Instability of Distillation Columns

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As recently recognized, distillation columns, operating with reflux and boilup as independent inputs, may have multiple steady-state solutions, even in the ideal binary case. Two fundamentally different sources may cause the multiplicity, and in both cases some operating points are found to be unstable. This article provides evidence for the instability and discusses the effect of operating conditions on stability. Increasing the internal flow rates increases the probability of instability; when flows other than reflux and boilup are used as independent inputs, an operating point may become unstable if the level control is not sufficiently tight. In this case, a limit cycle, usually stable, appears as the steady state goes unstable.

Introduction

The dynamic behavior of distillation columns has been studied quite extensively over the past decades and several general qualitative properties have been proposed. One suggested property is that the operating points of distillation columns, at least in the binary case, always are globally asymptotically stable (with level and pressure control). This conjecture is based on results published over the years on the uniqueness and stability of distillation columns (for example, Acrivos and Amundson, 1955; Rosenbrock, 1960, 1962; Doherty and Perkins, 1982; Sridhar and Lucia, 1989). Doherty and Perkins (1982) provide a review of results published on this subject and conclude that multiplicity and instability is impossible in any binary distillation column. However, it is important to realize that all these studies include restrictive assumptions. First, all the studies assume that the flows, for example, reflux $L$ and boilup $V$, are fixed on a molar rate basis. As Jacobsen and Skogestad (1991) argue, this is rarely the case in operating columns, especially for liquid flows. For instance, fixing the valve position will normally correspond closely to fixing the geometric average of mass and volumetric flow rate.

Secondly, most studies include the assumption of constant molar flows (neglected energy balance). Sridhar and Lucia (1989) include the energy balance in their study, but conclude that also in this case the operating points of binary distillation columns will be unique. They do, however, only study a limited number of configurations (sets of specifications), namely the $QDQb$ and $LB$ configurations. (The term “configuration” is used in distillation control to denote the two independent variables which remain for composition control.)

In a recent article, Jacobsen and Skogestad (1991) analyze models without the two above mentioned assumptions and show that distillation columns, even in the ideal binary case, may display multiple steady states. They identify two different sources that may cause the multiplicity:

- Most operating columns will have the flows fixed on a mass or volume basis, while the separation is determined by the size of the molar flows. The transformation from mass or volume flows to molar flows is nonlinear due to the composition dependence and may in some cases become singular. A singularity in the input transformation will imply that several solutions exist in terms of the outputs (for example, compositions) for a given specification of inputs (flows).
- When the energy balance is included in the model, even molar inputs may yield multiple solutions. The multiplicity is caused by interactions between flows and compositions through the material and energy balances.

Jacobsen and Skogestad (1991) treat the multiplicity from a steady-state point of view only. In this article we study the dynamics of columns with multiple solutions and provide proof of instability for some configurations (specifications).

It is well known that for the simple distillation columns studied in this article, with given feed stream, two products, and no intermediate heaters or coolers (see Figure 1), there are only two degrees of freedom at steady state, that is, only two independent specifications are possible. A large number of specifications (configurations) are possible for distillation columns. One typical specification is $L$ and $D$ ($LD$ configuration), and others are $QDQb$, $LV$, $LQb$, $yDxS$ and so on. Note from the last specifications that one may at steady state also specify dependent variables (in this case product compositions). However, in terms of dynamics and control there is a fundamental
difference between independent variables ("inputs" in control) and dependent variables ("outputs" in control). In an operating column only the former may be specified directly, while the latter only may be specified indirectly through the manipulation of the former, for example, through feedback control. Mathematically, we require any dynamic model to be causal and this is satisfied only when independent variables are specified. Also, in the dynamic case we usually have at least three additional degrees of freedom because the pressure (vapor holdup) and the reboiler and condenser levels (liquid holdups) may vary dynamically. When studying the dynamic behavior of distillation columns in this article, we assume that the pressure and the two levels are controlled, that is, we are studying a partly controlled system. This is reasonable since otherwise all distillation columns are unstable because the two levels behave as pure integrators. In any case, usually the levels and pressure are tightly controlled so that we practically are left with two degrees of freedom also in the dynamic case.

We will assume that the cooling $Q_B$ always is used for pressure control and restrict ourselves to consider as independent variables the flows $L$, $V$, $D$, and $B$ (note that boilup rate $V$ is closely related to heat input $Q_B$). These flows may be specified on a molar basis (in which case we use no subscript) or on a mass basis (in which case we use subscript $w$). Typically, the product flows $D$ and $B$ are used to control the levels, which leaves $L$ and $V$ as independent variables and we get the $L,V$ configuration. This is the most widespread configuration in industry and in this article we mainly discuss this configuration. However, there are also other possibilities for controlling the levels and therefore many possible configurations (see, for example, Skogestad and Morari, 1987).

We review the results presented in Jacobsen and Skogestad (1991) on steady-state multiplicity caused by singularities in the input transformations. We provide evidence for the instability of some of the operating points for this case and discuss the effect of operating conditions on the stability of distillation columns. The multiplicity and instability caused by singularities in the input transformations is independent of the energy balance and, for simplicity, we therefore assume constant molar flows. We then include the energy balance in the model and provide evidence for the instability that may result from interactions between flows and compositions through the material and energy balances. The effect of operating conditions on this type of instability is then discussed.

At the end of the article we consider the $D,V$ and $L,B_o$ configurations. We show that while steady-state multiplicity is unlikely, they may have unstable operating points if level control is slow. It is shown that the instability in this case results from a Hopf bifurcation and that a limit cycle hence appears as the steady state goes unstable.

In this article we concentrate on the theoretical aspects of the dynamic behavior of distillation columns. In a separate article (Jacobsen and Skogestad, 1991b) we study the practical implications of the observed instability on operation and control.

**Steady-State Multiplicity in Ideal Distillation with $L,V$ Configuration**

We give here a brief review of the results on multiplicity caused by singularities in the input transformation presented in Jacobsen and Skogestad (1991). By "ideal" we mean that the thermodynamic behavior is ideal and that we have constant molar flows. Specifically, we assume that the vapor-liquid equilibrium (VLE) is described by constant relative volatility $\alpha$:

$$y_i = \frac{\alpha x_i}{1 + (\alpha - 1)x_i}$$

and that at steady state we have for all stages (except at feed locations):

$$V_i = V_{i+1}; \quad L_i = L_{i+1}$$

where the subscript denotes the stage number. With assumption 2 the energy balance is not needed. Note that in order to make our dynamic model more realistic we have included liquid flow dynamics (Table 1) so that dynamically $L_i \neq L_{i+1}$. However, the flow dynamics do not affect the stability and all analytical results we present are therefore valid also if the flow dynamics are neglected. Throughout the article we also assume negligible vapor holdup and constant pressure.

