Feasible Products and Cost Indicators for Vapour-Liquid Equilibrium Separation Processes

Megan Ruth Jobson

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Declaration

I declare that this thesis is my own unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

Megan Jobson

[illegible]st January 1996

Abstract

The aim of process synthesis is to select process equipment and interconnections in order to achieve some performance goal, such as the composition of one or more products, in an optimal manner. This work focuses on the synthesis and optimization of vapour-liquid equilibrium (VLE) separation processes.

The regions of feasible products for a range of VLE separation processes (including simple distillation, simple condensation and processes comprised of one or two flash stages and mixing) are determined and analyzed. Binary and ternary systems, both ideal and non-ideal, are considered. It is shown that the products of VLE separation processes are not inherently restricted; limitations in product composition are therefore introduced by the choice of separation equipment. The products on the boundary of the region of feasible products are often found to be associated with infinite costs. Therefore costs and product composition should be considered simultaneously in process synthesis.

This work introduces a pair of variables which are proposed as cost indicators for VLE separation processes. These variables, which are called "capacity variables", pertain to distillation columns and a wide range of other VLE separation processes, allowing their comparison. The variables incorporate both capital and energy costs of a process and are thus related to total annual costs. They accommodate costs of both boiling and condensing. They are simple to calculate from the mass balance equations. The capacity variables are analogous to mean residence time, which serves as a cost indicator for processes involving reaction.

The capacity variables are evaluated for a range of processes separating binary and ternary mixtures and a range of thermodynamic systems. The capacity variables reflect the impact of the operating parameters, such as product specifications and

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The capacity variables are evaluated for a range of processes separating binary and ternary mixtures and a range of thermodynamic systems. The capacity variables reflect the impact of the operating parameters, such as product specifications and reflux ratio, on process costs. In distillation processes, the optimum reflux ratio is found to be close to the heuristic value of 1.2 times the minimum reflux ratio. The capacity variables are proposed as useful tools for the initial stages of process synthesis.

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Nomenclature

A	Antoine constant; Margules constant
$\dot{a}$	molar rate of addition of material
B	molar flow rate of bottoms; Antoine constant
$bubble(\overline{x})$	bubble-point composition of a liquid of composition $\overline{x}$
C	Antoine constant; cost
$\dot{c}$	molar rate of condensation
D	molar flow rate of distillate
$dew(\overline{x})$	dew point composition of a vapour of composition $\overline{x}$
dia	diameter
F	molar flow rate of feed
f	sum defined in eq. (B.199)
g	sum defined in eq. (B.200)
h, h'	number of distillation stages (continuous formulation)
L	liquid quantity or flow rate (molar)
N	total number of stages in rectification section
n	arbitrary number of stages in rectification section
M	total number of stages in stripping section
m	arbitrary number of stages in stripping section
p	vapour pressure
r, R	reflux ratio
s	reboil ratio; sum defined in eq. (B.146)
$\dot{s}$	molar rate of addition of material
t	time
V	vapour quantity or flow rate
$\dot{v}$	molar rate of vaporization
$\overline{x}$	liquid composition vector
$\overline{y}$	vapour composition vector
$\overline{z}$	feed composition vector

Greek

α	scalar ($0 \leq \alpha \leq 1$)
β	scalar ($0 \leq \beta \leq 1$)
γ	activity coefficient
Δ	increment
κ	boiling capacity variable
λ	condensing capacity variable
ξ	scalar non-linearly related to time
σ	sum defined in eq. (B.153)
τ	mean residence time
ϕ	fraction of feed vaporized

Subscripts

B	bottoms stream
col	column
D	distillate stream
F	feed stream
i	i^{th} component; i^{th} stage
m, min	minimum
o	initially, or feed stream
opt	optimum
ov	overall

Superscripts

$*$	mixture; extreme point
$'$	additional material (batch systems) or stripping section
$\overline{}$	mean

Abbreviations

TAC	total annual cost
VLE	vapour-liquid equilibrium

Chapter 1

Introduction

Distillation and other vapour-liquid equilibrium separation processes are very widely used in the chemical and petrochemical industries. Distillation was practised as an art before it developed as a science, and currently the scientific understanding of distillation technology is still incomplete (Porter, 1995). According to Porter (1995), there are three disciplines in distillation technology: process design, vapour-liquid equilibrium studies and equipment design, and all of these areas are not yet fully understood. In particular, process design, which is the area of interest of this work, is based largely on "rules of thumb" and trial-and-error optimization procedures.

In process design, or process synthesis, the design engineer attempts to fulfil a performance goal of a process. For example, the composition of one or more products or the fraction of raw material lost may be specified. A primary aim of process synthesis is to generate a process flowsheet by selecting processing units of the flowsheet and interconnections between these units which will achieve this performance goal (Nishida *et al.*, 1981). More than one process flowsheet may obtain the specified products; one of these flowsheets would be selected as the optimal, or nearly optimal, process. Optimality may be defined in terms of cost-effectiveness, selectivity to a particular product, waste minimization, or some other criterion. In this work, the optimization criterion will be taken to be cost-effectiveness.

This research concentrates on the design of vapour-liquid equilibrium (VLE) separation processes. In particular, binary and ternary, homogeneous, non-reacting mixtures separated at constant pressure are considered. The study of distillation processes is mainly restricted to individual columns rather than networks of columns.

Two major issues concerning the synthesis of distillation processes have been discussed in the literature. The first issue pertains to the compositions of the feasible products of a distillation process. Previous research has shown that not every product composition which is specified for a given feed is a feasible product of processes comprised of one or more distillation columns. Several researchers have attempted to determine what product compositions may be attained by a distillation column separating a given feed. The second issue concerns the cost of distillation processes. There is generally no unique distillation process which can obtain a specified pair of products. The aim of synthesis of distillation processes is to determine which is the most cost-effective process amongst several processes that may be used to obtain a desired product.

Much of the previous research has focused on distillation; this work considers the synthesis and optimization of distillation processes as well as some other VLE separation processes. The other separation processes investigated include simple distillation (batch boiling), simple condensing (batch condensing) and processes comprised of one equilibrium flash stage or two equilibrium flash stages (arranged in series, parallel or in series with reflux). The two issues discussed above, namely the compositions of feasible products and the costs of the process, are studied in this work.

The first objective of this work is to determine and analyse the region of feasible products for a range of processes separating binary and ternary mixtures, both ideal and non-ideal. The second objective of this work is to develop one or more variables which can be used for comparing the costs of a range of separation processes, in such a way that alternative separation processes can be compared for their cost-effectiveness, and that separation processes may be optimized.

In the design and optimization of processes involving chemical reaction, costs are generally found to be strongly related to the volume of the reactor or reactors used (Levenspiel, 1972). Mean residence time, which is the ratio of the volume of the reactor required to the volumetric flow rate of the feed, is therefore a cost indicator for such processes. This cost indicator can be used to compare different types and configurations of reactors, allowing the evaluation of alternative process flowsheets during the initial stages of process synthesis.

Vapour-liquid separation processes other than distillation have received little attention in previous research. Consideration of other VLE separation processes should allow the development of a deeper understanding of VLE separation than has been acquired to date. In particular, since a distillation column is a complex network of interlinked equilibrium flash stages, this work should lead to a better understanding of distillation processes.

A unified and rational basis for the comparison of costs of a wide range of VLE separation processes, which this work aims to develop, is not currently available. Such a costing variable could prove useful for the synthesis and optimization of separation processes, and could also enhance the understanding of the issues pertaining to the synthesis and optimization of distillation and other VLE separation processes.

The feasible products of a number of binary and ternary mixtures and a range of VLE separation processes are determined by process simulation. A pair of variables, which are proposed for indicating the costs of separation, are defined for a single equilibrium separation stage and applied to a range of processes. A range of separation processes are simulated and the proposed cost indicators of these processes are evaluated.

The two main issues considered in this work, namely the compositions of feasible products and the costs of separation processes, are initially treated separately in this thesis. Chapter 2 presents a review of the literature on the feasible products of VLE separation processes, and Chapter 3 presents results of simulated separations of a non-ideal ternary mixture. A review of the literature on the synthesis and optimization of VLE separation processes is presented in Chapter 4. The proposed cost indicators for separation processes are defined and developed theoretically in

Chapter 5. In Chapter 6, the issues of product composition and process costs are combined. A number of case studies are presented, in which the relationships between process costs and product composition are explored for a range of separation processes. The conclusions to this thesis are presented in Chapter 7.

Chapter 2

Review of the Literature on Feasible Products of Separation Processes

2.1 Introduction

Process synthesis is concerned with developing a cost-effective process flowsheet for obtaining a particular product or set of products from a given feed. There are two main sub-problems embedded in this objective: it must be established whether particular products are feasible for the proposed flowsheet and its processing units (Fidkowski *et al.*, 1993), and it must be established whether the proposed flowsheet is a cost-effective flowsheet (Foucher *et al.*, 1991). Considerable attention has been devoted to both aspects of the problem. This chapter reviews previous work which considers the feasible products of separation processes. Chapter 4 examines previous work focusing on optimization of separation processes.

The evaluation of process flowsheets at the preliminary stages of process design requires a method which balances speed and accuracy (Motard and Westerberg, 1978). Too simplistic an approach will lead to optimal process flowsheets being overlooked, while too detailed an approach is time-consuming and inappropriate to the quality of the solutions required.

Vapour-liquid equilibrium (VLE) separation processes, especially distillation, have developed on a largely empirical foundation, the science of which is still not fully understood (Porter, 1995). In spite of being well-established, homogeneous (that is, with a single liquid phase), ternary distillation processes have been the focus of much research activity in recent years. This review examines some of this research.

2.2 Background concepts

Much of the discussion about feasible products lends itself to visual representation and has been presented graphically. Some of the graphical forms used in the literature will be introduced briefly.

2.2.1 Composition space

A mixture comprised of c components may be described by a set of c-1 of the component mole fractions, $x_1, x_2, \ldots, x_{c-1}$. The c^{th} mole fraction is not independent of the others, since the sum of the mole fractions is 1. A vector $\bar{x} = (x_1, x_2, \ldots, x_{c-1})$ may be defined to describe the composition of this mixture.

For ternary systems, the composition vector (x_1, x_2) is easily represented in two-dimensional space. The space of all possible compositions is bounded by the axes $x_1 = 0$, $x_2 = 0$, and the diagonal line $x_1 + x_2 = 1$ (Doherty and Perkins, 1978). This chapter focuses on the separation of ternary mixtures.

