

# Multiple Steady States in Ideal Two-Product Distillation

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## Abstract

Results are presented showing that simple distillation columns with ideal thermodynamics may display multiple steady state solutions. The multiplicity may have two different sources. The first type of multiplicity is found for columns with mass or volume inputs (eg. reflux and boilup). In this case we find that the transformation between the actual input units and molar units may become singular. This may be the case even for ideal thermodynamics and constant molar flows. The singularity will result in multiple steady-state solutions, one of which will be unstable. The results are highly relevant in practice as industrial columns will have inputs on a mass or volume basis.

The second type of multiplicity is found for specifications on a molar basis and depends on the presence of an energy-balance in the model. In this case the multiplicity is caused by an interaction between flows and compositions in the column. Also this type of multiplicity may be experienced in industrially operated columns as it is the size of the molar flows that determines the separation in distillation.

# 1 Introduction

The issue of multiple steady-states (multiplicity) in distillation columns has been studied extensively over the last 30 years. A literature review on homogeneous (one liquid phase) distillation is given by Doherty and Perkins (1982). Rosenbrock (1960,1962) was the first to prove, using a Krasovski form of the Lyapunov function, that multiplicity is impossible for ideal cases with constant molar flows. Doherty and Perkins (1982) study models of different complexity, and conclude that multiple steady states is impossible for single-staged "columns" and for any multistage column separating a binary mixture. They assume constant molar flows, ie. neglect the energy balances, and do not draw any conclusions for the multicomponent multistage case. Sridhar and Lucia (1989) include the energy balance in the model and conclude that also in this case binary distillation columns will exhibit unique solutions. They do however only study two different sets of specifications (ie.  $LB$  and  $Q_D Q_B$ ).

In a simulation study Magnussen et.al. (1979) report multiple solutions for a non-ideal mixture of water-ethanol-benzene. The authors do not give any explanation for their results, and the multiplicity was only predicted by the NRTL and UNIQUAC activity coefficient models. Their results have been studied and reproduced in several other simulation papers (Prokopakis and Seider, 1983; Kovach and Seider, 1987; Venkataraman and Lucia, 1988). The main reason for the multiplicity in this case is the non-ideality in terms of potential liquid-liquid phase split in the mixture (Lucia et al., 1989). Widagdo et.al (1989) report multiplicity for another heterogenous system.

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

In this paper we present two fundamentally different types of multiplicity: I) Multiplicity in input unit transformations and II) multiplicity for molar flows.

I. Multiplicity in input unit transformations. Common for all the work 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, in this paper we argue that in practice most streams, in particular liquid streams, are *not* given on a molar 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 also 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 is dependent 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 present in real columns as it is the size of the molar flows that determines separation in distillation. This type of multiplicity will in addition be important in simulations where specifications most often are done on a molar basis.

The term “multiplicity” used above refers to the case of *output multiplicity*, that is, when there for a given value of the independent variables (inputs, eg. reflux and boilup) exists several possible sets of dependent variables (outputs, eg. product compositions). This is similar to the classical example of multiplicity in exothermic chemical reactors in which there exists two stable and one unstable steady-state.

Another kind of multiplicity which is only briefly discussed in this paper is *input multiplicity*. This is when there for a given value of the output exists several possible sets of inputs. It is quite common within chemical engineering, and may occur whenever there is an extremum in the relationship between the input and the output. For example, for distillation columns the relationship between product flow and concentration of intermediate component generally has a maximum (see discussion 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).

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

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

### 2 Introductory example

*Example 1.* Data for a methanol-propanol column are given in Table 1. We have assumed constant relative volatility as well as constant molar flows. The last assumption implies constant vapor and liquid molar flows through the column (except for 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 2. For  $L_w$  between 48.8 and 52.2 kg/min there exists three steady-state solutions. For example, with  $V = 2.5$  kmol/min and  $L_w = 50$  kg/min we get the three steady-states II, III and IV given

in Table 2. With fixed values of  $V$  and  $L_w$  the solution on the upper and lower branches on Fig.2 are stable, whereas the intermediate branch (steady-state III) is unstable. The reason for this multiplicity is the transformation  $L = L_w/M$  between mass and molar reflux. As seen from Fig.2 this transformation is not unique for  $L_w$  in the region 48.8 and 52.2 kg/h.

The objective of the next chapters is to discuss and explain the results presented in this example.

### 3 Specification of Flows in Distillation Columns.

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

*Configurations.* Consider the two-product distillation column in Figure 1. If the feed to the column is given there are 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, that is, only two of these flows may be specified independently. In the following we shall denote a specific choice of two independent flows as a "configuration". This word comes from process control where these are the independent variables from a control point of view.

*Notation.*  $n$  (or with no subscript) denotes molar flow in kmol/min,  $w$  (or as subscript) denotes mass flow in kg/min,  $q$  (or as subscript) denotes volumetric flow in m<sup>3</sup>/min. For example,  $L$  is reflux in kmol/min,  $L_w$  in kg/min and  $L_q$  in m<sup>3</sup>/min. Furthermore,  $v$  (m/min) is the linear velocity,  $M$  (kg/kmol) is the molecular weight,  $\rho$  (kg/m<sup>3</sup>) is the density, and  $A$  (m<sup>2</sup>) is the cross-sectional area. We have

$$w = Mn \tag{1}$$

$$w = \rho q \tag{2}$$

$$q = Mn/\rho \tag{3}$$

$$q = Av \tag{4}$$

For example,  $L_w = \rho L_q = ML$ .  $M$  is often a strong function of composition (operating point). For liquids  $\rho$  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 weakly dependent 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  $\Delta p_V = \hat{k}(z)\rho v^2 = k(z)qw$  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,  $\sqrt{qw}$ . In the second case assume 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 conclusion, in this case it is most natural to specify the flow on a volumetric or mass basis

(as noted above these are usually not too different). Special case: If a partial condenser is used then the reflux may be indirectly given 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 restriction in a pipe, eg. an orifice or venturi. As noted above the pressure drop is proportional to the product  $qw$ , and hence one gets a measure of the geometric average of the mass and volumetric flowrate. Other measuring devices give a direct measure of volumetric flowrate  $q$ , eg. displacement meters, turbine meters and magnetic meters. Direct measurements of mass flow rates also exist. However, for liquids no direct measurement of molar flowrate is in common use.

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

$$Q = V(H_{V1} - H_{L2}) + B(H_{L1} - H_{L2}) \quad (5)$$

where  $H_{Vi}$  and  $H_{Li}$  are the molar enthalpies on tray  $i$  of the vapor and liquid phases respectively. Neglecting variations in the liquid enthalpy yields

$$Q \approx V(H_{V1} - H_L) = V\Delta H_{vap1} \quad (6)$$

where  $\Delta H_{vap1}$  is the heat of vaporization in the reboiler. In many cases  $\Delta H_{vap}$  is only weakly dependent on composition and specifying  $Q$  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.

*Summary.* 1) 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. Since the mole weight  $M$  often depends strongly on composition, this implies that the molar flow rate  $n$  may change considerably during operation even though the volumetric flow rate  $q$  or mass flow rate  $w$  is constant. 2) It seems reasonable in many cases to assume the boilup  $V$  to be given on a molar basis.

## 4 Transformation between Actual Flow and Molar Units

Doherty and Perkins (1982) have shown that multiplicity is impossible in the binary, constant molar flow case, ie. for a given  $L$  and  $V$  (molar basis) there exist 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 a specific case almost any combination of units is possible, and only rarely will it be reasonable

to assume that both flows are specified on a molar basis. In the following we shall mainly consider the  $L_wV$ -configuration, that is, with reflux specified on mass basis and with boilup on molar basis. We shall also discuss the effect of choosing other flows as independent inputs, for example, the  $D_wV$ - and  $LQ$ -configuration. In the latter case the heat input  $Q$ , which indirectly sets  $V$ , is used as an independent variable.

#### 4.1 $L_wV$ -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:

$$L = L_w/M; \quad M = y_D M_1 + (1 - y_D) M_2 \quad (7)$$

Here  $M_i$  denotes the mole weight of the individual components. We might expect  $L$  to increase uniformly with  $L_w$ , that is,  $dL/dL_w > 0$  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 the molar boilup  $V$  is fixed, and differentiate both sides of  $L_w = LM$  with respect to  $L$

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

This slope is negative when

$$M_1 y_D + M_2 (1 - y_D) - L(M_2 - M_1) \left( \frac{\partial y_D}{\partial L} \right)_V < 0 \quad (9)$$

which will correspond to an unstable operating point. The possible negative slope 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  $L$ . 1) Initially,  $L_w = LM$  always increases because  $M$  is unchanged. 2) However, as a result of the increase in  $L$  the fraction of light component will start increasing<sup>1</sup> 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 never 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  $\Delta y_{D1}$ .

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<sup>1</sup>The gain  $(\partial y_D / \partial L)_V$  is positive for any column with constant molar flows provided the stage efficiency is not reduced drastically as  $L$  increases, see Häggblom (1988). This also applies to the light key component in a multicomponent separation if pseudobinary compositions are used. However, when the energy-balance is included  $\left( \frac{\partial y_D}{\partial L} \right)_V$  may be negative as shown in Part II of this paper.