Jacobsen and Skogestad (1991) provide an example of steady-state multiplicity in a column separating a mixture of methanol and $n$-propanol. The column has mass reflux $L_w$ and molar boilup $V$ as independent variables, that is, $L_w,V$-configuration. Data for the column are given in Table 1. Some steady-state solutions are given in Table 2, and we see that for a specification of mass reflux $L_w = 50.0$ kmol/min and molar boilup $V = 2.0$ kmol/min there are three possible solutions II, III and IV in terms of compositions. The multiplicity is graphically illustrated in Figure 2.

The observed multiplicity is caused by the transformation between the actual flow rates (mass) and the molar flow rates which determine separation. For a binary mixture the trans-
Table 1. Data for Methanol-Propanol Column

<table>
<thead>
<tr>
<th>$z_F$</th>
<th>$F$</th>
<th>$\alpha$</th>
<th>$N$</th>
<th>$N_F$</th>
<th>$M_1$</th>
<th>$M_2$</th>
</tr>
</thead>
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<tr>
<td>0.50</td>
<td>1.0</td>
<td>3.55</td>
<td>8</td>
<td>4</td>
<td>32.0</td>
<td>60.1</td>
</tr>
</tbody>
</table>

- Feed is saturated liquid.
- Total condenser with saturated reflux.
- Liquid holdups are $M_{1}/F = 0.5$ min, including reboiler and condenser except for $D,V$ configuration where $M_{1}/F = 5.0$ min.
- Liquid flow dynamics: $L_{w} = L_{0} + (M_{L0} - M_{L0})/\tau_{L}$, $\tau_{L} = M_{L0}/3L_{0}$
- Negligible vapor holdup.
- Constant pressure (1 atm).

Table 2. Steady-State Solutions for Methanol-Propanol Column with $V = 2.0 \text{ kmol/min}$ and $L_{w} = 48$ to $53 \text{ kg/min}$

<table>
<thead>
<tr>
<th>$L$</th>
<th>$D$</th>
<th>$L_{w}$</th>
<th>$y_{D}$</th>
<th>$x_{B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.064</td>
<td>0.936</td>
<td>48.00</td>
<td>0.534</td>
</tr>
<tr>
<td>2</td>
<td>1.143</td>
<td>0.857</td>
<td>50.00</td>
<td>0.584</td>
</tr>
<tr>
<td>3</td>
<td>1.463</td>
<td>0.537</td>
<td>50.00</td>
<td>0.9237</td>
</tr>
<tr>
<td>4</td>
<td>1.555</td>
<td>0.445</td>
<td>50.00</td>
<td>0.9969</td>
</tr>
<tr>
<td>5</td>
<td>1.650</td>
<td>0.350</td>
<td>53.00</td>
<td>0.9984</td>
</tr>
</tbody>
</table>

*Constant molar flows (no energy balance); see also Figure 2.

Figure 2. Methanol-propanol column with constant molar flows: multiple steady-states for $L_{w},V$ configuration.

Mass reflux $L_{w}$ is varied while molar boilup $V$ is fixed at 2.0 kmol/min. On upper plot, corresponding maximum eigenvalue is shown at some steady-state solutions. Broken line represents unstable solutions.

Instability with $L_{w},V$-Configuration

Methanol-propanol example

The "maximum eigenvalue" (the eigenvalue with the largest real part) at selected operating points of the methanol-propanol column with constant molar flows is indicated in Figure 2. The eigenvalues were obtained by linearizing a nonlinear dynamic model with two states per tray (fraction of light component and liquid holdup). The steady-state values used for the liquid holdups are given in Table 1. Note that the nonlinear model is used in all simulations. From Figure 2 we observe that the maximum eigenvalue at the upper and lower branches (positive slope) is negative, implying stability, while the one at the intermediate branch (negative slope) is positive, implying instability of the operating points. There is only a single eigenvalue in the RHP at any unstable operating point. The eigenvalue at the singular points, which correspond to limit points, are zero as expected. The open-loop instability at the intermediate branch is illustrated by the nonlinear simulations in Figure 3 which shows the responses in top composition $y_D$ to small changes in mass-reflux $L_{w}$ (keeping boilup $V$ fixed) starting from equilibrium at the unstable operating point III (initial holdups are as given in Table 1). The simulations indicate that the two stable solutions II and IV have equally large regions of attraction as seen from the unstable solution III.

Below we provide evidence for the observed instability and discuss under which operating conditions instability is most likely to occur.
Figure 3. Nonlinear open-loop simulation of methanol-propanol column starting at unstable operating point III in Figure 2.

1) = increase in mass reflux \( L \), of 0.01 kg/min; 2) = decrease in mass reflux \( L \), of 0.01 kg/min. Boilup \( V = 2.0 \) kmol/min. Constant molar flows.

Conditions for instability

One-Stage Column. It is useful to study the simplest case for which the above-mentioned instability may occur (Jacobsen and Skogestad, 1991). To this end, consider the simple column in Figure 4 with one theoretical stage (the reboiler) and a total condenser (of course, such a column will never be operated in practice because the reflux is simply wasting energy and has no effect on separation). Assume binary separation, liquid feed, constant holdup in the reboiler \( M_L \) and negligible holdup in the condenser. The dynamic model of the column becomes:

\[
M_L \frac{dx_b}{dt} = Fz_F - D y_D - B x_b
\]  (5)

Here \( D = V - L \) and \( D + B = F \) and with \( L \) and \( V \) as independent variables we get:

\[
M_L \frac{dx_b}{dt} = F(z_F - x_b) + L(y_D - x_b) + V(x_b - y_D)
\]  (6)

Linearization, Laplace transformation and introduction of deviation variables assuming \( F, z_F, \) and \( V \) constant yields:

\[
sM_L dx_b(s) = -D^* dy_D(s) - B^* dx_b(s) + (y_D^* - x_b^*) dL(s)
\]  (7)

where \( s \) is the Laplace variable and a superscript \( * \) shows that these are the nominal steady-state values (this superscript is deleted in the following to simplify notation). Linearizing the expression for the vapor-liquid equilibrium (for example, expression 1 for the case of constant relative volatility) yields:

\[
dy_D = K(x_b) dx_b
\]  (8)

As all terms in Eq. 10 are positive, the eigenvalue (pole) of the linearized system, \( -\alpha/M_L \), is always negative, implying that all operating points are stable when molar reflux \( L \) and molar boilup \( V \) are used as independent variables.