2.2.2 Mixing in composition space

The composition simplex may be used to represent separation processes and their mass balances and composition profiles. When two fluids of composition $\bar{x}_1$ and $\bar{x}_2$ and quantities F_1 and F_2, respectively, are mixed, the result is a mixture of composition $\bar{x}*$, where $\bar{x}* = \alpha\, \bar{x}_1 + (1\text{-}\alpha)\, \bar{x}_2$. The variable α is a scalar and a measure of the relative quantities of the two fluids: $\alpha = F_1/(F_1 + F_2)$. The points $\bar{x}_1$, $\bar{x}_2$ and $\bar{x}*$ are collinear. This means that the compositions of the feed and the products of a separation process with only two products must lie on a straight line. The distances between the points are determined by the relative quantities of the products, as given by the lever-arm rule.

2.2.3 Vapour-liquid equilibrium

At some temperature and pressure, a liquid of composition $\bar{x}$ may be in equilibrium with a vapour of composition $\bar{y}$, determined by the thermodynamics of the system. For a system at fixed pressure, at every point $\bar{x}$ in the composition space there is a unique vector, $\bar{x}-\bar{y}$, associated implicitly with some temperature. These vectors or tie-lines are not restricted from crossing each other (see for example, Koehler *et al.*, 1991). Constant pressure processes are assumed throughout the following discussion.

2.3 Simple distillation and condensation

2.3.1 Simple distillation

Simple distillation is also known as simple boiling and differential distillation. In this process, a liquid of composition $\bar{x}$ is slowly boiled and the vapour of composition $\bar{y}$, which is in equilibrium with the liquid, is removed as it is formed, at a molar rate $\dot{v}$. The quantity of liquid in the still at any time is L moles. Doherty and Perkins (1978) developed the mass balance for the process for a homogeneous, non-reacting, but not necessarily ideal, system:

$$\frac{d\bar{x}}{dt} = \frac{\dot{v}}{L}\,(\bar{x}-\bar{y}) \tag{2.1}$$

Or equivalently:

$$\frac{d\bar{x}}{d\xi} = \bar{x} - \bar{y} \tag{2.2}$$

where ξ is a scalar quantity non-linearly related to time.

The original liquid feed composition, the liquid composition at any time, and the accumulated vapour composition must lie on a straight line, by the mixing rule.

Residue curves and residue curve maps

The trajectory of these differential equations in composition space shows the composition of the liquid residue with time or ξ, and is known as a residue curve. The map of such trajectories with various starting points is known as the residue curve map. The singular points of this map occur where the differential equations are equal to the zero vector, that is, where $\overline{x} = \overline{y}$. These singular points are pure component vertices and azeotropes.

The mathematical results of work on residue curves and residue curve maps may be summarized as follows:

- The tangent to the residue curve at $\overline{x}$ and the vector $\overline{x}-\overline{y}$ are collinear (Doherty and Perkins, 1978).
- Temperature increases monotonically with ξ or time along the residue curve (Doherty and Perkins, 1978).
- Given the location and boiling temperature of all singular points, a single (*i.e.*, unique) residue curve map may be constructed (Doherty, 1985). However, Fien and Liu (1994, citing the PhD thesis of Knight, 1986) showed a rare case where the same boiling point data resulted in more than one residue curve map.
- Residue curves cannot intersect (Doherty and Perkins, 1978), but they may converge in a tangential manner.
- The singular points of the residue curve map may only be comprised of nodes or saddles (Doherty and Perkins, 1979b).

Simple distillation regions and boundaries

It may be observed that, for certain non-ideal ternary mixtures, the composition space is divided into regions. Doherty and Perkins (1978) defined the regions in this way: "If two residue curves are initially close together and are still close together after a long time, then we shall say that both these residue curves belong to the same distillation region". The simple distillation boundary divides the composition space into these regions. The definition of the simple distillation boundary may be extended to systems of higher dimension, but the boundary will no longer be a curve, but a (*c*-2)-dimensional hypersurface.

A separatrix is a residue curve which starts or ends at a singular point, "such that it is the side of a hyperbolic sector" (Doherty and Perkins, 1978). Singular points always form the terminus and origin of a separatrix in two dimensions. An unstable separatrix is a residue curve from which adjacent residue curves diverge, while a stable separatrix is flanked by converging trajectories (Van Dongen and Doherty, 1985a).

Not all researchers agree on what constitutes simple distillation boundaries. According to Doherty and Perkins (1978), simple distillation boundaries are specifically unstable separatrices. Rev (1992) also makes the distinction between separatrices, which join any two singular points, and boundaries, which are separatrices which *arrive* at saddle points. However, Doherty and Caldarola (1985), stated that residue curves starting *or* ending at binary saddles form simple distillation boundaries. Laroche *et al.* (1992a) and Bekiaris *et al.* (1993) specify that in a distillation region, all the residue curves must originate from the same low-boiling node and end at the same high-boiling node. Fien and Liu (1994) implied that azeotropes invariably result in simple distillation boundaries. Stichlmair (1991) identified the boundary with valleys and ridges in the boiling temperature surface. (This relationship was shown not to be identical by Van Dongen and Doherty (1984).) These definitions are not always as precise as they might be, and are not mutually consistent. There remains some confusion in this area.

Two examples present some of these inconsistencies in the literature. In Fig. 2.1, a stable separatrix joining a high-boiling binary saddle at the A-B azeotrope to the stable node at pure C is not found to represent a boundary by Doherty and Perkins (1978), Van Dongen and Doherty (1985a) and Rev (1992). However, Doherty and Caldarola (1985), Stichlmair (1991), Laroche *et al.* (1992a), Bekiaris *et al.* (1993) and Fien and Liu (1994) diagnose two distillation regions in this case.

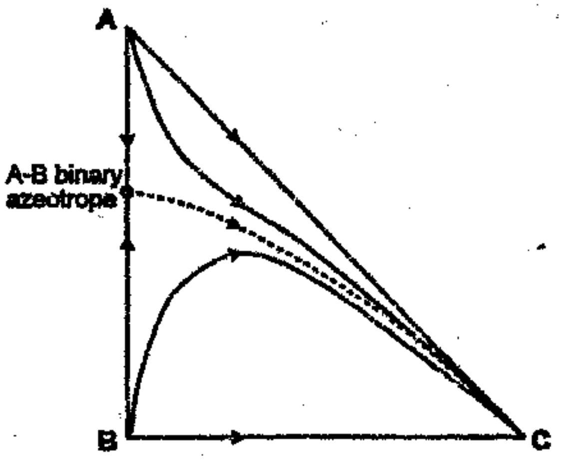


Fig. 2.1 The separatrix joining the A-B binary azeotrope to the pure C vertex may or may not represent a simple distillation boundary.

In the residue curve map shown in Fig. 2.2, Foucher *et al.* (1991) found that there are three distillation regions, in spite of their rule that a residue curve joining two nodes cannot form a residue curve boundary. (The curve joining the low-boiling ternary azeotrope, which is an unstable node, and the high-boiling A-B binary azeotrope, which is a stable node, is such a curve.) Applying the definitions of Doherty and Perkins (1978), Rev (1992), Laroche *et al.* (1992a) and Bekiaris *et al.* (1993) to this case gives only two simple distillation regions, that containing both the A and B vertices, and that containing the C vertex.

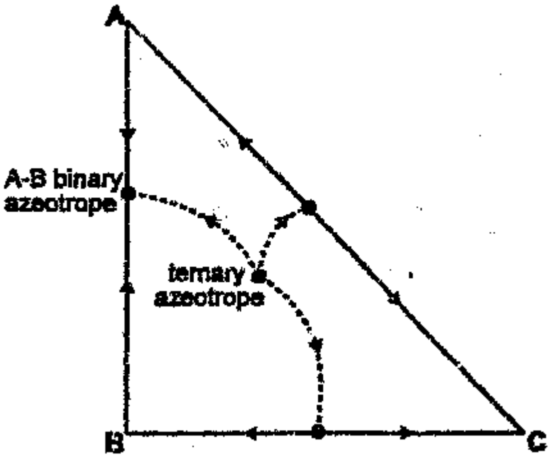


Fig. 2.2 The separatrix joining the low-boiling ternary azeotrope to the high-boiling A-B binary azeotrope may or may not represent a simple distillation boundary.

Residue curves may not intersect, so the simple distillation boundary cannot be crossed by the liquid composition trajectory of a simple distillation process (Doherty and Perkins, 1978). Consider an arbitrary liquid residue curve close to and on the concave side of the boundary. Although the residue curve itself does not cross the simple distillation boundary, the equilibrium vapour composition may lie on the other side of the boundary, as shown in Fig. 2.3, because the vector $\bar{x}-\bar{y}$ is tangential to the residue curve (Doherty and Perkins, 1978). A perfectly straight boundary may not be crossed. However, in practice, separatrices are found not to be mathematically straight (Doherty and Perkins, 1978, citing Schreinemakers, 1902). Thus, although a single simple distillation residue curve is restricted by the boundary, the simple distillation boundary does not restrict possible product compositions in a more general sense.

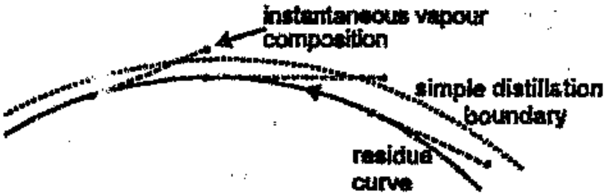


Fig. 2.3 The vapour product from a residue curve may lie on the other side of a simple distillation boundary.

2.3.2 Simple condensation

Simple condensation is a process analogous to simple distillation. A vapour of quantity V and composition $\bar{y}$ is condensed and the liquid of composition $\bar{x}$ which is in equilibrium with the vapour is removed as it is formed, at a molar rate $\dot{c}$. The differential equation rising out of the mass balance is:

$$\frac{d\bar{y}}{dt} = \frac{-\dot{c}}{V}\,(\bar{x}-\bar{y}) \tag{2.3}$$

Or equivalently (Nikolaev *et al.*, 1979):

$$\frac{d\bar{y}}{d\xi} = \bar{y} - \bar{x} \tag{2.4}$$

It is expected that the properties of a liquid residue map for a simple distillation process would be similar to those of a vapour residue map for a simple condensation process. Equations (2.2) and (2.4) may be rewritten as follows, using *bubble*($\bar{x}$) and *dew*($\bar{x}$) to represent the bubble point composition and the dew point composition of $\bar{x}$, respectively:

$$\frac{d\bar{x}}{d\xi} = \bar{x} - bubble(\bar{x}) \tag{2.2a}$$

$$\frac{d\bar{y}}{d\xi} = \bar{y} - dew(\bar{y}) \tag{2.4b}$$

The points *dew*($\bar{x}$), $\bar{x}$ and *bubble*($\bar{x}$) are not generally collinear. Therefore the tangent to the simple distillation trajectory at some $\bar{x}$ is not identical and opposite in direction to the tangent to the simple condensation trajectory at that point. That is, the liquid and vapour residue curves, although similar, are not coincident. It follows that both processes may have boundaries, but that these boundaries are not strictly coincident, as shown by Nikolaev *et al.* (1979).