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

$$\left( \frac{\partial y_D}{\partial L} \right)_V \left( \frac{\partial L}{\partial y_D} \right)_{L_w} > 1 \quad (10)$$

which may shown to be equivalent to having a negative slope in (8). 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  $V$ . 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 the introductory example, 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 between  $L_w$  and  $L$  is singular (ie.,  $\partial L / \partial L_w = \infty$ ). Singular points occur when we have equality in (9).

*Example 2. One-stage column.* Consider the simple column in Fig.3 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. Nevertheless, this is an excellent example for demonstrating the presence of instability and multiple steady-states. Assume binary separation, constant relative volatility and liquid feed. The following equations apply

$$Fz_F = Dy_D + Bx_B \quad (11)$$

$$D = V - L; \quad B = L + F - V \quad (12)$$

$$\alpha = \frac{y_D(1 - x_B)}{(1 - y_D)x_B} \quad (13)$$

$$L_w = LM; \quad M = y_D M_1 + (1 - y_D) M_2 \quad (14)$$

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 (11)-(14) 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 graphically in Fig.4b. 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 Fig.4c where  $V$  has been increased from 4.7 to 7 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 Fig.4a where  $V = 4$  kmol/min.

## 4.2 $D_wV$ -configuration

We have

$$D = D_w/M \quad (15)$$

where  $M$  is defined by Eq. 7. Differentiating yields the following condition for instability

$$\left(\frac{\partial D_w}{\partial D}\right)_V = M + D(M_1 - M_2) \left(\frac{\partial y_D}{\partial D}\right)_V < 0 \quad (16)$$

Since  $(\partial y_D/\partial D)_V$  always is negative for the case of constant molar flows, we see from (16) that a necessary condition for instability or singularity is that  $M_1 > M_2$ , ie. 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.

## 4.3 LQ-configuration

Above we 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,  $Q$ , to the reboiler. The energy balance for the reboiler when liquid enthalpy changes are neglected yields (Eq.6)

$$V \approx Q/\Delta H_{vap}(x_B) \quad (17)$$

Here we have indicated that the heat of vaporization,  $\Delta H_{vap}$ , 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 molefraction of light component. The differential of  $Q$  with respect to  $V$  becomes

$$\left(\frac{\partial Q}{\partial V}\right)_L = \Delta H_{vap} + V \frac{d\Delta H_{vap}}{dx_B} \left(\frac{\partial x_B}{\partial V}\right)_L \quad (18)$$

and we have instability if this slope is negative. As  $(\partial x_B/\partial V)_L$  is essentially always negative, we see from Eq. 18 that a necessary condition for instability or singularity is that  $d\Delta H_{vap}/dx_B > 0$  for the actual value of  $x_B$ . This will usually be the case when the lightest component has the largest heat of vaporization, but may also happen for non-ideal systems where this is not the case.



*Example 3. One-Stage propanol-acetic acid column* (Fig. 3). Propanol is the more volatile component and the relative volatility,  $\alpha$ , is in the range 1.85 to 2.25. The heat of vaporizations are 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 (5), 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  $Q = 349$  MJ/min. We obtain two steady-state solutions for these specifications: 1)  $y_D = 0.596$  and 2)  $y_D = 0.787$ . Solution 1) is unstable while solution 2) is stable. The multiplicity is illustrated graphically in Fig. 5.

## 4.4 Other Configurations

As seen from the above, possible singularities in the transformation of streams depends on the choice of configuration, or in terms of steady-state simulation, which flows we choose to specify. The analysis of other configurations follows the same lines as for the ones discussed above. It is obvious from the above that a necessity for singularity to occur in the transformation between molar units and other units is that there are opposing effects included in the transformation. This means that an input which when increased on a molar basis affects composition so that the molar weight or molar volume *decreases*, may have a singularity in the transformation from mass or volume basis to molar basis. 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  $V_w$  requires the opposite, ie.  $M_1 > M_2$ . This is easily seen from the sign of the respective gains. However, as we shall see below it seems unlikely that singularity will occur for  $D_w$  or  $B_w$ . For ratio inputs instability is also unlikely in most cases. For example,  $(L/D)$  is independent of composition provided the column has a total condenser and  $L$  and  $D$  are measured in the same units.

## 5 Analytical Treatment

The analytical results presented here are for the ideal case with constant molar flows and constant relative volatility.

### 5.1 $L_wV$ -configuration

From (9) we know that instability will occur at operating points where

$$y_D + L \left( \frac{\partial y_D}{\partial L} \right)_V > \frac{M_2}{M_2 - M_1} \quad (19)$$

Here we have assumed  $M_2 > M_1$  which we have shown is a necessary condition for instability for this configuration. To understand the implications of condition (19) 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.

### 5.1.1 One-stage column

Differentiating (11)-(13) yields the following exact expression for the gain

$$\left(\frac{\partial y_D}{\partial L}\right)_V = \frac{(1 - y_D)y_D(y_D - x_B)}{Bx_B(1 - x_B) + Dy_D(1 - y_D)} \quad (20)$$

Condition (19) for instability then becomes

$$y_D + L \frac{(1 - y_D)y_D(y_D - x_B)}{Bx_B(1 - x_B) + Dy_D(1 - y_D)} > \frac{M_2}{M_2 - M_1} \quad (21)$$

The gain (20) varies only moderately with operating conditions for a single-stage column. Thus we conclude from (21) 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 the instability condition  $L > 4.0$ . Since we have  $L=4.2$  the operating point is unstable.

### 5.1.2 Multistage column

Somewhat surprisingly, the analytical results for the one-stage column carry over almost directly to the multistage case. For example, expression (20) for the gain  $(\partial y_D/\partial L)_V$  is a good approximation for multistage columns with constant molar flows (eg., Skogestad and Morari, 1987b). The reason is that the overall separation factor

$$S = \frac{y_D(1 - x_B)}{(1 - y_D)x_B} \quad (22)$$

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  $\alpha$ ). Eq.(22) then takes the place of Eq.(13) 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

$$\left(\frac{\partial y_D}{\partial L}\right)_V = \frac{(1 - y_D)y_D(y_D - x_B)}{Bx_B(1 - x_B) + Dy_D(1 - y_D)} \left(1 + \frac{Bx_B(1 - x_B)}{y_D - x_B} \left(\frac{\partial \ln S}{\partial L}\right)_V\right) \quad (23)$$

The only assumptions made here are those of constant molar flows and negligible subcooling such that (12) applies. (23) shows that the effect of changes in  $S$  on the gain is always negligible when the bottom product is pure, ie.,  $x_B \approx 0$ .]

The main difference from the single-stage case is that in a multistage column the compositions and the gain (20) may change drastically with operating conditions. To study this effect consider the following three cases:

I) Top impure, bottom pure ( $x_B \ll (1 - y_D)$ ). (20) simplifies to:

$$\left(\frac{\partial y_D}{\partial L}\right)_V \approx \frac{y_D - x_B}{D} \approx \frac{y_D}{D} \quad (24)$$

II) Equal purity in top and bottom ( $x_B \approx (1 - y_D)$ ). (20) simplifies to:

$$\left(\frac{\partial y_D}{\partial L}\right)_V \approx \frac{y_D - x_B}{F} \approx \frac{1}{F} \quad (25)$$

III) Top pure, bottom impure ( $x_B \gg (1 - y_D)$ ). (20) simplifies to:

$$\left(\frac{\partial y_D}{\partial L}\right)_V \approx \frac{1 - y_D}{Bx_B} \approx 0 \quad (26)$$

Recall the instability condition (19). We conclude that instability is unlikely in case III, that is, 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

$$y_D(1 + L/D) > \frac{M_2}{M_2 - M_1} \quad (27)$$

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.

In practice, conditions 2 and 3 are often 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) are usually 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.

*Methanol-Propanol Example.* Consider a methanol-propanol column (example 1) which is operated manually with the  $L_wV$ -configuration. For this mixture we have  $M_2/(M_2 - M_1) = 2.14$ , and if the column is operated such that the bottom product (propanol) is much purer than the top product, instability will occur for  $L/D > 1.14$  (here we have assumed  $y_D \approx 1$ ).

*Additional examples.* Skogestad and Morari (eg., 1987) have studied the dynamics and control of seven example columns. The data for the columns are given in Table 4 together with the critical mole weight ratio  $M_2/M_1$  needed to make the operating points unstable for the  $L_wV$ -configuration according to equation (19). The ratio is in the region 1.23 - 223 for the seven examples. The exact gains given in Skogestad and Morari (1987) were used in these calculations. Column C with a pure bottom product requires the smallest ratio for instability. It has  $L/D = 4.93$  and  $\alpha = 1.5$ . It is likely that a real mixture with this relative volatility would have  $M_2/M_1 > 1.23$ . For example, the mixture methanol-ethanol has  $M_2/M_1 = 1.44$  and  $\alpha \approx 1.5$  at 2 bar.

## 5.2 $LQ$ -configuration

A similar analysis for the case where boilup  $V$  is determined by heat input  $Q$ , shows that instability is most likely when the internal streams are large and when the bottom product is relatively unpure.