Now consider mass reflux \( L \) as an input instead of molar reflux \( L = L_w/M \). By linearizing Eq. 3 we obtain for binary mixtures:

\[
dL(s) = \frac{1}{M} dL_w(s) + L \frac{M_2 - M_1}{M} dy_D(s)
\]  (11)

Substituting Eq. 11 into Eq. 9 and using Eq. 8 we obtain the following transfer-function between liquid composition, \( dx_b(s) \), and mass reflux \( dL_w(s) \):

\[
dx_b(s) = \frac{y_D - x_b}{M_L s + a_w} \frac{dL_w(s)}{M}
\]  (12)

where

\[
a_w = KD + B
\]  (10)

The operating point is unstable for \( a_w < 0 \). We now want to compare this condition for instability with the condition for a negative slope for \( (\partial L_w/\partial L)_v \) given in Eq. 4. At steady-state we have \( s = 0 \) and Eqs. 8, 9, and 10 yield:

\[
\left( \frac{\partial y_D}{\partial L}_v \right)_0 = \frac{y_D - x_b}{D + B/K}
\]  (14)

which inserted into Eq. 4 yields:

\[
\left( \frac{\partial L_w}{\partial L}_v \right)_0 = \frac{M}{KD + B} a_w
\]  (15)
and we find for the simple one-stage column that instability \(a_{\nu} < 0\) is equivalent to a negative steady-state slope for \(\frac{\partial L_{\nu}}{\partial L_{\nu}}\).

**Multistage Column.** The dynamic model of a multistage column will in general be of relatively high order and it is difficult, if not impossible, to calculate the eigenvalues analytically. In order to assess the stability of a multistage column we will therefore employ the Routh-Hurwitz stability criterion and derive a sufficient condition for instability. To do this we first need to derive an expression for the transfer-function \(\frac{\partial y_{D}}{\partial L_{\nu}}(s)\). With \(V\) constant the total differential of \(y_{D}\) may be written:

\[
dy_{D}(s) = \left(\frac{\partial y_{D}}{\partial L_{\nu}}\right)_{V}(s) dL(s)
\]

We have \(L = L_{\nu}/M\) and for binary mixtures \(M\) is a (static) function of \(y_{0}\) only. Thus, for binary separations Eq. 11 applies. Combining Eqs. 16 and 11 yields:

\[
\left(\frac{\partial y_{D}}{\partial L_{\nu}}\right)_{V}(s) = \frac{1}{M} \left(\frac{\partial y_{D}}{\partial L_{\nu}}\right)_{V}(s) + \frac{1 - L(M_{2} - M_{1})}{M} \left(\frac{\partial y_{D}}{\partial L_{\nu}}\right)_{V}(s)
\]

To use the Routh-Hurwitz criterion write the transfer-function from molar reflux \(L\) to top composition \(y_{D}\) on the following form:

\[
\left(\frac{\partial y_{D}}{\partial L_{\nu}}\right)_{V}(s) = \frac{k_{L_{\nu}}^{y_{D}}(1 + b_{1}s + b_{2}s^{2} + \cdots + b_{m}s^{m})}{1 + a_{1}s + a_{2}s^{2} + \cdots + a_{n}s^{n}}
\]

is the steady-state gain. The response is assumed to be strictly proper, that is, \(n > m\). We also assume that this transfer function is stable, that is, we have "molar" stability. This always holds for the case of constant molar flows (Doherty and Perkins, 1982). From the Routh-Hurwitz stability criterion, which says that the system is stable only if all the coefficients in the pole polynomial (denominator of Eq. 18) have the same sign, we conclude that all \(a_{i}\)'s in Eq. 18 are positive. Inserting Eq. 18 into Eq. 17 yields:

\[
\left(\frac{\partial y_{D}}{\partial L_{\nu}}\right)_{V}(s) = \frac{1}{M} k_{L_{\nu}}^{y_{D}}(1 + b_{1}s + b_{2}s^{2} + \cdots + b_{m}s^{m}) - \frac{k_{L_{\nu}}^{L}(M_{2} - M_{1})}{M} (1 + b_{1}s + b_{2}s^{2} + \cdots + b_{m}s^{m})
\]

Since \(n > m\) we know that the highest-order term in the denominator is \(a_{n}s^{n}\) where \(a_{n}\) is positive. From the Routh-Hurwitz condition we then find that Eq. 20 is unstable if the constant term in the denominator is negative, and we conclude that a sufficient criterion for instability with the \(L_{\nu}V\)-configuration is:

\[
k_{L_{\nu}}^{y_{D}}L(M_{2} - M_{1}) > 1
\]

This is exactly the same criterion as given in Eq. 4 in order to have a negative slope between mass and molar reflux. Thus, we have proven for binary mixtures that a sufficient condition for instability with the \(L_{\nu}V\)-configuration is that at steady state:

\[
\left(\frac{\partial L_{\nu}}{\partial L_{\nu}}\right)_{V} < 0
\]

In conclusion, we have proved that solution branches with a negative slope between mass and molar reflux. Thus, we have proven for binary mixtures that a sufficient condition for instability with the \(L_{\nu}V\)-configuration is that at steady state:

\[
\left(\frac{\partial L_{\nu}}{\partial L_{\nu}}\right)_{V} < 0
\]
We see that the instability condition (Eq. 21) corresponds to having the static term in the denominator negative:

\[
\left( \frac{\partial L}{\partial y_D} \right)_{L,v} (0) \left( \frac{\partial y_D}{\partial L} \right)_{v} (0) > 1
\]

(25)

