analysis as in step 2 above then yields:

$$\left(\frac{\partial x_i}{\partial B}\right)_L > 0 \quad (\text{A4})$$

for all  $i$ . This also applies to the reboiler where  $x_i = x_B$ .

### Appendix B: Sign of Gains $(\partial y_D/\partial L)_V$ and $(\partial x_B/\partial V)_L$ for the Case of Constant Molar Flows

The gain  $(\partial y_D/\partial L)_V$  may be written as:

$$\left(\frac{\partial y_D}{\partial L}\right)_V = \left(\frac{\partial y_D}{\partial D}\right)_V \left(\frac{\partial D}{\partial L}\right)_V \quad (\text{B1})$$

For the case of constant molar flows  $(\partial D/\partial L)_V = -1$ , and Eq. B1 becomes  $(\partial y_D/\partial L)_V = -(\partial y_D/\partial D)_V$ . From Appendix A it then follows that

$$\left(\frac{\partial y_D}{\partial L}\right)_V > 0 \quad (\text{B2})$$

Similarly, we find:

$$\left(\frac{\partial x_B}{\partial V}\right)_L < 0 \quad (\text{B3})$$

When the energy balance is included, the sign of the gains  $(\partial y_D/\partial L)_V$  and  $(\partial x_B/\partial V)_L$  may take either sign as shown in Part II.

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