## 5.3 $D_wV$ -configuration

For the  $D_wV$ -configuration we see from (16) that multiplicity and instability is almost independent on the size of the internal streams. The gain  $(\partial y_D/\partial D)_V = -(\partial y_D/\partial L)_V$  is largest in magnitude when the bottom product is pure. In this case the gain is approximately  $-y_D/D$  and condition (16) for instability becomes  $M_2 < 0$  which of course is impossible to satisfy. This derivation has assumed constant molar flows, but nevertheless it seems very unlikely that multiple steady-states or instability may ever occur for this configuration. The same arguments apply to the  $LB_w$ -configuration.

# Part II. Multiple Steady States for Molar Inputs

To this point we have only discussed multiplicity in distillation due to input units other than molar. Models of binary distillation columns with constant molar flows will always exhibit unique solutions for molar specifications (Doherty and Perkins, 1982). However, here we provide an example showing that when the energy balance is included in the model, we may get multiplicity when molar reflux and boilup are used as specifications ( $LV$ -configuration). The occurrence of this multiplicity depends on the energy-balance, and is actually quite similar to the case with the  $LQ$ -configuration studied in Example 3 above.

## 6 $LV$ -configuration

*Example 4* We will again study the methanol-propanol column in Table 1. We now include an energy-balance on each tray where we previously assumed constant molar flows. The energy-balance on each tray is given by

$$Q_i + V_{i-1}H_{i-1}^V + L_{i+1}H_{i+1}^L - V_iH_i^V - L_iH_i^L + F_iH_i^F = 0 \quad (28)$$

where subscript  $i$  denotes tray number (trays are numbered from the bottom). We assume constant relative volatility as before, while enthalpies is computed from the equations given in Table 5.

Molar boilup  $V$  is kept constant constant at 4.5 kmol/min and we consider solutions for molar reflux between 4.6 and 4.75 kmol/min. Some solutions are given in Table 6. From the

table we see 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 graphically illustrated in Fig.6. The example

above shows that we may have multiplicity for the  $LV$ -configuration even in ideal binary distillation. In order to get an understanding of the source of the multiplicity we will consider the transformation between the  $DV$ -configuration, which yields unique solutions in terms of compositions, and the  $LV$ -configuration. A total mass balance around the condenser yields

$$L + D = V_T \quad (29)$$

where  $V_T$  denotes vapor flow from the top tray. For constant molar flows we have  $dV_T = dV$  and

$$\left(\frac{\partial L}{\partial D}\right)_V = -1 \quad (30)$$

However, due to the energy balance the flows inside the column will change as compositions change and we get

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

when  $\left(\frac{\partial V_T}{\partial D}\right)_V$  is not equal to zero. When  $\left(\frac{\partial V_T}{\partial D}\right)_V = 1$  the right hand side of Eq.31 becomes 0 and we will have singularity in the transformation between  $L$  and  $D$ . Instability will occur when

$$\left(\frac{\partial L}{\partial D}\right)_V > 0 \quad (32)$$

which corresponds to a negative slope between reflux  $L$  and top composition  $y_D$

$$\left(\frac{\partial y_D}{\partial L}\right)_V < 0 \quad (33)$$

We have  $\left(\frac{\partial L}{\partial D}\right)_V = -\left(\frac{\partial L_B}{\partial L}\right)_V$  and Eq. 32. is equivalent to

$$\left(\frac{\partial L_B}{\partial L}\right)_V < 0 \quad (34)$$

where  $L_B$  is liquid flow from the 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. This is illustrated in Fig.7 where we have plotted two liquid flow profiles in the unstable region for the methanol-propanol column. We see that an increase in reflux gives a decrease in liquid flows in the bottom part of the column. The profiles cross each other at the feed point in this case, but may in principal cross each other at any point.

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

$$\left(\frac{\partial V}{\partial B}\right)_L > 0 \quad (35)$$

and

$$\left(\frac{\partial x_B}{\partial V}\right)_L > 0 \quad (36)$$

We similarly find that in the unstable region profiles for different boilups have one crossing point, ie.

$$\left(\frac{\partial V_T}{\partial V}\right)_L < 0 \quad (37)$$

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 what we find for constant molar flows (eg.  $\left(\frac{\partial y_D}{\partial L}\right)_V < 0$ ) and we get multiple steady state solutions, one of which is unstable. Rademaker et.al. (1975) claim that the influence of compositions on flow rates usually will be negligible. The results we present here shows that the influence in many cases will be crucial, leading even to inversed gains and instability in some cases.

We do not present an analysis of when multiplicity is most likely for the case of molar flows in this paper. Such an analysis will be rather complicated. We only conclude that multiplicity is possible for the specification of molar reflux and boilup, and that instability seems to be most likely when internal flows in the column are large.

For the system studied we have that the most volatile component have the smallest heat of vaporization (usual case), but we also find multiplicity in systems where we have opposite relations, ie. where the most volatile component have the highest heat of vaporization. This implies that the type of multiplicity shown here is in principal possible in any system, ideal or non- ideal.

## 7 Combination of Mass Inputs and Energy Balance

In the first part of the paper we considered effect of mass inputs assuming constant molar flows. However, it is clear that the results will be altered somewhat when including the energy balance in the model. We discuss here short the implications of including an energy-balance in the model.

Figure 8 shows solutions for the methanol-propanol column for mass reflux in the range 57 to 60 kg/min while keeping molar boilup at 2.0 kmol/min. Compared to Fig.2 which shows the similar results for the case of constant molar flows, we see that the range of multiplicity in terms of mass reflux becomes more narrow when including the energy-balance. The reason for this is that with the energy-balance we get a more rapid change of  $y_D$  with molar reflux in the region where we would expect multiplicity ( $x_B \ll (1 - y_D)$ ). For this value of boilup there is no multiplicity between molar reflux and top composition.

Figure 9 shows solutions for the methanol-propanol column for mass-reflux in the range 95 kg/min to 103 kg/min while keeping boilup at 3.0 kmol/min. We see that we now have

two regions of multiplicity, and due to a partial overlap we get 4 solutions for mass reflux in the range 95.75 to 96.2 kg/min. If we could allow for negative product flows we would get five solutions as the upper branch would also overlap. The two lower singular points (high purity in top) are caused by a multiplicity between molar reflux  $L$  and top composition  $y_D$ , while the two upper singular points are caused by a multiplicity between mass reflux  $L_w$  and molar reflux  $L$ . This may be seen from the plot of mass reflux versus molar reflux in Fig.9. We see that for molar reflux around 3.0 kmol/min we have a multiplicity between molar reflux and mass reflux, ie. one molar reflux corresponds to three different mass-refluxes. This is caused by the multiplicity between molar reflux and top composition  $y_D$ .

In order to determine singularity or negative slope for the  $L_wV$ -configuration we should consider  $\left(\frac{\partial y_D}{\partial L_w}\right)_V$ , which may be written as

$$\left(\frac{\partial y_D}{\partial L_w}\right)_V = \left(\frac{\partial y_D}{\partial L}\right)_V \left(\frac{\partial L}{\partial L_w}\right)_V \quad (38)$$

We see that we will have a negative slope between  $L_w$  and  $y_D$  whenever one of the elements on the right hand side of Eq. 38 is negative. This will happen when 1) there is a negative slope between molar reflux and top composition or 2) when there is a negative slope between molar and mass reflux. Equation 38 tells us that we will have a positive slope between mass reflux  $L_w$  and top composition  $y_D$  if both 1) and 2) occur at the same time. However, from Eq.9 it is clear that when  $\left(\frac{\partial y_D}{\partial L}\right)_V$  is negative we will not have any singularity nor negative slope between mass and molar reflux (provided  $M_2 > M_1$ ). This implies that the instability for the molar reflux usually is preserved when using mass reflux.

## 8 Discussion

*Global stability.* We have derived conditions, e.g. (19), 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. To be specific, recall Example 1 and Table 2. It is easily shown using (19) that operating point III is unstable, and that operating points I, II, IV and V are (locally) stable. It is clear from Figure 2 that operating points I and V are globally stable (with the given  $L_w$  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 using molar inputs in a steady-state simulator, and then convert the results to the actual input units, that is, to generate a figure similar to Fig.2.

*Subcooling.* In this paper 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

composition. The separation in the column is determined by the effective reflux  $L_{eff} > L$  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 (10) is therefore reduced in magnitude, and we conclude that subcooling makes instability somewhat less likely for the  $L_wV$ -configuration.

*Multicomponent mixtures.* Introducing additional non-key components will generally make multiplicity and instability less probable for the case of mass or volume inputs. The reason is that the “dead weight” of the non-key components generally will reduce the effect of changes in the compositions of the key components on mole weight,  $M$ , and heat of vaporization,  $\Delta H_{vap}$ .

*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 only substitute the molecular weights with the molar volumes in the equations presented. For example, consider the  $L_qV$ -configuration. Similar to the mass case,  $V_2 > V_1$  is necessary for instability, and in this case the instability condition becomes

$$y_D + L \left( \frac{\partial y_D}{\partial L} \right)_V > \frac{V_2}{V_2 - V_1} \quad (39)$$

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  $795 \text{ kg/m}^3$  and a density of propanol of  $806 \text{ kg/m}^3$  at normal conditions and the results for volume inputs would be almost identical to what is found for mass inputs. For non-ideal 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 common in industry, it is surprising that there has 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 operation the presence of 1) instability and 2) multiple steady-states with the  $L_wV$ -configuration may be observed as follows: 1) Instability. 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 manual mode instability will occur. 2) Multiple steady states. 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 (Fig.10). Hysteresis may also be experienced during operation, that is, if one takes an input (eg.  $L_w$ ) through a singular point the outputs of the column will jump to totally different values. However, resetting the input to its original



value will not force the outputs back to their original values. This closed-loop hysteresis phenomena with jumps at the singular points is well known from catastrophe theory (see eg. Woodcock and Davis (1978)), and is illustrated in Fig. 10.