Note that Eq. 25 corresponds to a positive feedback loop with the product of the loop gains being larger than unity at steady state. The transfer-function from \( L_w \) to \( y_D \) in Eq. 24 may alternatively be written:

\[
\left( \frac{\partial y_D}{\partial L_w} \right)_{v} (s) = \frac{\left( \frac{\partial y_D}{\partial L} \right)_{v} (s)}{\left( \frac{\partial L}{\partial L_w} \right)_{v} (s)}
\]

(26)

and we see that provided \( \left( \frac{\partial L}{\partial L_w} \right)_{v} (0) > 0 \) (it is equal to \( 1/M \) for binary mixtures), the instability condition (Eq. 25) is equivalent to:

\[
\left( \frac{\partial L}{\partial L_w} \right)_{v} (0) < 0
\]

(27)

**Effect of operating conditions on stability**

Jacobsen and Skogestad (1991) provide analytical results on when a negative slope between mass and molar reflux, that is, instability according to the analysis above, is most likely. They show that a negative slope is most likely with large internal flows (that is, large \( L \) and \( V \)) and intermediate purities in the top (that is, intermediate \( L \) for given \( V \)). This corresponds to having \( L \) and \( k_{yD}^{L} \) large, and according to Eq. 21 this is the case for which instability is most likely. Note that the analytical treatment in Jacobsen and Skogestad (1991) was based on ideal separation with constant relative volatility and constant molar flows.

Figure 5 shows the stable and unstable regions in terms of boilup \( V \) and distillate flow \( D \) for the methanol-propanol column with the \( L,V \)-configuration. The regions were determined using the full nonlinear dynamic model. Note that the assumption of liquid feed and constant molar flows implies that \( L = V - D \). Thus, for a given \( V \), \( D = 0 \) corresponds to maximum reflux \( L_{\text{max}} \) and \( D = F \) to minimum reflux \( L_{\text{min}} \). From the figure we see that at low internal flows, that is, low values of \( V \), there is no unstable region and hence all operating points are unique and stable. However, for values of \( V \) above 1.32 kmol/min there exists a region of unstable operating points which, as expected from the analysis, expands with increasing \( V \). We also see from the figure that instability, as expected, is most likely for intermediate values of \( D \), that is, intermediate values of \( L \) for a given \( V \). Furthermore, from Figure 5 we see that instability is unlikely for values of the distillate flow \( D \) significantly less than 0.5 (\( = F_{\text{DP}} \)). This is explained by the fact that the top product becomes very pure with \( D \) significantly less than \( F_{\text{DP}} \), and that \( k_{yD}^{L} \) in Eq. 21 becomes correspondingly small.

The borders between the stable and unstable regions in Figure 5 correspond to limit-points with the \( L,V \)-configuration. Locally, two steady-state solutions exist around a limit-point (see, for example, Golubitsky and Schaeffer, 1985). One might expect that for values of \( V \) for which there are two singular points there exist three steady-state solutions for some value of \( L_w \), for example, as in Figure 2. However, this is not necessarily the case since the upper and lower solution branches (resulting from the two limit-points) may not overlap. (They will always overlap if we allow for negative product flows.)

We finally note that although the instability criteria (Eqs. 21 and 22) derived above only are sufficient, they give exact limits for instability in this example, for example, the border between the stable and unstable region in Figure 5 correspond to operating points with \( \left( \frac{\partial L_w}{\partial L} \right)_{v}(0) = 0 \). This is also the case for all examples with constant molar flows that we have studied. However, as we shall see below, when the energy balance is included in the model there may exist borders between stable and unstable regions which are not predicted by Eqs. 21 and 22.

**Instability Caused by the Energy Balance**

To this point we have assumed "molar stability" which always holds for the binary case with constant molar flows. However, Jacobsen and Skogestad (1991) show that when the energy balance is included in the model, even molar specifications may yield multiplicity in distillation. The multiplicity is in this case caused by interactions between the flows and compositions inside the column. The flows will affect the compositions through the material balance while the compositions will affect the flows through the energy balance.

**Methanol-propanol example**

Figure 6 and Table 3 show steady-state solutions for the methanol-propanol column with the \( L,V \)-configuration and the energy-balance included in the model. The heats of vaporization of the two pure components at 1 atm are approximately \( \Delta H_{L,\text{VC}} = 35 \text{ kJ/mol} \) and \( \Delta H_{v,\text{DP}} = 41 \text{ kJ/mol} \).
heat of vaporization. The maximum eigenvalue at selected operating points is shown in Figure 6, and we see that the solution branch with a negative slope between molar reflux \( L \) and top composition \( y_D \) corresponds to unstable solutions. The eigenvalues were obtained using the same dynamic model as was used for the \( L,V \) configuration above apart from the inclusion of the energy balance. For simplicity we used a static energy balance, that is, the term \( \frac{dU_L}{dt} \) was neglected in the dynamic model.

**Conditions for instability with \( L,V \)-configuration**

To consider the stability properties for the \( L,V \) configuration with the energy balance included we utilize the fact that the \( D,V \) configuration in all known cases yields unique solutions (Sridhar and Lucia, 1989; Jacobsen and Skogestad, 1991) which are stable under the assumption of perfect level control (see the section on instability with \( D,v \)-configuration). We will again employ the Routh-Hurwitz criterion to derive a sufficient condition for instability and hence need an expression for \( \frac{\partial y_D}{\partial L} \). The transfer function from molar reflux \( L \) to top composition \( y_D \) may be written:

\[
\left( \frac{\partial y_D}{\partial L} \right) (s) = \left( \frac{\partial y_D}{\partial D} \right) (s) \left( \frac{\partial L}{\partial D} \right)^{-1} (s)
\]

Write the transfer-function from \( D \) to \( y_D \) on the form:

\[
\left( \frac{\partial y_D}{\partial D} \right) (s) = \left[ k_{y_D D} \right] n_1(s) d(s) = k_{y_D D} \frac{1 + b_s + \cdots + b_s^a}{1 + a_s + \cdots + a_s^a}
\]