Simple distillation and simple condensation are similar processes with similar residue curve maps. By convention, liquid residue curves are more widely discussed. This work will also largely neglect simple condensation processes, except where there are specific advantages to including them.

2.4 Column distillation

2.4.1 Modelling column performance

In order to investigate the feasible products of a column distillation process, a number of authors (including Levy *et al.*, 1985; Laroche *et al.*, 1992a; Wahnschafft *et al.*, 1992 and Fidkowski *et al.*, 1993) have modelled a simple column, with a single feed and two products, and no heat transfer other than to the condenser and reboiler. Non-reacting, homogeneous liquid systems, with a saturated liquid feed are generally assumed. The key assumptions used by a number of authors for modelling distillation columns are:

- Constant molar overflow in the column. This incorporates the assumptions that heat losses in the column are negligible, that the molar heat of vaporization is constant, that heats of mixing are negligible and that the changes in sensible heat with temperature are negligible (Barbosa and Doherty, 1988b).
- Ideal equilibrium stages are used, that is, the streams leaving a stage are in equilibrium.

From these assumptions it follows that the liquid molar flow rate in the rectification section (above the feed tray), L, is constant, and that in the stripping section (below the feed tray), the liquid flow rate, L', is also constant. The vapour flow rate, V, is constant throughout the column. The reflux ratio, r, is defined by the ratio L/D, where D is the distillate product flow rate; the reboil ratio, s, is defined by the ratio V/B, where B is the bottoms product flow rate. By the assumption of constant molar overflow, the quantities r and s are constant in any given column.

For a distillation column for which the composition of the distillate product, $\bar{x}_D$, is specified, the mass balance over n stages of the rectification section, numbering stages from the total condenser downwards, may be written (Van Dongen and Doherty, 1985b):

$$\bar{x}_n = \frac{r+1}{r}\bar{y}_{n+1} - \frac{1}{r}\bar{x}_D \tag{2.5}$$

The mass balance over m stages of the stripping section, where the bottoms product composition is $\bar{x}_B$, and the stages are numbered from the reboiler upwards, may be written as:

$$\bar{x}_{m+1} = \frac{s}{s+1}\bar{y}_m + \frac{1}{s+1}\bar{x}_B \tag{2.6}$$

Where the feed composition is given by $\bar{x}_F$, the overall mass balance relates the reflux ratio and reboil ratio as follows (Van Dongen and Doherty, 1985b):

$$\bar{x}_D = \frac{s+r+1}{s}\bar{x}_F - \frac{r+1}{s}\bar{x}_B \tag{2.7}$$

The difference equations (2.5) and (2.6) give the liquid compositions on each stage of the column starting at either the distillate composition (eq. 2.5) or at the bottoms composition (eq. 2.6). These points may be plotted and connected to give the liquid composition profiles in the two sections of the column, as shown in Fig. 2.4. The feed, bottoms and distillate compositions are collinear, according to the overall mass balance for the column.

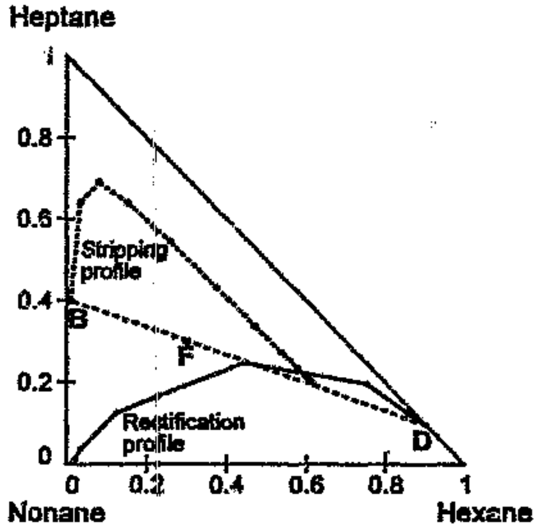


Fig. 2.4 An example of product profiles for a distillation column. Since the profiles intersect, the separation is feasible for the chosen reflux ratio. B: Bottoms, F: Feed, D: Distillate compositions.

When two such column profiles intersect, the separation is feasible (Van Dongen and Doherty, 1985b) because then the mass balance and equilibrium constraints have been simultaneously satisfied (Wahnschafft *et al.*, 1992). The total number of stages in the column is the sum of the number of stages in each profile up to the intersection. The composition of the liquid at the intersection is the feed tray liquid composition, but is not necessarily the same as the feed composition. Only if the intersection of profiles occurs at an integral number of stages in both column sections does the intersection represent the physical composition at the feed tray (Wahnschafft *et al.*, 1992).

Instead, Stichlmair and Herguijuela (1992) proposed that the column profiles do not intersect for a feasible distillation process, but illustrated a mixing condition across the feed tray. This construction is not explained, and differs from the condition given above, which is used by many researchers in the field. In this work, the condition for a feasible distillation process will be that the composition profiles of the rectification and stripping sections intersect.

Differential equations modelling column performance

Van Dongen and Doherty (1985b) approximated the finite difference equation (2.5) for the rectifying section by the following first-order ordinary differential equation:

$$\frac{d\bar{x}}{dh'} = -\frac{r+1}{r}\bar{y} + \bar{x} + \frac{1}{r}\bar{x}_D \tag{2.8}$$

The boundary condition is $\bar{x}|_{h'=1} = \bar{x}_D$, where h' is the number of stages in the rectification section.

The following differential equation is an approximation of eq. (2.6) for the stripping section:

$$\frac{d\bar{x}}{dh} = \frac{s}{s+1}\bar{y} - \bar{x} + \frac{1}{s+1}\bar{x}_B \tag{2.9}$$

The boundary condition is $\bar{x}|_{h=1} = \bar{x}_B$, where h is the number of stages in the stripping section.

Saturated liquid products are assumed, which means that $\bar{x}_D$ and $\bar{x}_B$ lie on the liquid composition profiles. This condition assumes the use of a total condenser. The assumption of saturated liquid products is not essential to this work.

The model assumes that each theoretical tray has been broken into an infinite number of differential plates over the interval from n to $n+1$, with each performing a differential amount of mass transfer according to eq. (2.8) and (2.9). (Laroche *et* *al.* (1992b) showed how the differential equations also describe the composition profile in a packed column.) The variables h and h' are related to the number of stages, not to the actual height of the plate in the column, or the actual depth of packing in a packed column (Van Dongen and Doherty, 1985b).

Van Dongen and Doherty (1985b) illustrated the column profiles generated by these differential equations. In their example, the columns profiles arising from the difference equations, eq. (2.5) and (2.6), and those arising from the differential equations, eq. (2.8) and (2.9), were indistinguishable after about the fourth stage. However, Barbosa and Doherty (1988a) found that the first-order approximation was only good where x_i changed little from one stage to the next, and for large numbers of stages. Caution should therefore be exercised when using these differential equations. In this work, difference equations will be used to describe column distillation.

2.4.2 Distillation at total reflux

The two limiting cases of distillation are total (or infinite) reflux and reboil, and minimum reflux and reboil, also called reversible operation (Doherty and Perkins, 1979b). Distillation under total reflux has been extensively researched, using both difference and differential equations to describe column behaviour. Both conventions will be discussed in this section.

Under total reflux conditions, the difference equation (2.5) for the rectifying section becomes:

$$\overline{x}_n = \overline{y}_{n+1} \tag{2.10}$$

The differential equation (2.8) describing the rectification section reduces to:

$$\frac{d\overline{x}}{dh'} = \overline{x} - \overline{y} \tag{2.11}$$

When the reflux ratio is large, the reboil ratio, s, also becomes large, and difference equation (2.6), modelling the stripping section, becomes:

$$\overline{x}_{m+1} = \overline{y}_m \tag{2.12}$$

The differential equation (2.9), which describes the stripping section, simplifies to:

$$\frac{d\overline{x}}{dh} = \overline{y} - \overline{x} \tag{2.13}$$

When differential equations are used to model column behaviour, it is found that eq. (2.11) is exactly the equation describing simple distillation (eq. 2.2). Equation (2.13) is equal to eq. (2.11) but opposite in sign, which is a result of the numbering convention used. The column profile at total reflux is thus identical to the residue curve passing through the product compositions.

A difference equation analysis of column compositions gives the following results. From eq. (2.10) it may be seen that, at total reflux conditions, the liquid composition of each stage in the rectification section is simply the dew point composition of the liquid of the stage above. Similarly, it follows from eq. (2.12), that the liquid composition of each stage in the stripping section is the bubble point composition of the liquid on the stage below. These difference equations give rise to a sequence of points, each of which is the bubble point composition of the previous point. When these points are joined smoothly and in the direction of decreasing temperature, a distillation line is obtained, as defined by Stichlmair *et al.* (1989). The mathematical method for obtaining a smooth curve was not described. Distillation lines describe the composition profile of staged distillation columns operated under conditions of total reflux.

Distillation lines are similar, but not identical, to residue curves (Fidkowski *et al.*, 1993). Residue curves are tangential to the vector $\overline{x}-bubble(\overline{x})$ at every point $\overline{x}$, but do not actually contain $dew(\overline{x})$ or $bubble(\overline{x})$. Wahnschafft *et al.* (1992) illustrated how a distillation line may cross several residue curves, especially in wide-boiling systems or regions of high curvature, but added that the "difference between residue curves and distillation lines ... is not normally very significant". Rev (1992) also showed how a distillation line may cross residue curves and how residue curve boundaries may be crossed by distillation lines. However, it would be more logical to look at boundaries defined in terms of distillation lines, when considering columns modelled using finite difference equations, and boundaries defined in terms of residue curves when considering columns modelled using differential equations.

Boundaries, similar to those for residue curves, arise for distillation lines, dividing distillation lines into regions. Residue curves and distillation lines point in opposite directions, since residue curves point in the direction of increasing temperature and distillation lines point in the direction of decreasing temperature. Therefore an unstable separatrix in a distillation line map is associated with a stable separatrix in a residue curve map. Several examples occur where unstable separatrices in distillation line maps are called simple distillation boundaries (Stichlmair *et al.*, 1989; Wahnschafft *et al.*, 1992 and Fien and Liu, 1994), which does not conform to the definition of simple distillation boundaries as given by Doherty and Perkins (1978), and adds further to the inconsistencies described at the end of Section 2.3.1.