*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  $y_M \approx y_M^* = z_M/(1 - z_H) > z_M$ . 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, as illustrated in Fig.11, the relationship between  $D$  and  $y_M$  has a maximum. If  $y_M$  is specified between  $z_M$  and  $y_M^*$  there exists two possible values for  $D$ , that is, 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.

## 9 Conclusions

1. 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.
2. The behavior may be caused by two different effects:
  - I) Possible singularities in the transformation between the actual independent flows and 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 1) The mole weight of the light component is much smaller than of the heavy component, but relative volatility still reasonably close to 1. 2) Bottom product relatively pure ( $x_B \ll (1 - y_D)$ ), and 3)  $L/D$  large.
  - II) Possible singularities between top composition  $y_D$  and molar reflux  $L$  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. High internal flows will in most cases favor instability.
3. For the  $L_wV$ -configuration the following three operating regimes exist :

-Internal flows low. No multiplicity, no instability.

-Internal flows intermediate. Multiple steady-states, one of which is unstable. (In some cases there may be two unstable states due to both molar- and mass-input multiplicity in the same area of operation)

-Internal flows high. No multiple steady-states, all operating points unstable.

## NOMENCLATURE (also see Fig. 1)

$B$  - 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)

$\Delta H_{vap}$  - 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)

$Q$  - heat input to reboiler (kJ/min)

$S = \frac{y_D(1-x_B)}{(1-y_D)x_B}$  - separation factor (binary mixture)

$v$  - linear velocity (m/s)

$V$  - boilup from reboiler (kmol/min) (determined indirectly by heating  $Q$ )

$V_T$  - vapor flow rate from top tray (kmol/min) (determined indirectly by cooling)

$V_1$  - pure component molar volume of most volatile component (m<sup>3</sup>/kmol)

$V_2$  - pure component molar volume of least volatile component (m<sup>3</sup>/kmol)

$x_B$  - mole fraction of most volatile component in bottom product

$y_D$  - mole fraction of most volatile component in distillate (top product)

$z_F$  - mole fraction of most volatile component in feed

### Greek symbols

$\alpha = \frac{y_i/x_i}{(1-y_i)/(1-x_i)}$  - relative volatility (binary mixture)

$\rho$  - density (kg/m<sup>3</sup>)

### Subscripts

$q$  - flow rate in m<sup>3</sup>/min

$w$  - flow rate in kg/min

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**Table 1.** Data for example columns.

Example	$z_F$	$F$	$\alpha$	$N$	$N_F$	$M_1$	$M_2$
1.Methanol – Propanol	0.50	1	3.55	8	4	32.04	60.10
2.One – stage column	0.50	1	4.0	1	1	20	40
3.Propanol – Acetic acid	0.50	1	*)	1	1		

Feed is saturated liquid

Total condenser with saturated reflux

\*)  $\alpha$  varies since non-ideal thermodynamics are used

**Table 2.** Steady-state solutions for methanol-propanol column with  $V=2.0$  kmol/min and  $L_w$  in the range 48 to 53 kg/min.

	$L$ kmol/min	$D$ kmol/min	$L_w$ kg/min	$y_D$	$x_B$
<i>I</i>	1.064	0.936	48.00	0.534	$3.10e - 3$
<i>II</i>	1.143	0.857	50.00	0.584	$3.50e - 3$
<i>III</i>	1.463	0.537	50.00	0.9237	$7.60e - 3$
<i>IV</i>	1.555	0.445	50.00	0.9969	0.104
<i>V</i>	1.650	0.350	53.00	0.9984	0.233

**Table 3.** Steady-state solutions for one-stage column with  $V = 4.7$  kmol/min and  $L$  in the range 3.7 to 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

**Table 4.** Critical mole weight ratio  $M_2/M_1$  needed for instability in example columns of Skogestad and Morari (1987)

Column	$z_F$	$\alpha$	$N$	$N_F$	$1 - y_D$	$x_B$	$L/D$	$M_2/M_1$
<i>A</i>	0.5	1.5	40	21	0.01	0.01	5.41	1.42
<i>B</i>	0.1	1.5	40	21	0.01	0.01	25.3	1.25
<i>C</i>	0.5	1.5	40	21	0.10	0.002	4.93	1.23
<i>D</i>	0.65	1.12	110	39	0.005	0.10	19.3	1.69
<i>E</i>	0.2	5	15	5	0.0001	0.05	1.43	223
<i>F</i>	0.5	15	10	5	0.0001	0.0001	0.45	5.10
<i>G</i>	0.5	1.5	80	40	0.0001	0.0001	5.27	1.44

**Table 5.** Equations used for computing enthalpies for methanol-propanol system at a pressure of 1 atm.

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

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

**Table 6.** Steady-state solutions for methanol-propanol column with boilup  $V=4.5$  kmol/min. The energy balances are included in the model.

	$L$ kmol/min	$D$ kmol/min	$\log(1 - y_D)$ kg/min	$x_B$
<i>I</i>	4.60	0.535	-1.1701	$2.474e - 3$
<i>II</i>	4.70	0.505	-1.8097	$6.344e - 3$
<i>III</i>	4.70	0.406	-3.1662	0.1587
<i>IV</i>	4.70	0.0866	-3.5164	0.4526

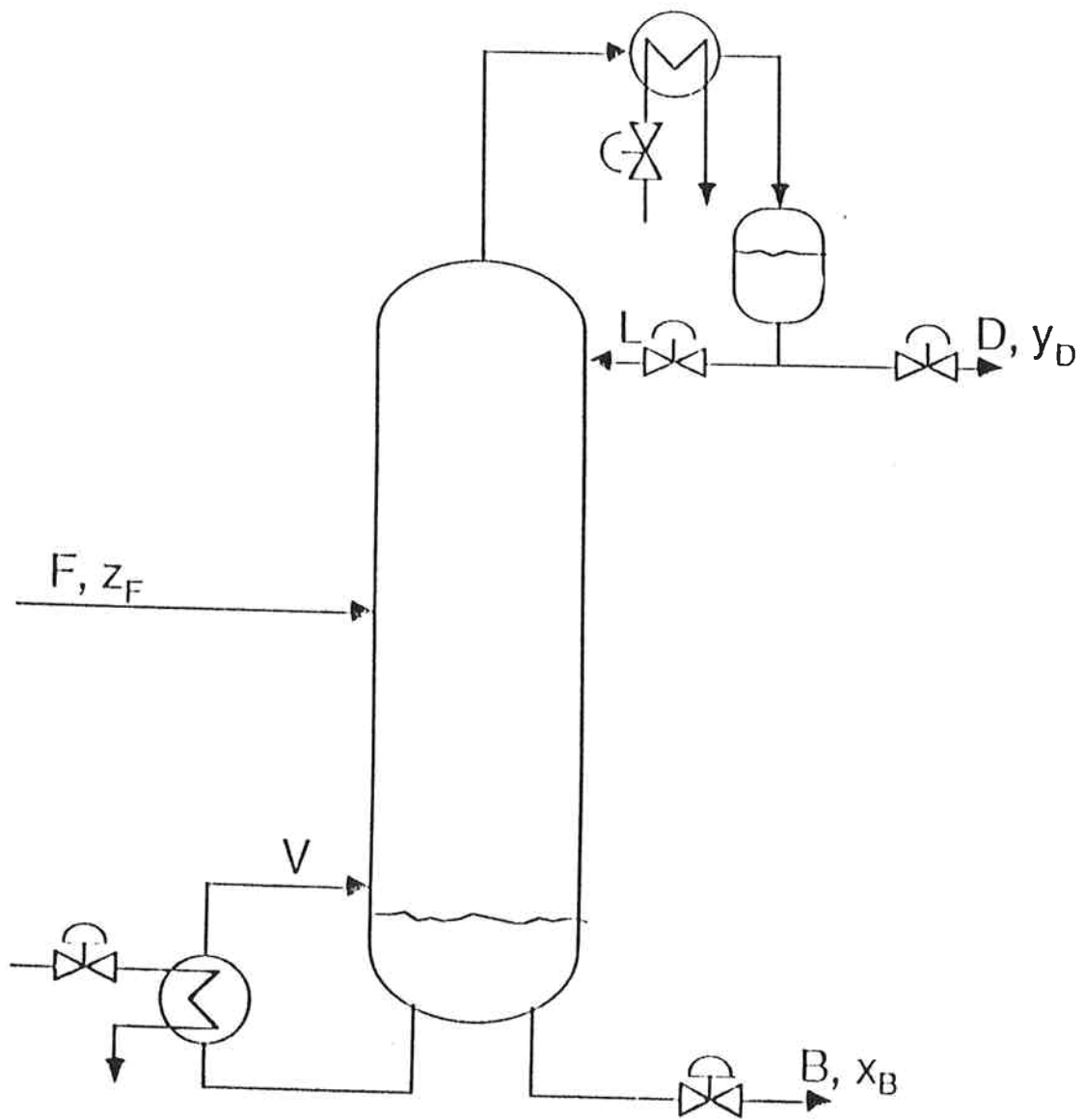
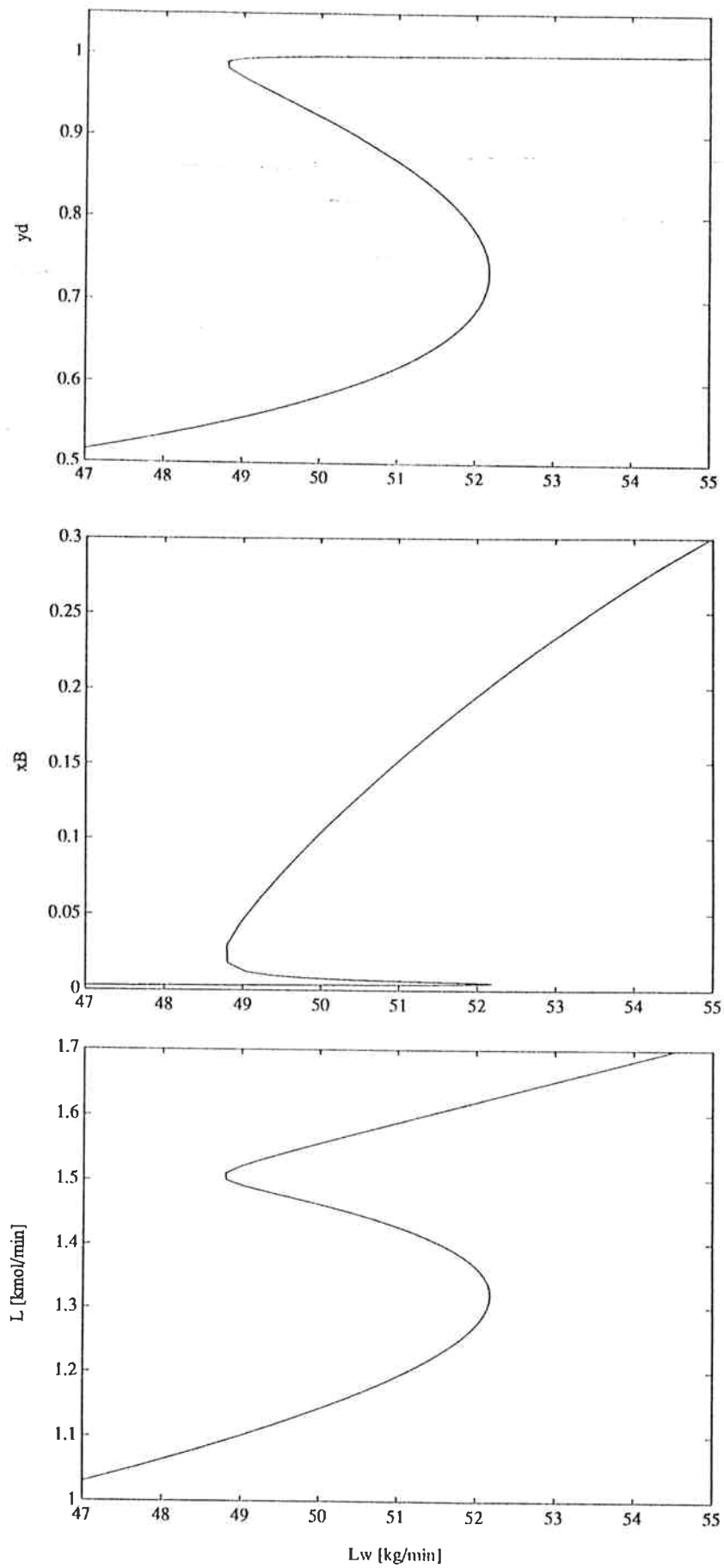