Note that the constant terms in the polynomials \( n_1(s) \) and \( d(s) \) are equal to 1. Stability implies that all \( a_i \)'s in Eq. 29 are positive. A material balance around the condenser yields (assuming perfect level control):

\[
L = V_T - D
\]

where \( V_T \) denotes vapor flow to the condenser. Next consider the energy balance, and let \( \bar{H}^V(y) \) denote the molar enthalpy of the vapor with each component as pure saturated liquid at column pressure as reference. For simplicity we will here assume saturated liquid feed and neglect changes in the liquid enthalpy with composition. An overall energy balance then yields (see Appendix for details):

\[
V_T = \bar{H}_b^V \bar{H}_r^V (31)
\]

where

\[
\bar{H}_b^V = \bar{H}_b^V (y_b); \quad \bar{H}_r^V = \bar{H}_r^V (y_r)
\]

\( y_b \) is the composition of the vapor leaving the reboiler and is assumed to be in equilibrium with \( x_b \). \( y_r \) is the composition of the vapor on the top stage, which at steady state is equal to \( y_D \). Inserting Eq. 31 in the material balance (Eq. 30) and differentiating yields for a binary mixture:

\[
\left( \frac{d\bar{H}^V}{dy} \right) y = \left( \frac{\partial y_D}{\partial D} \right) (s) \bar{H}_r^V - \left( \frac{\partial y_D}{\partial D} \right) (s) \bar{H}_b^V \frac{(\bar{H}_r^V)^2}{(\bar{H}_r^V)}
\]

where the transfer functions from \( D \) to \( y_b \) and \( y_r \) may be written:

**Table 3. Steady-State Solutions for Methanol-Propanol Column with Boilup \( V = 4.5 \) kmol/min**

<table>
<thead>
<tr>
<th>( L ) kmol/min</th>
<th>( D ) kmol/min</th>
<th>( y_D )</th>
<th>( x_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.60</td>
<td>0.535</td>
<td>0.9324</td>
</tr>
<tr>
<td>11</td>
<td>4.70</td>
<td>0.505</td>
<td>0.9845</td>
</tr>
<tr>
<td>111</td>
<td>4.66</td>
<td>0.406</td>
<td>0.9993</td>
</tr>
<tr>
<td>1111</td>
<td>4.72</td>
<td>0.0866</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

*The energy balance is included in the model (enthalpy data are given in Table 4); see also Figure 6.
as a sufficient condition for instability with the LV configuration. Applying Routh-Hurwitz stability criterion to the pole-polynomial in Eq. 38 yields:

\[
\left(\frac{\delta H_v}{\delta y}\right)_v (s) = k_{D, v}^V P_i (s) \frac{\partial y_v}{\partial D} (s) + k_{D, v}^V \frac{\partial y_v}{\partial D} (s) \frac{d(s)}{d(s)} (34)
\]

since all the transfer functions share the pole-polynomial \(d(s)\). Finally, inserting Eqs. 29, 33, and 34 into Eq. 28 yields

\[
(\partial y_v/\partial L)_v (s) = \frac{k_{D, v}^D \left(\bar{H}_n^V \right)^2 n_1 (s)}{V \left(\frac{d\bar{H}_n^V}{dy} \right)_{y=g} - \left(\frac{d\bar{H}_n^V}{dy} \right)_{y=g} \frac{k_{D, v}^V \left(\bar{H}_n^V \right)^2 n_1 (s)}{k_{D, v}^V \left(\bar{H}_n^V \right)^2 n_1 (s)} (35)
\]

Applying Routh-Hurwitz stability criterion to the pole-polynomial in Eq. 35 yields:

\[
\left(\frac{d\bar{H}_n^V}{dy} \right)_{y=g} \left(\frac{d\bar{H}_n^V}{dy} \right)_{y=g} > 0 (36)
\]

as a sufficient condition for instability with the LV configuration. Comparing Eqs. 36 and 33 finally yields that instability will occur if \((\partial L/\partial D)_v > 0\) at steady state.

Remarks. (1) In the above derivation we have assumed a binary mixture such that the saturated vapor enthalpy, \(\bar{H}_n^V\), is a function of one composition only (pressure is assumed constant) as shown in Eq. 32. We have also selected the reference state for energy such that it is reasonable to set the liquid enthalpy equal to zero at all stages, that is, \(H^L = 0\) (see Appendix for details). This assumption is very good for many mixtures.

(2) From the exact steady-state balances \(D = V + L - F + \frac{V}{V_B}\) we derive for \(F\) constant the following equivalent steady-state conditions for instability:

\[
(\partial L/\partial D)_v > 0 \iff (\partial V/\partial L)_v > 1 \iff (\partial L_B/\partial L)_v < 0 (37)
\]

Thus, we find that an unstable operating point corresponds to a situation where at steady state an increase in liquid flow, \(L\), in the top of the column, yields a decrease in liquid flow, \(L_B\), at the bottom of the column (to observe this in practice one would need feedback to stabilize the operating point).

(3) Since \((\partial y_v/\partial D)_v\) usually is negative at steady-state (see Appendix I in Jacobsen and Skogestad, 1991; counter examples are given by Jacobsen, 1993), we see from Eq. 28 that the instability condition \((\partial L/\partial D)_v (0) > 0\) corresponds to \(k_{P, v}^L = (\partial y_v/\partial L)_v (0) < 0\). That is, at the unstable operating points we have the unexpected situation where the separation gets worse with increasing reflux. This is in accordance with the numerical results in Figure 6.

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

\[
\begin{array}{c|c}
H^L & 16.67e^{-1.06k_B} \\
H^V & 13.49e^{-1.06k_B} + 43.97e^{-0.87kJ}
\end{array}
\]

\*Reference state: Pure components as liquid at 0°C. x denotes mole fraction methanol in liquid phase.

(4) In industrial practice it is more common to specify the heat input to the reboiler \(Q_B\) rather than the molar boilup \(V = Q_B/\Delta H^{vap}\). In many cases the molar heat of vaporization \(\Delta H^{vap}\) is nearly constant and the \(LQ_B\)-configuration is very similar to the \(LV\)-configuration. However, the instability we find with the \(LV\) configuration is related to changes in the heats of vaporization and we therefore need to consider whether the instability persists with the \(LQ_B\) configuration. Assuming \((\partial y_v/\partial D)_{z_0} (s)\) stable and neglecting changes in liquid enthalpy with composition yields:

\[
\frac{(\partial H_v)/dy}{(\bar{H}_n^V)^2} > 1
\]

as a sufficient criterion for instability with the \(LQ_B\) configuration. According to Eq. 38 instability is unlikely with the \(LQ_B\) configuration in the usual case where \(d\bar{H}_n^V/\partial y < 0\) and \(k_{D, v}^V > 0\). Thus, while the energy balance may cause instability with the \(LV\) configuration it is unlikely to cause instability with the \(LQ_B\) configuration. The exception is for cases where \(d\bar{H}_n^V/\partial y > 0\) for which Eq. 38 predicts that instability may occur. Note that we have in deriving Eq. 38 neglected changes in liquid enthalpy with composition and that instability with the \(LQ_B\) configuration is possible also in the normal case when this assumption is removed. However, we do not include any proof here since instability in this case only is predicted in regions of operation where the internal flows are unrealistically high.