Distillation product regions at total reflux

Either the differential equation approach (Van Dongen and Doherty, 1985b) or difference equations (Stichlmair, 1991) may be used to model distillation column behaviour. When a column is operated at total reflux, it follows that both the distillate and the bottoms products lie on the same residue curve or distillation line, depending on which model is used to describe the column. From the overall mass balance, the feed, bottoms and distillate compositions must lie on a straight line (Petlyuk, 1978a). These two constraints allow the region of feasible products for distillation under total reflux to be determined.

Stichlmair (1991) and Stichlmair and Herguijuela (1992) combined these two constraints to develop product regions for distillation at total reflux. Part of the boundary of these regions is the residue curve which passes through the feed; part of the boundary is formed by the simple distillation boundary. The straight lines representing sharp direct and indirect splits (pure low-boiling distillate product and pure high-boiling bottoms product, respectively) also make up the boundary of the product region.

Wahnschafft *et al.* (1992) discussed further how, if there are inflections in the feed residue curve, the residue curve boundary may be "crossed" in the manner illustrated in Fig. 2.5. Although the feed, distillate and bottoms compositions all lie on a straight line, the feed may lie in a different distillation region to the two products. However, the column profile itself does not cross the boundary. The total reflux product region is extended, in places, beyond the feed residue curve, by the locus of points at which the tangent to the residue curve passes through the feed composition and intersects the same residue curve twice.

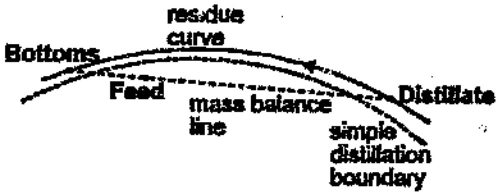


Fig. 2.5 The mass balance line of a total reflux distillation process may cross the simple distillation boundary.

2.4.3 Reversible distillation

The second limiting condition of distillation column operation is reversible operation, also called "thermodynamically reversible fractionation" (Petlyuk, 1978a) and "thermodynamically optimum operation" (Wahnschafft *et al.*, 1992). In this process, a finite amount of product is obtained using minimum work and infinitely many stages and intermediate reboilers and condensers, while distillation under total reflux conditions produces a zero-quantity product using minimum work input and infinite internal flow rates (Wahnschafft *et al.*, 1992).

Koehler *et al.* (1991) gave a clear description of this limiting process. A reversible column has infinitely many stages and is everywhere at equilibrium. That is, the liquid stream approaching a stage and the vapour leaving it are at equilibrium at every stage, unlike conventional columns, where streams leaving a stage are assumed to be in equilibrium. Heat is transferred continuously to and from the column. This causes the reflux ratio to change at every stage. Reversible distillation is a constant pressure process. Koehler *et al.* (1991) used the term "adiabatic column" to refer to columns with heat transferred only to the reboiler and condenser.

In order to obtain reversible mixing at the feed stage, the feed may be partially vaporized at saturation temperature. The liquid and vapour feed streams have exactly the same temperature, pressure and compositions as the liquid and vapour streams at the feed tray.

A mass balance for an envelope over the rectifying section (eq. 2.5) may be rewritten to give the difference equation:

$$(r+1)(\bar{x}-\bar{y}) = \bar{x}-\bar{x}_D \tag{2.14}$$

For the stripping section, the mass balance (eq. 2.6) gives:

$$-s(\bar{x}-\bar{y}) = \bar{x}-\bar{x}_B \tag{2.15}$$

For a reversible column, the differential equations (2.8) and (2.9) both tend to the zero vector and reduce to exactly the same form as the equations above; that is, the difference and differential equations agree.

The geometrical interpretation of this process was discussed by Petlyuk (1978a) and Wahnschafft *et al.* (1992). For example, in the rectification section, the lines joining the product composition, $\bar{x}_D$, and the liquid composition, $\bar{x}$, are everywhere collinear with the tie-line $\bar{x}-\bar{y}$ at $\bar{x}$, *i.e.*, they are tangential to the residue curve at $\bar{x}$. Similarly, the lines $\bar{x}-\bar{x}_B$ and $\bar{x}-\bar{y}$ are collinear everywhere in the stripping section. The relative distances between $\bar{x}$, $\bar{y}$ and the product composition, $\bar{x}_D$ or $\bar{x}_B$, give the reflux or reboil ratio.

Associated with a particular point $\bar{x}$ on the reversible column profile is a unique reflux ratio, r, or reboil ratio, s. An adiabatic column composition profile starting at the same product composition and operating under that fixed value of r or s, will end at the same point $\bar{x}$. The profile ends because additional stages do not lead to a change in composition. This is known as a pinch point. For an adiabatic column with a given product composition, a locus of pinch points may be calculated as the reflux or reboil ratio changes. The reversible column operates everywhere at a pinch point, so its composition profile is exactly this locus. This pinch point curve is also known as a "zone of constant concentrations" (Petlyuk, 1978b).

Product regions of reversible distillation columns

Petlyuk (1978a) investigated the boundaries of the product region for the reversible distillation of an n-component mixture. The upper and lower sections of the column are restricted by two different boundaries. The composition profile of the upper section may not cross the locus of points where the equilibrium coefficients, $K_i = y_i/x_i$, of the two highest boiling species are equal or the curve containing points where the equilibrium coefficient of the least volatile component is equal to 1. In the lower section of the column, the profile may not cross the locus of points where the equilibrium coefficients of the two lowest boiling components are equal or the locus of points where the equilibrium coefficient of the most volatile component is equal to 1.

For a ternary system, the $K_1 = K_2$ curve is the locus of points at which the tangent to the residue curve passes through the vertex representing pure component 3 (Petlyuk, 1978a). This curve will form a semi-boundary for the upper section of the column (that is, it is not a boundary for the lower section of the column) if components 1 and 2 are the two highest boiling species, or a semi-boundary for the lower section of the column if components 1 and 2 are the two lowest boiling species of the mixture. The curves $K_1 = K_3$ and $K_2 = K_3$, similarly, may form semi-boundaries for this process. The $K_i = 1$ boundary is the locus of points where the tangent to the residue curve is parallel to the $x_i = 0$ axis. Petlyuk (1978a) did not illustrate such a boundary.

In comparing these reversible column boundaries with simple distillation boundaries, Petlyuk (1978a) stated that the boundaries do not coincide and do not pass through the same singular points. Since the boundaries at the two limiting conditions of total reflux and reversible operation do not coincide, Petlyuk (1978a) concluded that there are no restrictions on compositions of attainable products. However, for a ternary mixture, he illustrated a $K_1 = K_3$ boundary which ends at the 1-3 azeotrope, which is a singular point through which the simple distillation boundary also passes.

Koehler *et al.* (1991) proposed that the two straight lines passing through the feed composition, $\bar{z}$, and its dew point composition, *dew*($\bar{z}$), and joining the feed composition and its bubble point composition, *bubble*($\bar{z}$), and extended to the boundaries of the composition triangle, form the boundaries of the product region for a reversible column.

Little other interest has been shown in the reversible distillation product regions. The results of Petlyuk (1978a) and Koehler *et al.* (1991) do not appear to have been reconciled.

2.4.4 Product regions for distillation processes at non-limiting conditions

The two limiting conditions of distillation are total reflux and reversible distillation (Wahnschafft *et al.*, 1992). Considerable emphasis has been placed on determining feasible product regions at total reflux. This section reviews research into determining the region of feasible products for columns operating at non-limiting conditions, namely at finite reflux ratios and using finite numbers of stages.

For the purpose of process synthesis, the products of a distillation column with a known feed may be specified. The following questions may be raised as part of the synthesis process:

- Given some feed, what products may be obtained using a distillation column?
- Is some specified product pair feasible for the distillation of a given feed?
- For some binary azeotrope, what entrainer (third component) should be

selected to allow separation of the mixture into the two components making up the azeotrope, using some sequence of distillation columns?

These questions are closely related, as they deal with feed, feasible products and the profiles joining these.

This review focuses on the product regions of individual columns for a given ternary mixture. Research relating to the choice of entrainer for separating a binary azeotrope will not be discussed here.

It is well known that distillation profiles at finite reflux ratios are quite different to residue curves and distillation lines, and that column profiles may cross simple distillation boundaries (Wahnschafft *et al.*, 1992). Some researchers have regarded as significant the extent to which a column profile may cross these boundaries, while others, for the sake of simplicity, have chosen to consider only products lying within simple distillation regions.

Van Dongen and Doherty (1985b) illustrated a bow-tie shaped product region containing all the feasible products for a given feed. Fien and Liu (1994) explained how to construct these bow-tie regions for estimating the region of feasible products for a given feed. The boundaries of these regions are given by the simple distillation boundary, the residue curve passing through the feed composition and mass balance lines for very sharp direct and indirect splits.

Stichlmair *et al.* (1989) and Koehler *et al.* (1991) used the distillation line which passes through the feed composition as a boundary for distillation processes at finite reflux ratios. This followed from strictly applying the requirements that the feed and product compositions lie on a straight line, and that the products must lie on the same residue curve. Profiles at finite reflux ratios are assumed to follow closely total reflux ratio profiles.

Doherty and Caldarola (1985) used a "reasonable working assumption" that column profiles do not cross the simple distillation boundary. This assumption was slightly relaxed by Stichlmair and Herguijuela (1992) and Bossen *et al.* (1993), who considered the crossing of the simple distillation boundary by the overall mass balance line, as shown in Fig. 2.5, but still assumed that column profiles do not cross the boundary.

Foucher *et al.* (1991) and Doherty and Caldarola (1985) gave a sufficiency condition for separability that products lie in the same simple distillation region. Fidkowski *et al.* (1993) concluded that it is "better engineering practice not to attempt to cross a simple distillation boundary unless all other alternatives have been explored". Fien and Liu (1994), in their excellent review of the use of residue curve maps, declared that "the error in approximating the boundaries with 'simple distillation boundaries' often is so small as to be inconsequential, especially at the flowsheet synthesis stage".

However, it is well known that distillation profiles may cross the simple distillation boundary (Nikolaev *et al.*, 1979), and Laroche *et al.* (1992a) maintained that excluding this possibility may restrict flowsheet development.

Separability at total reflux implies separability at finite reflux ratios, but the converse is not true (Laroche *et al.*, 1992b): for a specified separation, a maximum reflux ratio may exist, above which the separation is no longer feasible. Fidkowski *et al.* (1993) went so far as to say that there is almost always a maximum reflux ratio associated with a feasible specified separation. Certainly, even ideal mixtures are subject to this phenomenon, contrary to the belief of Laroche *et al.* (1992a). It therefore seems necessary to consider not only total reflux, but also finite reflux distillation processes when investigating regions of feasible products. It also follows that the assumption that distillation profiles follow total reflux profiles closely appears to be unjustified.