Figure 1. Two product distillation column



**Figure 2.** Multiple steady-states for mass reflux  $L_w$  for the methanol-propanol column assuming constant molar flows. Boilup  $V=2.0$  kmol/min.



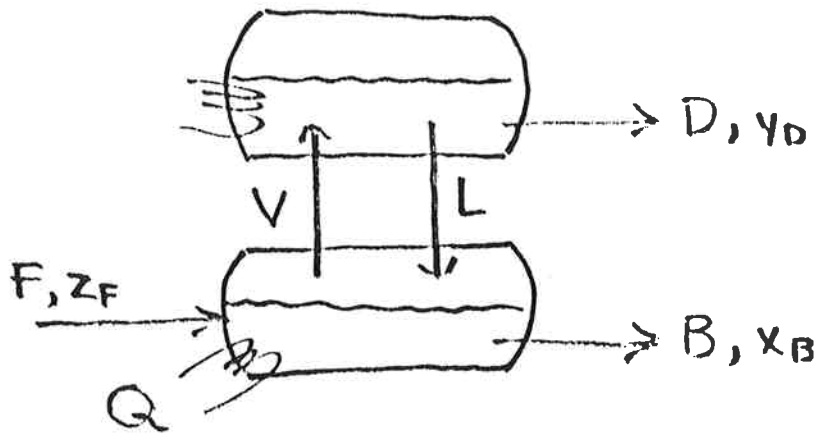
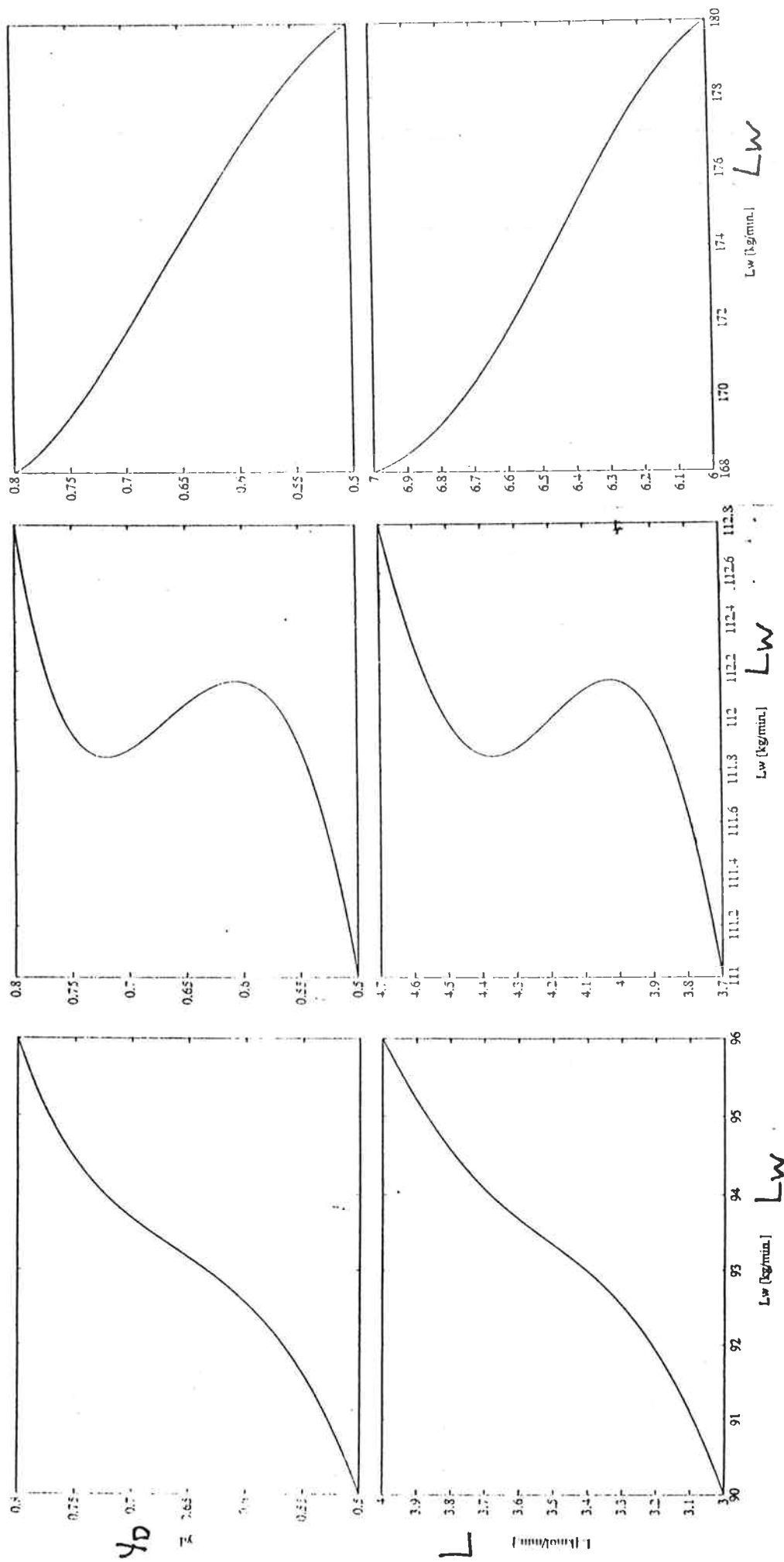


Figure 3. . One-stage column with total condenser.



a)  $V = 3.0$  kmol/min - Unique stable solution.      b)  $V = 4.7$  kmol/min - Multiple solutions.      c)  $V = 6.0$  kmol/min - Unique unstable solution.