The fact that the energy balance is unlikely to yield instability with the \(LQ_B\) configuration does not render the results for the \(LV\)-configuration of no interest from a practical viewpoint. First, some industrial columns are effectively operated with molar boilup \(V\) as an independent input. This is usually achieved by inferring the boilup rate \(V\) from the differential pressure across a column section and manipulating \(Q_B\) to keep the boilup constant (Kister, 1990). Secondly, many simulation models use the molar boilup \(V\) as a specification rather than the heat input \(Q_B\). Our results show that it may be crucial to choose the correct specification in simulations in order to correctly predict the behavior of the real column.

**Effect of operating conditions on stability**

From Eq. 36 we see that the probability of instability with the \(LV\) configuration will increase with internal flows (that is, \(V\)). This is similar to what was found for the instability caused by a singularity in the input transformation with the \(L, V\) configuration.

If we assume ideal vapor phase and neglect the small contribution from vapor heat capacity, we have for a binary mixture:

\[
\bar{H}_n^V = y_1 \Delta H_1^{vap} + (1-y) \Delta H_2^{vap} (39)
\]
and we derive \( dH^V/dy = \Delta H_1^{\text{vol}} - \Delta H_2^{\text{vol}} \) which is the difference in heats of vaporization for the light and heavy component at their boiling point. Usually, the most volatile component has the smallest heat of vaporization and we get \( dH^V/dy < 0 \). We also usually have \( k_{Lp}^{PV} < 0 \) and \( k_{Vp}^{PV} < 0 \) (Jacobsen and Skogestad, 1991), and we see from Eq. 36 that in this case instability is most likely when \( |k_{Vp}^{PV}| \) is large relative to \( |k_{Lp}^{PV}| \), which corresponds to having high purity in the top relative to the bottom. Note that this is different from what was found for the instability caused by the transformation between molar and mass reflux for the \( L,V \) configuration where instability was found to be most likely with a relatively impure top product.

Figure 7 shows the stable and unstable regions in terms of boilup \( V \) and distillate flow \( D \) for the methanol-propanol column with the \( L,V \) configuration. For low internal flows, that is, low values of \( V \), we see that there is no unstable region and thus a unique stable operating point for all values of \( L \). For values of \( V \) above 2.56 kmol/min there exist a region of unstable operating points and, as expected from the analysis above, the unstable region expands with increasing \( V \), that is, increasing internal flows. We also see from Figure 7 that for high values of \( D \), corresponding to low purity in the top relative to the bottom, there are no unstable operating points. This is true even at high values of the internal flows, and is also as expected from the above analysis.

The borders between the stable and unstable regions in Figure 7 correspond to limit-points with the \( L,V \) configuration and locally there are thus two steady-state solutions around these points.

Note that we in our derivation of Eq. 36 as a sufficient criterion for instability neglected changes in the liquid enthalpy with composition while the region of unstable operating points in Figure 7 was computed using a model with composition dependent liquid enthalpy. Because of this the unstable region is not predicted exactly by the criterion (Eq. 36). However, we note that the instability criterion \((\partial L/\partial D)_s(0)=0\) predicts the unstable region in Figure 7 exactly. This is not surprising as the border between the stable and unstable regions corresponds to \((\partial y_p/\partial L)_s(0)\) being singular, that is, it has a single zero eigenvalue at the border, and from Eq. 28 we see that this corresponds to having \((\partial L/\partial D)_s^{-1}(0)\) singular or \((\partial D/\partial L)_s(0)=0\).

**Combining mass flows and energy balance**

Jacobsen and Skogestad (1991) show that both types of multiplicities may be present in the same region of operation. They show that a column operating with the \( L,V \) configuration may have up to five different steady-state solutions, two of which they find to be unstable.

Figure 8 shows the stable and unstable operating regions in terms of boilup \( V \) and distillate flow \( D \) for the methanol-propanol column with the \( L,V \) configuration and the energy balance included in the model. The unstable region appearing in the upper part of the figure is caused by singularities in the transformation from \( L,V \) to \( L,D \) while the unstable region in the lower part is due to the presence of the energy balance. As seen from Figure 8, the two regions coincide at high values of \( V \), that is, high internal flows, and all solutions are therefore unstable for \( V>12.2 \text{ kmol/min} \).

Note that all the unstable operating points have only a single RHP pole. Some readers might believe that both types of instability may be present in some operating points thereby possibly giving rise to two unstable poles. However, instability with the \( L,V \)-configuration, due to energy balance effects, corresponds to \((\partial y_p/\partial L)_s(0)<0\) which implies that instability due to the input transformation is not possible according to Eq. 21 (when \( M_1<M_2 \)).

**Instability with \( D,V \)-Configuration**

We have so far only considered using reflux and boilup as independent variables. However, as discussed in the introduction, there are many possible configurations. For instance, changing condenser level control from using distillate \( D \) to using reflux \( L \), results in the \( D,V \)-configuration. Jacobsen and...
Skogestad (1991) show that multiplicity is unlikely with this configuration. Dynamically, with perfect level control, the operating points are found to be asymptotically stable in all examples we have considered. However, here we show that without the assumption of perfect level control an operating point may become unstable also with the \( D,V \)-configuration. We start by considering an example and will then explain the results thereof using analytical results.

**Methanol-propanol example**

Consider the methanol-propanol column in Table 1. The holdups in the reboiler and condenser are increased to \( M_D/F = M_B/F = 5.0 \) min. We consider the case with constant molar flows, and use distillate flow \( D \) and boilup \( V \) as independent inputs, that is, \( D,V \)-configuration. With this configuration the condenser level is controlled by reflux \( L \), and the reboiler level is controlled by bottoms flow \( B \). The nominal operating point we consider has \( D = 18.36 \) kg/min and \( V = 2.0 \) kmol/min. For these specifications we obtain \( y_D = 0.9237 \) and \( x_B = 0.0078 \), and the steady state is unique. Note that the operating point corresponds to solution III in Table 2 and Figure 2, that is, the operating point is unstable with the \( L,V \)-configuration.