Wahnschafft *et al.* (1992) provided substantial insight in their development of feasible composition profile regions. For a specified distillate composition, this region is shown to be bounded by the residue curve and the reversible column profile through the product composition: that is, all possible rectification profiles lie between these two limiting conditions. A stripping profile region may be constructed in a similar manner. A necessary condition for a feasible separation is that these profile regions intersect. A point of interest in the intersection of the regions is the point where the tangent to the residue curve is collinear with the overall mass balance line: that is, it passes through both product compositions and the feed composition. This point lies on the feed pinch point curve, which is the locus of points where the tangent to the residue curve passes through the feed composition.

Wahnschafft *et al.* (1992) and Fidkowski *et al.* (1993) set up feasible product regions for a given feed, incorporating all reflux ratios. The boundaries of the region are found in part by feed pinch point curves, and indicate the existence of a pinch point in the column. Wahnschafft and Westerberg (1993) extended the work of Wahnschafft *et al.* (1992) for columns with more than one feed stream. It is significant that the boundaries of the feasible product region for distillation columns are given by the loci of products which are achievable only in the limit – at the limiting conditions of pinch points, which are associated with reversible distillation.

A range of feasible product regions for the distillation of a given feed have been proposed in the literature. These regions are obtained using more or less sophisticated assumptions. It is beyond the scope of this review to assess the validity of these assumptions. For example, it is not clear exactly how much poorer the optimal flowsheets are when it is assumed that distillation regions lie within simple distillation regions than when this assumption is not made. It is clear that making simplifying assumptions may allow problems to be solved relatively easily, but may also result in promising alternative flowsheets being overlooked. While it is not appropriate to become involved in detailed process design at the process synthesis stage, it is not desirable to use such crude assumptions that good alternative flowsheets are discarded prematurely.

In any of these product regions, only one of the two column products may be specified. Every composition in a feasible product region is attainable, but not every point on the mass balance line passing through the feed and lying in the opposite product region to the specified product is attainable. (Specifically, it is not possible to distinguish which bottoms products are feasible for a distillate product lying in the region of feasible products.) It is not possible to represent in two-dimensional space all sets of feasible co-products associated with all attainable products for some ternary mixture.

2.5 Feasible products of VLE separation processes

Column distillation is probably the most commonly used VLE separation process, and almost all the previous work on feasible product regions of separation processes has focused on distillation processes. Some of this work on achievable products has been presented in Section 2.4.4 above.

For the simple distillation process, the locus of compositions of the liquid residue with time is the residue curve starting at the initial liquid composition. More general questions about the possible products from simple distillation processes do not appear to have been addressed.

In passing, Koehler *et al.* (1991) illustrated, but did not discuss, the set of possible product pairs when the feed to a distillation column is partially vaporized (that is, the feasible products of a single equilibrium flash stage). The set of feasible products is a pair of arcs, one from the feed composition, $\overline{z}$, to the bubble point composition of the feed, *bubble*$(\overline{z})$, the other between the feed composition and the dew point composition of the feed, *dew*$(\overline{z})$. Other investigations into the feasible products of flash processes are not known.

2.6 Conclusions

This discussion has restricted itself to considering ternary, homogeneous mixtures and constant pressure, equilibrium separation processes. It has focused on the attainable products of individual distillation columns, since previous work on feasible products has concentrated almost exclusively on column distillation processes. Some ambiguities in this work have still not been resolved, and this continues to be an area of research activity. The far less complex process of simple distillation has received some attention, but even this relatively simple process has led to unresolved ambiguities relating to the definition of simple distillation boundaries. The feasible products of other VLE separation processes have not received much attention.

A number of points pertaining to distillation should be highlighted. Considering distillation at total reflux only seems to neglect promising flowsheet alternatives, and would appear to be an over-simplification. Boundaries are seen to exist for regions of feasible products of distillation processes. The feasible products on these boundaries seem invariably to be obtained at limiting conditions, such as very sharp splits (that is, very nearly pure or azeotropic products), total reflux and reversible operation. The costs associated with these operating conditions have not been considered, but would tend to be prohibitively large. It is a limitation of working in composition space that costs are not made explicit. Product quantities and co-product compositions are also not easily represented in composition space.

Chapter 3

Feasible Products of VLE Separation Processes

3.1 Introduction

The review given in Chapter 2 shows that a considerable amount of research has been carried out into determining the feasible products of the distillation of homogeneous ternary mixtures. The feasible products of other VLE separation processes have not received as much attention. Distillation is a complex process, comprised of equilibrium flash stages and mixing steps. In this section, some processes of considerably reduced complexity are explored. The feasible products of one and two flash stages with mixing, and of simple distillation and condensation are presented.

The study is limited to ternary, homogeneous, non-reacting systems at constant pressure; results are presented in ternary composition space. A hypothetical ternary system is investigated, the activity coefficients and vapour pressures of which are described by models which characterize real components. The thermodynamic data used for all the examples studied in this chapter are presented in Table 3.1. All three components are assumed to behave ideally in the vapour phase. Components 1 and 2 form a low-boiling ternary azeotrope; a one-suffix Margules equation is used to characterize their liquid-phase interactions. The third component behaves ideally in the liquid phase.

Separation processes, by definition, produce more than one output stream from a process. The convention which will be used in this chapter is that any separation process will have exactly two products: the product of interest and the co-product, which is a mixture of all the other outputs from the process. Only one of the two products can be independently specified.

Table 3.1 Thermodynamic data for hypothetical azeotropic ternary system. * Antoine equation: $\ln(p_i\,[\mathrm{kPa}]) = A_i - B_i/(T[°C] + C_i)$. Low-boiling azeotrope: (0.6, 0.4, 0) at 70°C.

	A*	B	C	$\ln \gamma_i$	Boiling temp [°C]
1	7.9652	252	–	$1.5x_2^2$	80
2	8.3852	302.4	–	$1.5x_1^2$	75
3	6.8718	102	-27	0	72

The mixing which is considered in this work will be restricted to "forward" mixing; that is, feasible products and the feed may be mixed, but material may not be recycled.

The concern of this work is separation. Whether a stream is a liquid, a vapour, or of mixed phase will not be considered, and it will be assumed that a mixture may, at any point in a process, be condensed or vaporized, fully or partially, without composition change. Similarly, a liquid and a vapour may be mixed to form a product, of indeterminate phase, with composition given by the mixing rule.

The results presented in this chapter were calculated using Fortran 77 (SPARCompiler Fortran 2.0.1) and the Numerical Algorithms Group fortran library routines (Mark 16 — D02BBF for integrating one or more differential equations and C05PCF for solving non-linear equations simultaneously).

3.2 Feasible products of simple distillation, simple condensation and mixing

The simple distillation process was presented in Section 2.3.1. In this section an answer is sought to the question: what is the region of feasible products for a process comprised of simple distillation, simple condensation and mixing? A "constrained" process, comprised of a single simple distillation stage and mixing, and an "unconstrained" process, comprised of any number of simple distillation and condensation stages, are examined.

3.2.1 Feasible products of a constrained simple distillation process

The simple distillation boundary has been observed to be a boundary for the liquid product compositions of single simple distillation processes. For processes comprised of simple distillation and mixing, the boundary may be crossed in a number of ways. The instantaneous vapour composition may lie beyond the simple distillation boundary, as shown in Fig. 2.3; or, as shown in Fig. 2.5, the mixing line between two points on the same residue curve may cross the simple distillation boundary. Therefore, by mixing between two points in the same simple distillation region, a mixture lying on the other side of the separatrix may be obtained. Fig. 3.1 shows how the accumulated vapour product, for a given simple distillation process, may lie on the other side of the simple distillation boundary. A straight simple distillation boundary may not be crossed by one of these methods, but it is assumed that simple distillation boundaries always have some curvature. *Therefore the simple distillation boundary is not a boundary for processes comprised of simple distillation and mixing.*

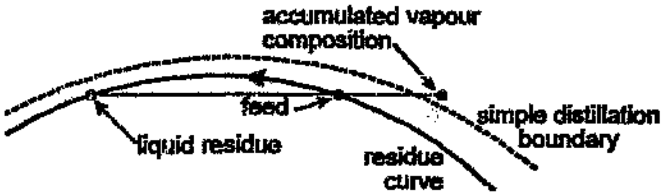


Fig. 3.1 The accumulated vapour may lie in a different simple distillation region to the residue curve.

The feasible products of processes comprised of a single distillation stage and mixing are investigated. The residue curve starting at a particular feed point and ending at a stable node in the residue curve map is the locus of feasible liquid products which may be obtained by a single simple distillation process. The instantaneous vapour composition profile is the locus of all feasible vapour products of the process, as shown in Fig. 3.2. The composition profile of the accumulated vapour product of the process is shown in Fig. 3.2. Since the accumulated vapour product at time t is the mixture of the instantaneous vapour products up to time t, the accumulated vapour product lies within the convex region bounded by the instantaneous vapour composition profile. The liquid residue at time *t* and the accumulated vapour product at time *t*, if mixed, would form a mixture with the same composition as the feed, so the compositions of the feed, the liquid residue and the accumulated vapour product must lie on a straight line in composition space at any given time.

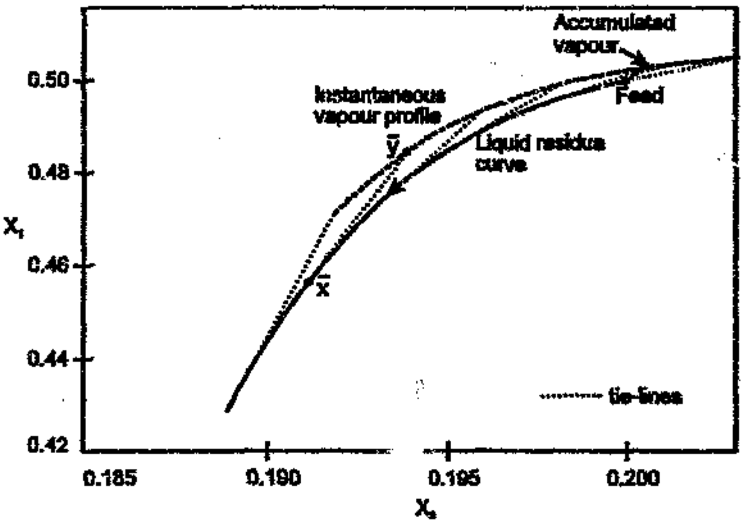


Fig. 3.2 Product profiles for a simple distillation process. The tangent to the liquid residue curve at $\bar{x}$ is equal to the vector $\bar{x}$-$\bar{y}$, where $\bar{y}$ is the instantaneous vapour composition.

The region of feasible products for the process comprised of a single simple distillation stage and forward mixing — the mixing of the products of such processes — is the convex region which contains the residue curve, the instantaneous vapour composition profile and all possible mixing lines. Such a region is illustrated in Fig. 3.3.