Figure 4. Steady-state solutions as a function of mass reflux  $L_w$  for one-stage column.

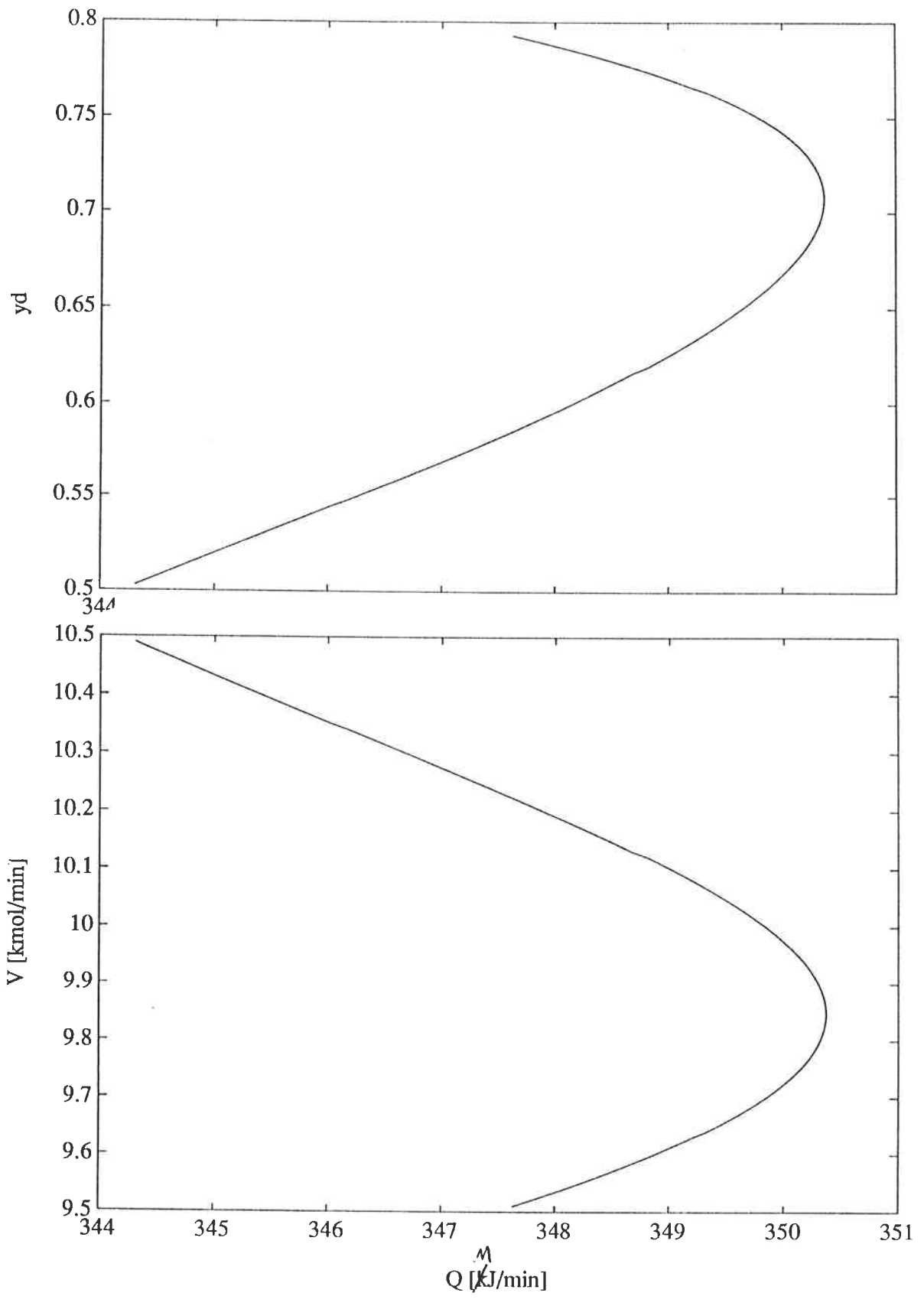
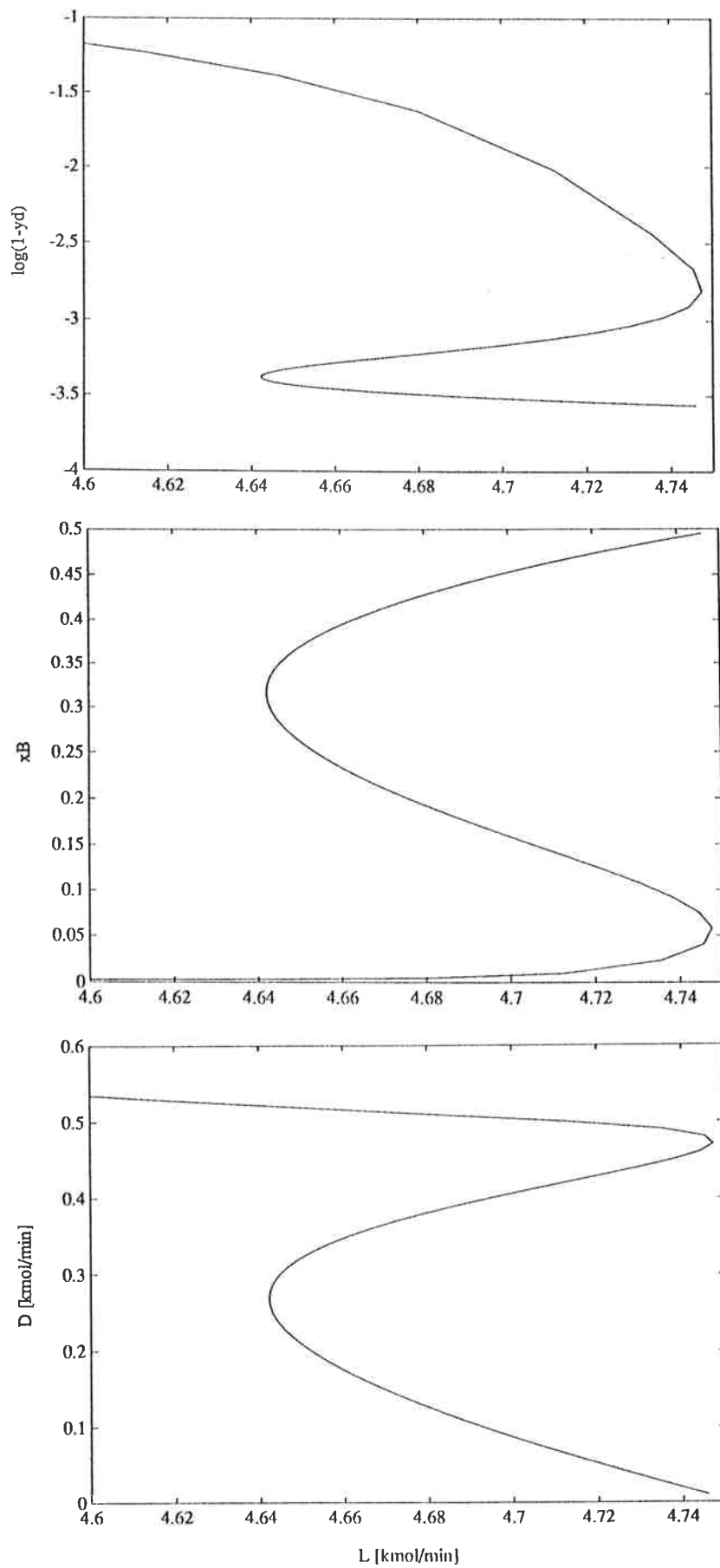
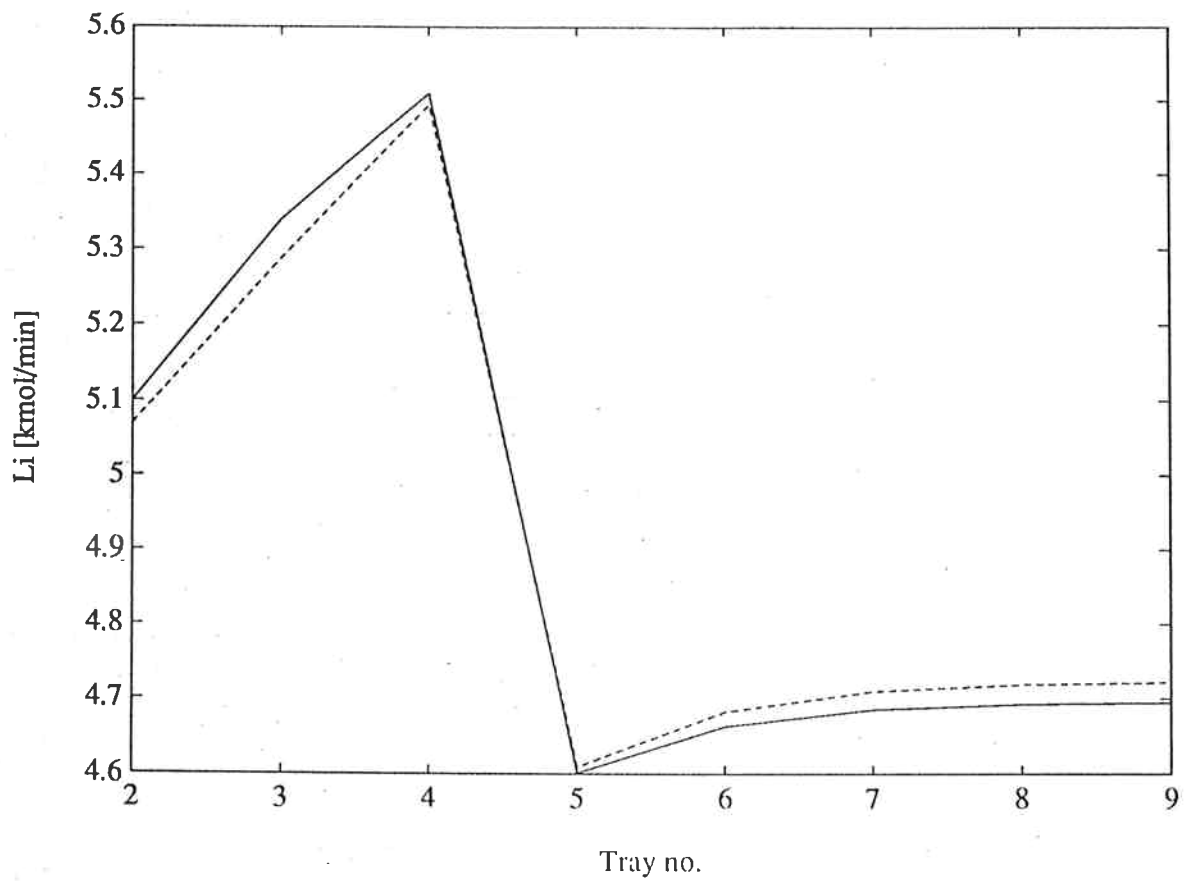