We now consider the response for different gains \( K_M \) in the condenser level controller. A pure proportional controller is used, that is, \( dL = K_M dM + (s) \). We assume perfect level control in the reboiler. The upper part of Figure 9a shows the response in top composition \( y_D \) to a small increase in \( D \), keeping \( V \) constant, with the level controller gain \( K_M = 0.10 \). We see that the response is stable and slightly oscillatory. The lower plot in Figure 9a shows the corresponding phase plot for \( y_D \) and \( B \), and we see that the steady state is a stable spiral attractor (sink). Figure 9b shows the corresponding response with \( K_M \) reduced to 0.05. The response is now more oscillatory, but the steady state is still a stable spiral. With \( K_M \) reduced to 0.03 the operating point becomes an unstable spiral (source) as seen from Figure 9c. However, the response settles into a stable periodic behavior. This implies that there, in addition to the unstable steady state, is a solution corresponding to a stable limit cycle.

The fact that the steady state changes from a stable spiral to an unstable spiral as the level control gain is reduced implies that a pair of complex conjugate eigenvalues cross the imaginary axis. This may be seen from Figure 10a which shows the largest eigenvalues as a function of level control gain \( K_M \), that is, the root locus. We see that as the gain is reduced below a value of 0.043, the eigenvalues cross the imaginary axis, and the operating point becomes unstable. The fact that a pair of complex conjugate eigenvalues crosses the imaginary axis as \( K_M \) is reduced below a certain value implies that the column undergoes a Hopf bifurcation and a limit cycle results as the steady state becomes stable. The bifurcation is supercritical in this case as the resulting limit cycle is stable (see for example, Guckenheimer and Holmes, 1983).

**Conditions for instability**

To understand why the steady state for the \( D,V \) configuration becomes unstable, consider the transfer function \( \frac{\partial y_D}{\partial D}(s) \) which may be written:
Figure 10. Root locus for methanol-propanol column with constant molar flows and $D,V$ configuration.

$D_v = 18.36$ kg/min and $V = 2.0$ kmol/min. Plot shows maximum eigenvalues as function of gain $K_{MD}$ in condenser level controller (arrows indicate increasing gain). a. Eigenvalues computed from full model; b. eigenvalues computed from simple expression (Eq. 45).

\[ \left( \frac{\partial y_D}{\partial D_n} \right)_V (s) = \left( \frac{\partial y_D}{\partial L_n} \right)_V (s) \left( \frac{\partial L_n}{\partial D_n} \right)_V (s) \]  

(40)

Here the transfer function $(\partial y_D/\partial L_n)_V (s)$ expresses the effect of reflux on top composition with the $L,V$-configuration. For simplicity we consider only the largest pole in the transfer function:

\[ \left( \frac{\partial y_D}{\partial D_n} \right)_V (s) = k_{\text{reflux}} \frac{\lambda_w}{s - \lambda_w} \]  

(41)

Here $\lambda_w$ denotes the largest eigenvalue with the $L,V$-configuration, and as we have seen it may become positive, either because of the input transformation or because of the energy-balance effects. Here we consider the first case only, that is, we assume constant molar flows. However, similar results are obtained for cases where the instability is caused by the energy balance.

The transfer function $(\partial L_n/\partial D_n)_V (s)$ may be computed from a material balance around the condenser:

\[ dL_n(s) = \frac{K_{MD}}{s} [dV_T(s) - dL_n(s) - dD_n(s)] \]  

(42)

Rearranging and using $V_T = VFM$ and assuming constant molar flows such that $dV_T = dV$ yields:

\[ \left( \frac{\partial y_D}{\partial D_n} \right)_V (s) = \frac{K_{MD}}{K_{MD} + s} \left( \frac{\partial y_T}{\partial D_n} \right)_V (s) - 1 \]  

(43)

Here $y_T$ denotes the composition of $V_T$. We consider only the dominant response and get $(\partial y_T/\partial D_n)_V (s) = (\partial y_D/\partial D_n)_V (s)$. Inserting Eqs. 41 and 43 into Eq. 40 yields:

\[ \left( \frac{\partial y_D}{\partial D_n} \right)_V (s) = \frac{-\lambda_w k_{\text{reflux}} K_{MD}}{s^2 + (K_{MD} - \lambda_w) s + \lambda_w K_{MD} (k_{\text{reflux}} V_T (M_1 - M_2) - 1)} \]  

(44)

The two eigenvalues (poles) of the transfer function (Eq. 44) become:

\[ \lambda = -\frac{1}{2} (K_{MD} - \lambda_w) \]

\[ \pm \frac{1}{2} \sqrt{(K_{MD} - \lambda_w)^2 + 4\lambda_w K_{MD} [1 - k_{\text{reflux}} V_T (M_1 - M_2)]} \]  

(45)

Figure 10b shows the root locus for the methanol-propanol column computed using Eq. 45, and we see that the simple expression of this equation yields a reasonable prediction of the behavior of the full model in Figure 10a. The deviation is explained by the assumption of first-order response and negligible condenser holdup in the analytical treatment.

Let us now use Eq. 45 to consider the stability of the $D,V$ configuration for the two cases when the operating point is stable or unstable with the $L,V$ configuration.

(1) Stable $L,V$-configuration ($\lambda_w < 0$ and $k_{\text{reflux}}^{L,V} > 0$): In this case the first term in Eq. 45 is negative for all values of $K_{MD} > 0$. Furthermore, the second term under the root in Eq. 45 is negative and the root will be real with a value less than $(K_{MD} - \lambda_w)$, or it will be imaginary. This implies that both eigenvalues in Eq. 45 are in the LHP, that is, the $D,V$-configuration is stable for all values of $K_{MD} > 0$.