For the example shown in Fig. 3.3, the feed is at *F*, and the end-point of the residue curve is at *D*. The outermost mixing lines of this region are those joining points *A* and *C* and joining points *B* and *D*. A point *M* on the line *BD* may be obtained by the following process: the feed, *F*, is boiled until vapour of composition *B* is obtained. This vapour is retained and the boiling process continued [illegible] the residue reaches composition *D*. The mixtures of compositions *B* and *D* are combined in suitable proportions to obtain a mixture at *M*. If it is assumed that the process has only two products, the second product must lie in a straight line through *M* and *F* and beyond *F*, as given by the mass balance. Points interior to the region *ABCDA* may also be obtained by some combination of boiling and mixing processes. The region *ABCDA* is a convex region.

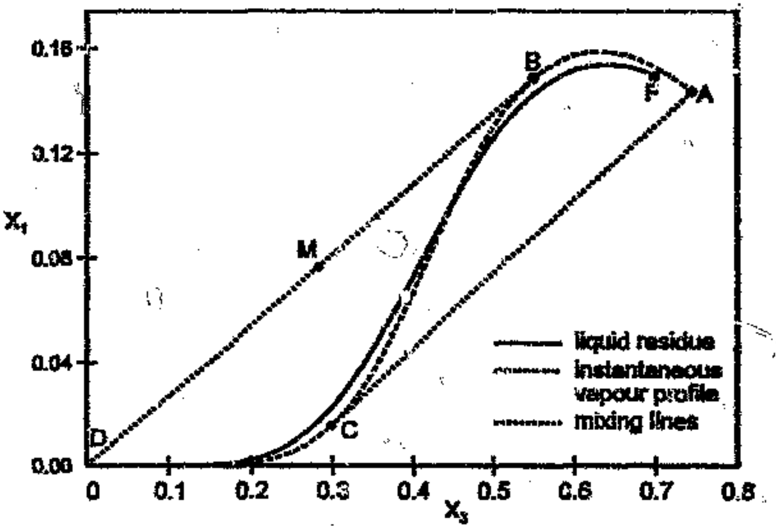


Fig. 3.3 Region of feasible products for a single simple distillation stage and mixing. The feed composition is at F: (0.15, 0.15, 0.7).

Since simple condensation is analogous to simple distillation, a convex region could be similarly constructed for a process comprised of a single simple condensation stage and mixing.

3.2.2 Feasible products of an unconstrained process comprised of simple distillation, simple condensation and mixing

This section addresses the question: what are the feasible products for any number of stages of simple distillation and simple condensation, mixing and phase change?

Residue curves do not intersect. However, by mixing between feasible points of a residue curve, or by collecting instantaneous or accumulated vapour products, points on other residue curves may be obtained. For example, the product region of Fig.

3.3 may sometimes be extended by initiating another simple distillation stage from a mixing line on the boundary of the product region. It will be shown that the region of feasible products of processes comprised of an unlimited number of stages of simple distillation, simple condensation and mixing is the entire composition space.

The region *R*, shown in Fig. 3.4(a), is proposed as the region of feasible products for an unconstrained process comprised of simple distillation, simple condensing and mixing. An arbitrary mixture with composition $\bar{p}$ is proposed as a point on the boundary of *R*. Initially it will be assumed that every point on the boundary of *R* is a ternary mixture, and not a binary mixture or pure component. It follows that *R* lies strictly within the composition triangle. It will further be assumed that $\bar{p}$ is not a ternary azeotrope. It will be shown how the processes of simple distillation, simple condensing and mixing may allow the region *R* to be extended, until *R* coincides with the composition triangle.

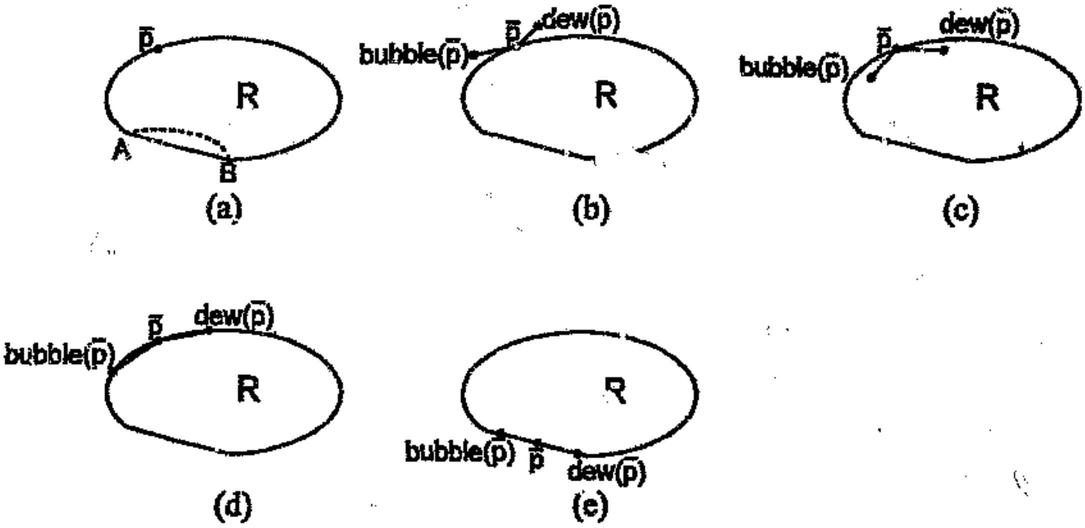


Fig. 3.4 A proposed region of feasible products, *R*. (a) *R* must be convex. (b) $dew(\bar{p})$ or $bubble(\bar{p})$ may lie outside *R*. (c) $dew(\bar{p})$ or $bubble(\bar{p})$ may lie inside *R*. (d) $dew(\bar{p})$ or $bubble(\bar{p})$ may lie on the boundary of *R* (e) $dew(\bar{p})$ or $bubble(\bar{p})$ may be collinear and lie on the boundary of *R*.

The dew-point composition of $\bar{p}$, *dew*($\bar{p}$), and bubble-point composition of $\bar{p}$, *bubble*($\bar{p}$), may be determined. The equation describing the composition of a liquid undergoing simple distillation is:

$$\frac{d\bar{x}}{d\xi} = \bar{x} - \bar{y} \tag{2.2}$$

The composition trajectory of the residual vapour in the simple condensing process is:

$$\frac{d\bar{y}}{d\xi} = \bar{y} - \bar{x} \tag{2.4}$$

that is, the tangent to the liquid residue curve for a simple distillation process initiated at $\bar{p}$ is the vector $\bar{p}$−*bubble*($\bar{p}$). Similarly, the tangent to the vapour residue curve at $\bar{p}$ for a simple condensation process initiated at $\bar{p}$ is the vector $\bar{p}$−*dew*($\bar{p}$).

1. The region *R* must be convex. If there were a concavity in the region, such as given by the dashed curve between *A* and *B* in Fig. 3.4(a), mixing lines, such as *AB*, could fill in the concavity.
2. If either *dew*($\bar{p}$) or *bubble*($\bar{p}$) lies outside the proposed product region, as shown in Fig. 3.4(b), then a mixture of one these compositions may be obtained which lies outside *R*, and *R* may be extended.

3. If either *dew*($\bar{p}$) or *bubble*($\bar{p}$) lies inside the product region *R*, as shown in Fig. 3.4(c), then the vector $\bar{p}$−*dew*($\bar{p}$) or $\bar{p}$−*bubble*($\bar{p}$) points out of the product region, since *R* is convex. Therefore, by eq. (2.2) or (2.4), respectively, the liquid or vapour residue curve must, at least initially, leave the proposed product region *R*, and compositions outside of *R* may be obtained. Therefore *R* may be extended.

4. If $\bar{p}$ is equal to *dew*($\bar{p}$) or *bubble*($\bar{p}$), then $\bar{p}$ is a singular point in the liquid residue curve map. In this case, $\bar{p}$ is either a pure component vertex or an azeotrope (Doherty and Perkins, 1978). All singular points, with the

exception of ternary azeotropes, therefore lie on the boundary of the composition triangle. No further separation is possible from such points by simple distillation or simple condensing.

If R consists of a single point of composition $\bar{p}$, which is a ternary azeotrope, then R cannot be extended. If, however, R consists of more than one point, not every point on the boundary of R may be a singular point, since singular points are isolated (Doherty and Perkins, 1979a). Then R may be extended from another point on the boundary of R by the methods of points 1, 2, 3 or 5.

5. If $\bar{p}$, *dew*$(\bar{p})$ and *bubble*$(\bar{p})$ all lie on the boundary of R and are not collinear, as shown in Fig. 3.4(d), then the vector $\bar{p}-\mathit{bubble}(\bar{p})$ or $\bar{p}-\mathit{dew}(\bar{p})$ points out of the region and the region may be extended. If $\bar{p}$, *dew*$(\bar{p})$ and *bubble*$(\bar{p})$ all lie on the boundary of R and are collinear, as shown in Fig. 3.4(e), then the region R cannot be extended by the processes of simple distillation and simple condensing at $\bar{p}$. If every point on the boundary of R has this property (*i.e.*, *bubble*$(\bar{p})$, *dew*$(\bar{p})$ and $\bar{p}$ lie on the boundary of R and are collinear) then the boundary is a perfectly straight line. In this case R cannot be extended. The only two types of lines which have this property are the boundaries of the composition triangle and perfectly straight residue curves, which are thought not to exist (Doherty and Perkins, 1978, citing Schreinemakers, 1902).

It has thus been shown that, in general, only the boundaries of the composition triangle may form boundaries to the region of feasible products for processes comprised of simple distillation, simple condensing and mixing.

It may be concluded that, by the processes of simple distillation, simple condensation, mixing and phase change, any composition may be achieved, and that the region of feasible products is the entire composition space. This result may seem trivial, but it indicates that *there are no absolute boundaries for VLE separation* *processes*. It follows that product limitations are not inherent to VLE separation, but arise out of the choice of separation equipment. In particular, that not every product may be obtained for a sequence of one or more distillation columns is a result of the choice of distillation columns.

The discussion on feasible products of simple distillation and condensing processes has concerned itself only with feasible product compositions and not with cost. The processes proposed (for example, that to obtain a mixture of composition *M* in the previous section) are achievable only in the limit. To obtain a finite amount of product, an infinite quantity of feed, an infinite amount of heating or condensing, and equipment of an infinite size would be required. A similar result was found by Wahnschafft *et al.* (1992) for distillation columns: the products on the boundary of the region of feasible products are obtained at the limiting conditions of reversible distillation, and are therefore associated with infinite costs. Clearly, there are limitations to working in composition space.