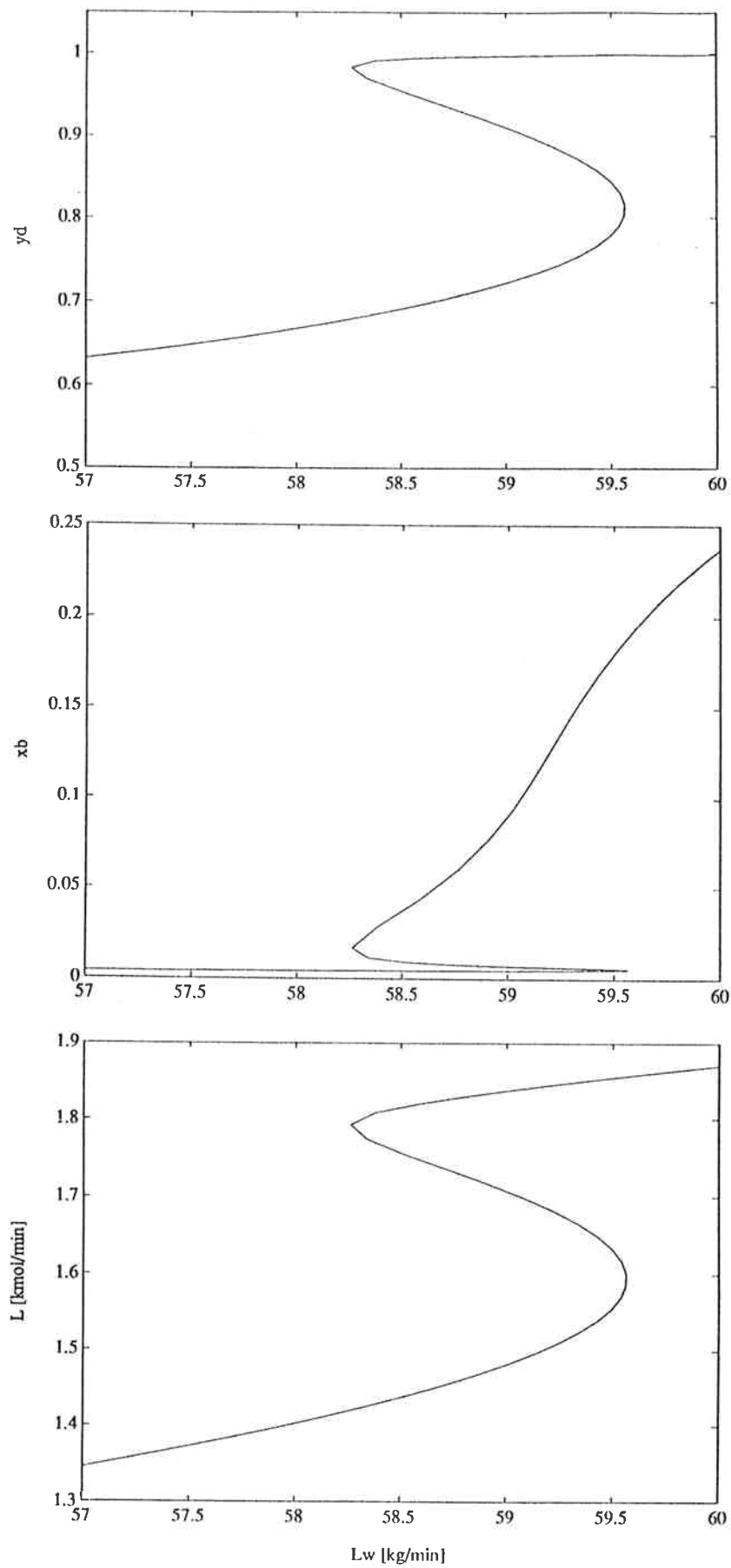
Figure 5. Multiple steady-states for heat input  $Q$  for one-stage propanol-acetic acid column. Reflux  $L = 9.5 \text{ kmol/min}$



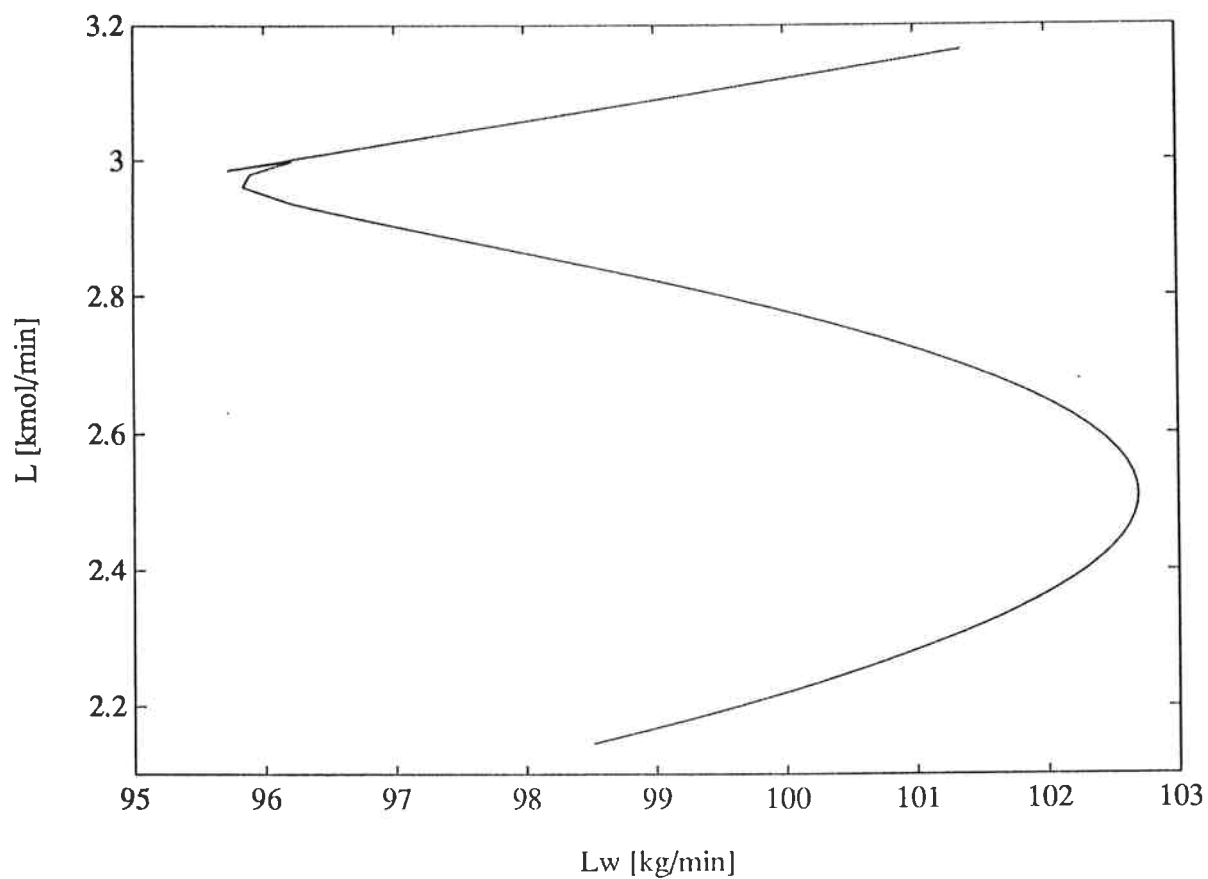
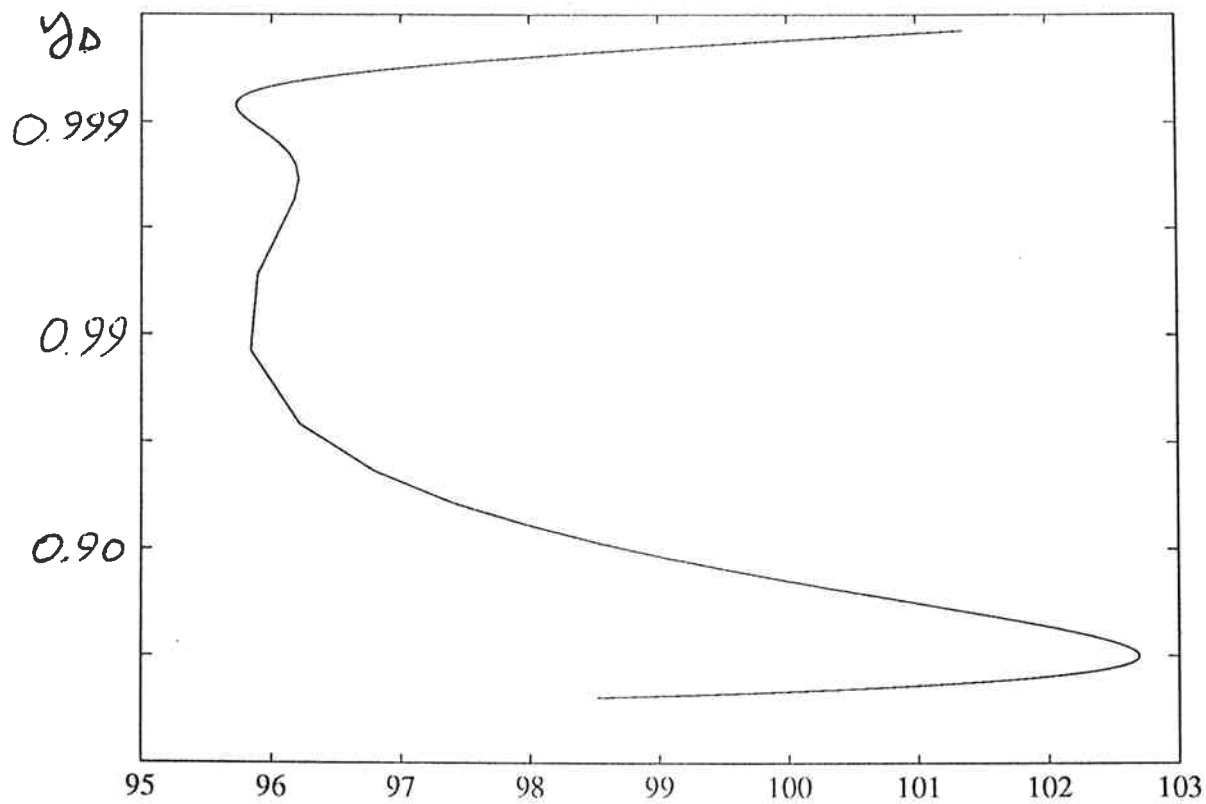
**Figure 6.** Multiple steady-states for molar reflux  $L$  for methanol-propanol column. Boilup  $V=1.5$  kmol/min.