(2) Unstable $L,V$-configuration ($\lambda_w > 0$ and $k_{\text{reflux}}^{L,V} < 0$): In this case the first term in Eq. 45 is positive if $K_{MD} < \lambda_w$, that is, at least one of the eigenvalues in Eq. 45 are in the RHP with $K_{MD} < \lambda_w$. The size of $K_{MD}$ will determine whether the root in Eq. 45 is imaginary. For $K_{MD} = \lambda_w$, that is, at the bifurcation point, the root is imaginary if $-k_{\text{reflux}}^{L,V} V_T (M_1 - M_2) > 1$ (note that we also assume $M_2 > M_1$). From Eq. 17 we get with $s = 0$ that $k_{\text{reflux}}^{L,V} = k_{\text{reflux}}^{L,V} / \left[ M - L (M_2 - M_1) \right]$, and we find that the root is imaginary if:

\[ \frac{V_T (M_1 - M_2) k_{\text{reflux}}^{L,V}}{L (M_2 - M_1) k_{\text{reflux}}^{L,V} - M} > 1 \]  

(46)

which is always satisfied since the denominator is positive and $V_T \geq L$. Thus, under the assumption of first-order response in
Eq. 41, the bifurcation point will always correspond to a Hopf bifurcation and a limit cycle is born as the steady state becomes unstable. In all examples that we have studied the bifurcation is supercritical, that is, the resulting limit cycle is stable.

We conclude from the above analysis that a prerequisite for instability with the $D,V$ configuration is that the operating point is unstable with the $L,V$ configuration. This is not surprising as the level control for the $D,V$ configuration may be viewed as a feedback effect on the $L,V$ configuration. If the feedback control is not sufficiently tight then we are not able to stabilize the column. With a gain $KM_0 = 0$, that is, no condenser level control, we see from Eq. 45 that there will be a RHP pole at $\lambda_c$ (in addition to a pole at 0), and we effectively have the stability properties of the $L,V$-configuration. This may also be seen from the root locus in Figure 10a for $KM_0 = 0$.

Also other configurations may display the type of instability found with the $D,V$ configuration above. For instance, it is easily shown that the $L,B_c$-configuration becomes unstable if the $L,V$ configuration is unstable and the reboiler level control is not sufficiently tight. The instability is also in this case resulting from a Hopf bifurcation.

**Discussion**

*Use of volumetric flows*

In this article we have only discussed using inputs on a mass basis, for example, reflux $L_w$ in kg/min. In many columns the flows are fixed on a volume basis [m$^3$/min]. If this is the case, and we assume ideal mixing, the molecular weights $M_1$ and $M_2$ (for example, in Eq. 21) should be replaced by the molecular volumes $V_1 = M_1/\rho_1$ and $V_2 = M_2/\rho_2$, where $\rho$ is the liquid density in kg/m$^3$ of component $i$. For most mixtures the difference in liquid density between the components is small, and very similar results are obtained with volume flows as those obtained with mass flows.

*Industrial columns*

The methanol-propanol column that we have studied in this article is not optimally designed for the product compositions at operating point III in Table 2. In fact it is doubtful that the column would be unstable when optimally designed as the internal flows then would be significantly smaller. This is probably true for many separations, that is, an optimally designed column will be open-loop stable. However, few industrial columns are operated close to the optimal operating point. One reason is that the desired compositions will change after the column is built. In addition, many operators prefer to use high mass flows (overpurification) in order to assure that specific-

*Is the instability caused by feedback?*

All the results in this article are for a partially controlled system where we assume feedback control of pressure and the two levels. One may ask whether the observed instability is a fundamental property or if it is an artifact caused by these feedbacks. We argue that it is indeed a fundamental property. Consider the $L,V$ or $L,Q_B$ configuration for which instability is most likely to occur in a practical situation. It is easily shown that the instability in this case is independent of the level control. Next consider the pressure. First, there are many cases where pressure may be kept constant without the need for feedback. As an example consider a typical lab-scale distillation column with an open vent to the surroundings, and where the pressure is "self-regulated" since the cooling adjusts itself to maintain atmospheric pressure at the top. Secondly, for the case of constant molar flows and constant relative volatility (independent of pressure), our analysis would be the same if we assumed constant cooling duty $Q_D$ rather than constant pressure. This follows since $Q_D = V_T/\dot{H}_c$ (Appendix 1) where $\dot{H}_c$ is independent of composition when we have constant molar flows. Thus, $Q_D$ constant implies that $V_T$ is constant such the vapor flow remains constant up the column. Also, if the relative volatility is independent of pressure, $(\partial y_D/\partial L)_v$ is the same both when $p$ or $V_T$ is constant. In conclusion, the instability for the $L,V$-configuration is not caused by feedback control of level and pressure.

On the other hand, for the $D,V$ configuration the feedback control is critical for the observed results. Indeed, without any condenser level control the $D,V$ configuration behaves as the $L,V$ configuration. It is therefore unstable with sufficiently slow level control when the $L,V$ configuration is unstable, but the level control may stabilize the system, and yield, for example, the stable limit cycle as shown in Figure 9c.

**Conclusions**

1. Two-product distillation columns operating with reflux and boilup as independent inputs may be open-loop unstable with a single right half plane pole. Two different effects may cause the instability:
   - Singularities in the transformation between the actual input units (mass or volume) and the molar units which determine separation.
   - Singularities between molar flows and compositions due to interactions through the material and energy balance. In both cases the probability of instability is increased with increased internal flows.

2. Distillation columns operating with distillate flow and boilup as independent variables may have unstable operating points if the condenser level control is not sufficiently tight. The instability will in this case correspond to a Hopf bifurcation, that is, a pair of complex conjugate eigenvalues cross the imaginary axis and a limit cycle (usually stable) is born as the steady state becomes unstable. A prerequisite for instability with this configuration is that the operating point is unstable with reflux and boilup as independent variables.

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**Notation**

- $B =$ bottoms flow (kmol/min)
- $a(s) = 1 + a_1 s + \cdots + a_n s^n =$ pole polynomial
Greek letters

\( \alpha = \frac{y_{i}/x_{i}}{(1-y_{i})/(1-x_{i})} \) relative volatility (binary mixture)

\( \lambda = \text{eigenvalue (pole) of system} \)

\( \lambda_{\text{max}} = \text{eigenvalue with largest real part} \)

\( \tau_L = \text{hydraulic time constant (min)} \)

Subscripts

0 = initial steady-state value

1 = most volatile component

2 = least volatile component

i = stage no.

w = flow rate in kg/min

Literature Cited