3.3 Feasible products of one and two flash stages

The product region for VLE separation processes is the entire composition space. In this section, the sub-regions of products for processes comprised of one or two flash stages will be presented. It has been seen that column distillation is a complex process which is not yet clearly understood. A distillation column is a series of flash stages, with the feed to each stage comprised of a mixture of the vapour product from the stage below and the liquid product from the stage above. This work aims to shed some light on the operation of distillation columns by examining and comparing the feasible product compositions of processes comprised of one or two flash stages and mixing.

The region of feasible products for a single flash stage may be extended by the use of a second flash stage. Three configurations of two flash stages are investigated in this section, namely, two flash stages arranged in parallel, in series and in series with reflux. Mixing is restricted to forward mixing, but the reflux in the third case forms an internal recycle.

3.3.1 Feasible products of a single flash stage

In a flash stage, a feed of quantity *F* and composition $\overline{z}$ is separated into a liquid product of quantity *L* and composition $\overline{x}$, and its equilibrium vapour product of quantity *V* and composition $\overline{y}$, as shown in Fig. 3.5. The mass balance for this process is given by:

$$\overline{z} = \phi\overline{y} + (1-\phi)\overline{x} \tag{3.1}$$

where ϕ is the fraction of the feed which is vaporized, equal to *V/F*, from which it follows that $0 \leq \phi \leq 1$; equivalently:

$$\overline{x} - \overline{z} = \phi(\overline{x} - \overline{y}) \tag{3.2}$$

That is, the vectors $\overline{x}-\overline{z}$ and $\overline{x}-\overline{y}$ are collinear, with their relative lengths given by the lever-arm rule.

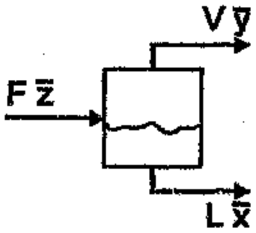


Fig. 3.5 Stream flow rates and compositions of a single flash stage.

When a mixture is flashed, its vapour and liquid products must be an equilibrium pair, and the feed, vapour product and liquid product must lie on a straight line, with the distance between the points given by the lever-arm rule. These criteria are valid for ternary as well as higher dimension systems, and combine to give a locus of feasible product pairs. For a ternary system, these pairs may be plotted in two-dimensional composition space. Fig. 3.6 shows a number of such product pairs for a particular feed, corresponding to a number of different values of ϕ.

The flash product locus has a structure of two contiguous arcs, one of which is the liquid product locus, and the other the vapour product locus. The arcs meet at the feed composition, $\bar{z}$, and have as end-points the dew-point composition of the feed (denoted by *dew($\bar{z}$)*) on the liquid locus, and the bubble-point composition of the feed (denoted by *bubble($\bar{z}$)*) on the vapour locus. The point *dew($\bar{z}$)* represents the liquid product in the extreme case where no liquid is formed ($\phi = 1$) and *bubble($\bar{z}$)* represents the vapour product in the extreme case where no vapour is formed ($\phi = 0$). In both cases the second product has the same composition and flow rate as the original feed. The arc-ends *dew($\bar{z}$)* and *bubble($\bar{z}$)* represent a limit on the amount of separation which can be achieved in a single flash stage.

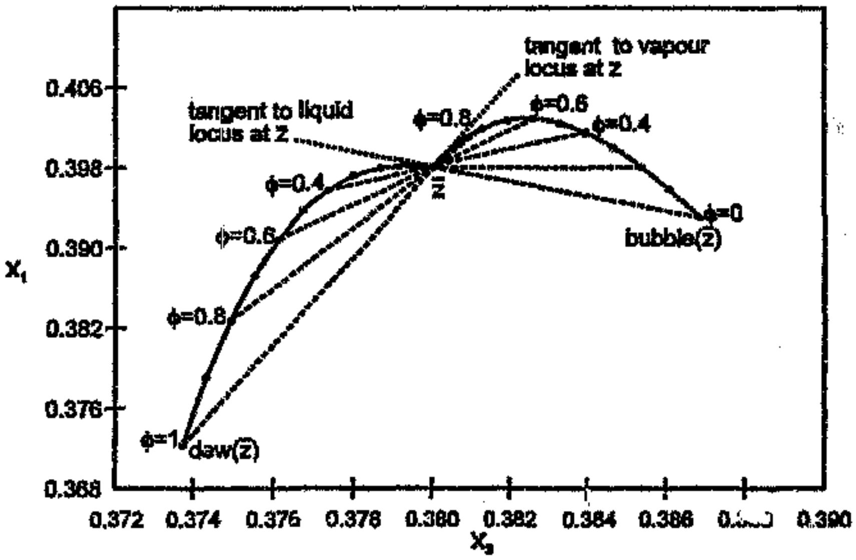


Fig. 3.6 The liquid and vapour product loci of a single flash stage with feed composition $\bar{z}$. Equilibrium liquid-vapour pairs are given for a range of ϕ values, where ϕ is the fraction of the feed which is vaporized.

There are restrictions on the geometry of this construction. Since, for example, a particular liquid has exactly one equilibrium vapour point associated with it, there can only be one intersection of the line through $\bar{x}$ and the feed $\bar{z}$ and the vapour product arc. Therefore, concavities in arcs, such as that illustrated in Fig. 3.7(a), are not feasible, because there would be two vapour products, of compositions $\bar{y}_1$ and $\bar{y}_2$ in equilibrium with a single liquid of composition $\bar{x}$.

The liquid loci of two different feeds ($\bar{z}_1$ and $\bar{z}_2$) also cannot intersect at $\bar{x}$ without the vapour loci also intersecting, as shown in Fig. 3.7(b). If they could, this would imply that two different vapour compositions were in equilibrium with $\bar{x}$ at the intersection point. Similarly, vapour product loci cannot intersect without the liquid loci also intersecting.

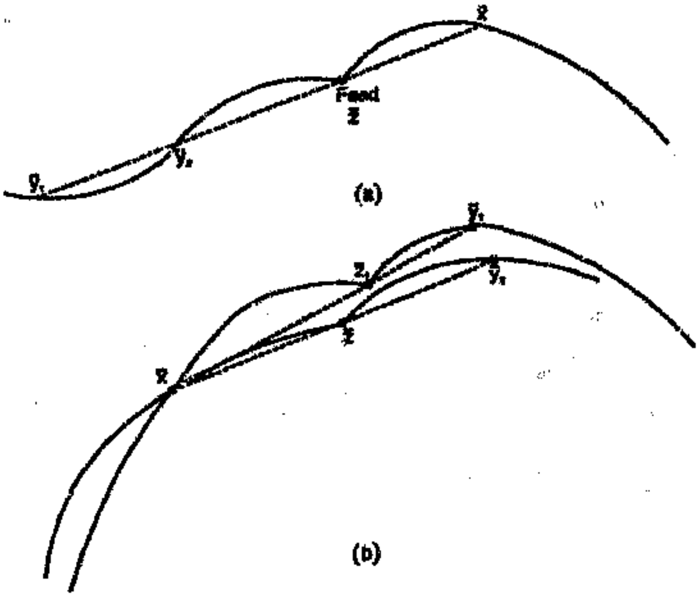


Fig. 3.7 Impossible geometries of flash product loci. (a) A concavity in the vapour product arc. (b) The liquid product arcs intersect while the vapour product arcs do not.

The limiting flash cases occur where an infinitesimal quantity of vapour or liquid is separated from the feed. The product loci near to the feed point are examined: at the limiting conditions. Equation (3.1) may be differentiated with respect to ϕ to obtain:

$$\frac{d\bar{z}}{d\phi} = \bar{0} = \bar{y} - \bar{x} + \phi\frac{d\bar{y}}{d\phi} + (1-\phi)\frac{d\bar{x}}{d\phi} \tag{3.3}$$

For ϕ approximately equal to one, $\bar{y}$ and $\bar{z}$ are equal, and $\bar{x}$ and *dew*($\bar{z}$) are equal. Therefore:

$$\bar{0} = \bar{y} - \bar{x} + \frac{d\bar{y}}{d\phi} \tag{3.4}$$

or, equivalently:

$$\frac{d\bar{y}}{d\phi}\Big|_{\bar{y}=\bar{z}} = \bar{y} - \bar{x} = \bar{z} - dew(\bar{z}) \tag{3.5}$$

For ϕ approximately zero, $\bar{x}$ is equal to $\bar{z}$ and $\bar{y}$ is equal to ***bubble($\bar{z}$)***. Hence:

$$\bar{0} = \bar{y} - \bar{x} + \frac{d\bar{x}}{d\phi} \tag{3.6}$$

or, equivalently:

$$\frac{d\bar{x}}{d\phi}\Big|_{\bar{x}=\bar{z}} = \bar{x} - \bar{y} = \bar{z} - bubble(\bar{z}) \tag{3.7}$$

These processes are identical to the simple condensation or distillation process when the first differential amount of liquid or vapour is removed from a feed of composition $\bar{z}$. The simple condensation and distillation processes are described, respectively, by eq. (2.4) and (2.2), from which it follows:

$$\frac{d\bar{y}}{d\xi}\Big|_{\bar{y}=\bar{z}} = \bar{y} - \bar{x} = \bar{z} - dew(\bar{z}) \tag{3.8}$$

$$\frac{d\bar{x}}{d\xi}\Big|_{\bar{x}=\bar{z}} = \bar{x} - \bar{y} = \bar{z} - bubble(\bar{z}) \tag{3.9}$$

It may be seen that the vapour product locus near $\bar{z}$, as given by eq. (3.5) is identical to the differential condensation trajectory at the feed, as described by eq. (3.8). The tangent to the vapour locus is equal to the vector $\bar{z}$−***dew($\bar{z}$)***, as shown in Fig. 3.6. Similarly, the tangent to the liquid locus near $\bar{z}$ is the vector $\bar{z}$−***bubble($\bar{z}$)***, as illustrated in Fig. 3.6.

The geometric properties of the ends of the arcs, *i.e.*, the product loci close to ***dew($\bar{z}$)*** or ***bubble($\bar{z}$)***, for the limiting processes of $\xi = 0$ and $\phi = 1$, have not been determined.

The arc between an equilibrium pair of points $\bar{x}$ and $\bar{y}$ is not unique. The vapour product arc for a flash with feed $\bar{x}$ is not identical to the liquid product arc for a flash with feed $\bar{y}$, although both arcs share the same end-points. The flash product loci for feed compositions $\bar{x}$ and *bubble*($\bar{x}$) are shown in Fig. 3.8.

The distance between the extreme compositions which are achievable for a process comprised of one or more flash stages and mixing, is defined as the "span" of the process. The span of a single flash stage is the distance from the dew-point composition of the feed to the bubble-point composition of the feed.