**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  $L$ ).



**Figure 8.** Multiple steady-states for mass-reflux  $L_w$  for methanol-propanol column with energy-balances included in model. Boilup  $V=2.0$  kmol/min.



**Figure 9.** Multiple steady-states for mass-reflux  $L_w$  for methanol-propanol column with energy-balances included in model. Boilup  $V=3.0$  kmol/min.

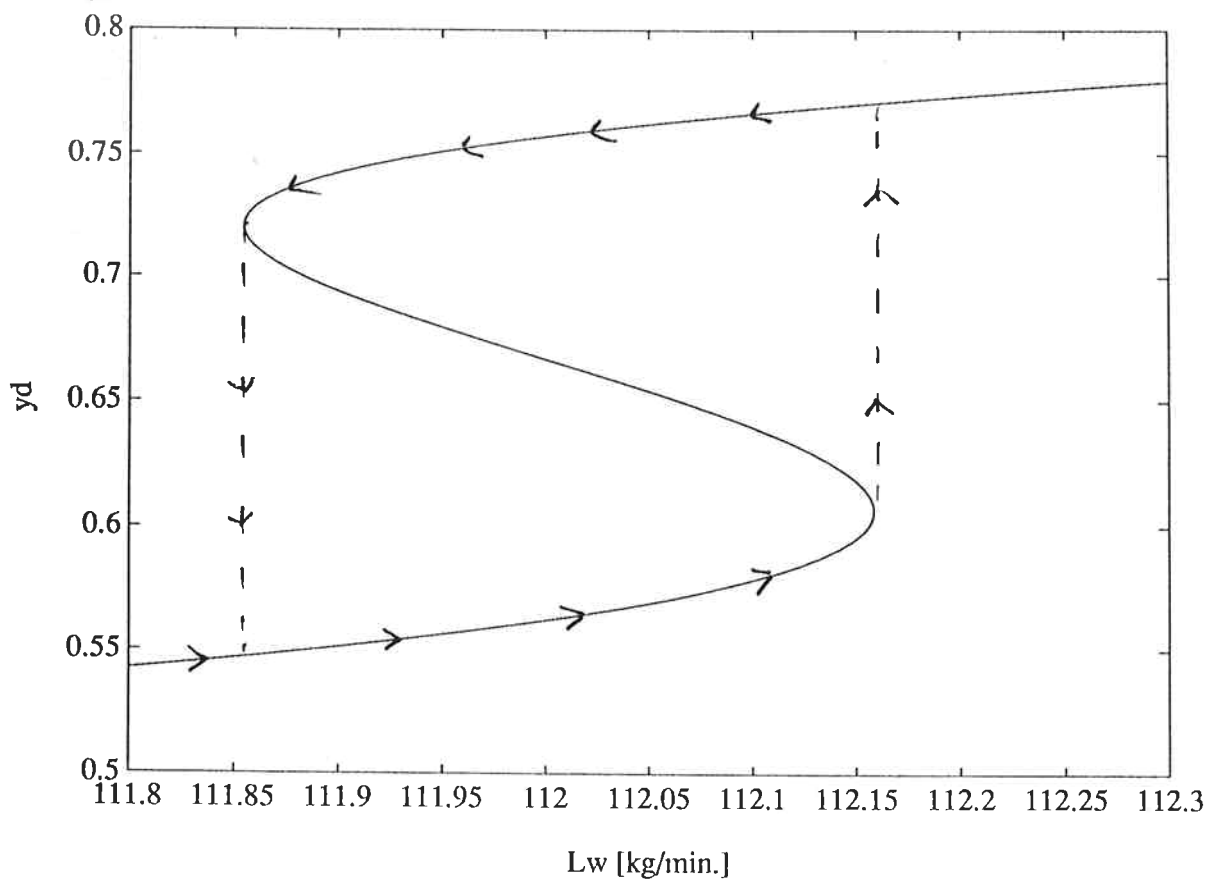
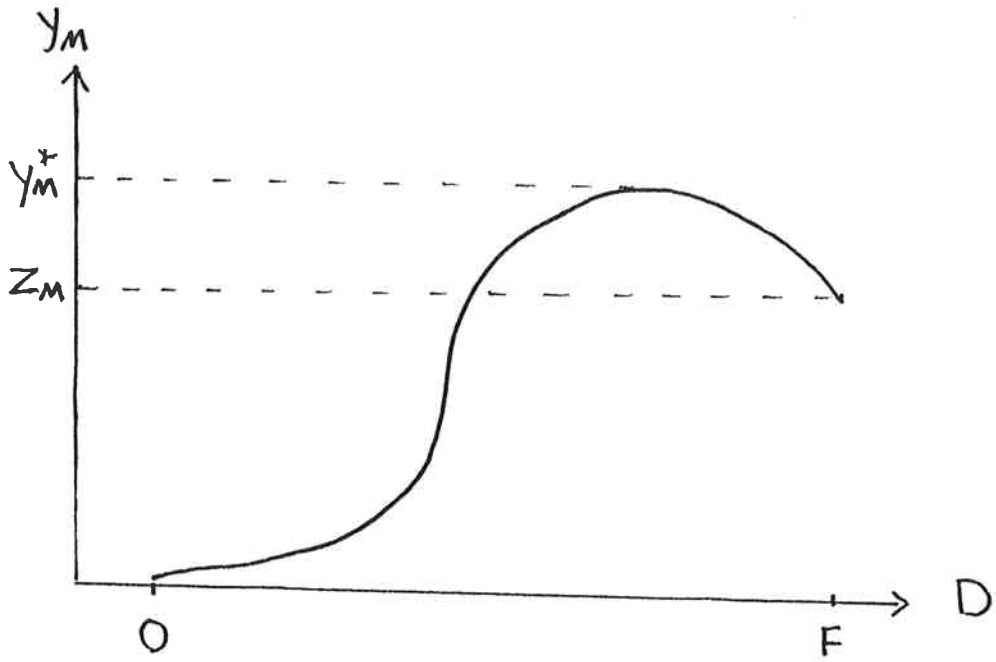


Figure 10. Illustration of hysteresis with jump phenomena in distillation.





**Figure 11.** Input multiplicity in distillation. Mole fraction of intermediate component in distillate,  $y_M$ , as a function of distillate flow rate,  $D$ .