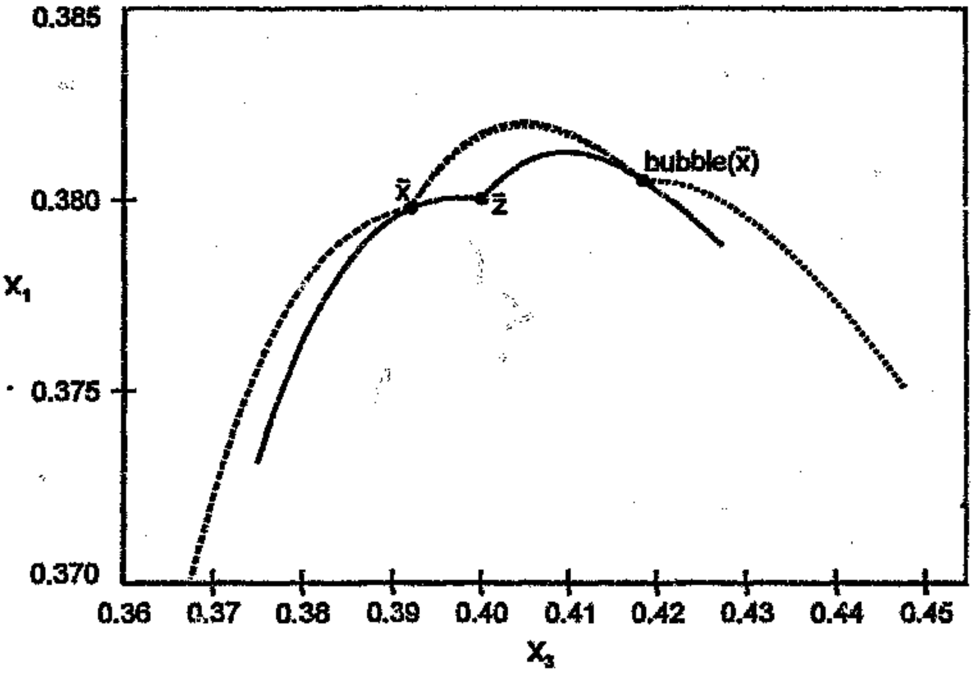


Fig. 3.8 The vapour-product arc of a flash with feed composition $\bar{x}$ is not identical to the liquid-product arc of a flash with feed composition *bubble*($\bar{x}$), although the end points are common.

Feasible products of a single flash stage and forward mixing

The arc-pair product locus of Fig. 3.6 is the set of all possible products for a single flash separation. For a process comprised of a single flash stage and forward mixing, appropriate quantities of some feasible $\bar{x}-\bar{y}$ product pair may be mixed to obtain any point on the mixing line $\bar{x}-\bar{y}$. The product region contains all such straight lines joining feasible product pairs. The region of feasible products is bounded by the arcs and the mixing lines joining the feed, $\bar{z}$, and *dew*($\bar{z}$), and joining $\bar{z}$ and *bubble*($\bar{z}$), as shown in Fig. 3.9.

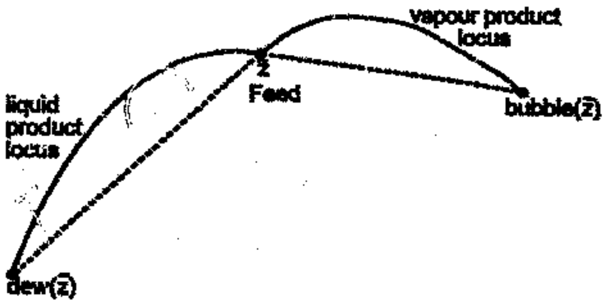


Fig. 3.9 The product region of a single flash stage and mixing, bounded by the mixing lines $\bar{z}$–*dew*($\bar{z}$) and $\bar{z}$–*bubble*($\bar{z}$) and the flash product arcs.

Feasible products of a single flash stage and recycle

Recycle is "reverse" mixing, where achievable downstream products are mixed with upstream process streams, such as the feed. It is the opposite of forward mixing, in which streams may be mixed but these mixtures are not reintroduced upstream in the process. A single flash stage with recycle is illustrated in Fig. 3.10. The nett feed composition to the flash stage is of composition $\bar{z}*$, but since $\bar{z}*$ is a mixture of $\bar{y}$ and $\bar{z}$, it follows that $\bar{x}$, $\bar{y}$, $\bar{z}$, and $\bar{z}*$ all lie on a straight line, as shown in Fig. 3.11; that is, $\bar{x}$ and $\bar{y}$ are an equilibrium product pair of a flash of feed $\bar{z}$. The same argument holds for all choices of $\bar{x}$–$\bar{y}$, whether it is the vapour or liquid product which is recycled. It follows that the product region for a single flash stage with recycle is identical to that shown in Fig. 3.9 for a single flash with forward mixing.

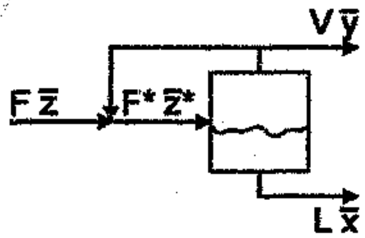


Fig. 3.10 Stream flow rates and compositions for a flash stage with recycle.

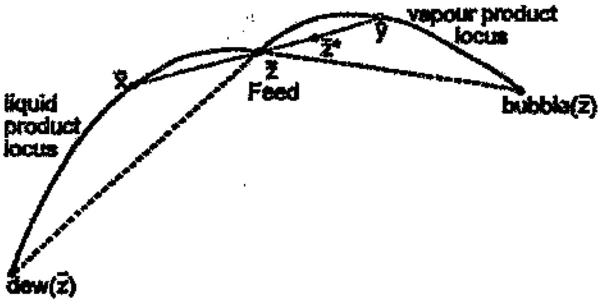


Fig. 3.11 The points $\bar{x}$, $\bar{z}$, $\bar{z}^*$ and $\bar{y}$ represent stream compositions for a single flash stage with recycle. The pair $\bar{x}-\bar{y}$ is a feasible product for a single flash stage of feed $\bar{z}^*$ or $\bar{z}$, *i.e.*, with or without recycle.

3.3.2 Feasible products of two flash stages arranged in parallel with mixing

The feasible products of two equilibrium flash stages arranged in parallel with forward mixing, as shown in Fig. 3.12, are investigated. The feed to the process, of composition $\bar{z}$, is split and fed to two flash stages, both of which have the same product locus. The products from the first stage are of composition $\bar{x}_1$ and $\bar{y}_1$, and those from the second stage of composition $\bar{x}_2$ and $\bar{y}_2$. The fractions of the feed vaporized in the first and second flash stages, respectively, are denoted by ϕ_1 and ϕ_2. Any combination of these four products may be mixed to form the final products. The product region for this process is found by examining the region of feasible products when both ϕ_1 and ϕ_2 are fixed, when only ϕ_1 is fixed, and when neither ϕ_1 nor ϕ_2 is fixed. It is noted that once a product composition, such as $\bar{p}_1$ in Fig. 3.12, is specified, the other product composition, $\bar{p}_2$, may not be independently specified.

Two feasible product pairs are shown in Fig. 3.13(a) for the case where ϕ_1 and ϕ_2 are specified. The products from the two stages may be mixed in any proportions. Therefore the region of feasible products of the process, for some arbitrary fixed values of ϕ_1 and ϕ_2, contain all possible mixing lines between these four products. The product region is bounded by the mixing lines joining the points $\bar{x}_1$, $\bar{y}_1$, $\bar{x}_2$ and $\bar{y}_2$, as shown in Fig. 3.13(a).

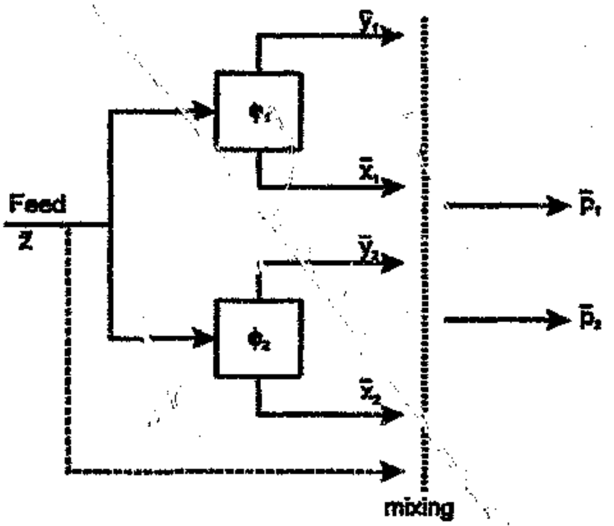


Fig. 3.12 Stream compositions for two flash stages arranged in parallel with mixing. The two final products, of composition $\bar{p}_1$ and $\bar{p}_2$, are some mixture of the intermediate products.

Where ϕ_1 is fixed at an arbitrary value and ϕ_2 is not fixed, the points $\bar{x}_2$ and $\bar{y}_2$ may lie anywhere on the one-stage product arcs for a feed of composition $\bar{z}$, as shown in Fig. 3.13(b). The stream of composition $\bar{x}_1$ may be mixed in any proportion with all possible liquid or vapour products of the second flash stage. Therefore the mixed product may lie on any mixing line between $\bar{x}_1$ and points on the vapour product locus, or on points on mixing lines joining $\bar{x}_1$ and points on the liquid product arc. Mixing lines between $\bar{x}_1$ and points on the liquid locus lie within the region of feasible products for a single flash stage; they do not, therefore, extend the product region, and will not be discussed further. A fan of mixing lines may be constructed joining $\bar{x}_1$ to points on the vapour product arc. The outermost lines of this fan are those joining $\bar{x}_1$ to *bubble*($\bar{z}$) and joining $\bar{x}_1$ to the point $\bar{y}$, where the tangent to the vapour product locus is collinear with the mixing line $\bar{x}_1-\bar{y}$, as shown in Fig. 3.13(b).

Similarly, the stream of composition $\bar{y}_1$ may be mixed in any proportion with points on the liquid product arc. A fan of mixing lines from $\bar{y}_1$ to points on the liquid product arc may be constructed, as shown in Fig. 3.13(c). The outermost lines of this fan are those joining $\bar{y}_1$ and *dew*($\bar{z}$) and joining $\bar{y}_1$ to the point $\bar{x}$ where the tangent to the liquid product arc is collinear with the mixing line $\bar{y}_1$–$\bar{x}$. Lines joining $\bar{y}_1$ to points on the vapour product arc do not extend the one-stage product region, and will therefore not be examined further.

For the mixing fans shown in both Fig. 3.13(b) and 3.13(c), it may be seen that products with compositions in the concavity near the feed are achievable, which was not the case for a single flash stage.

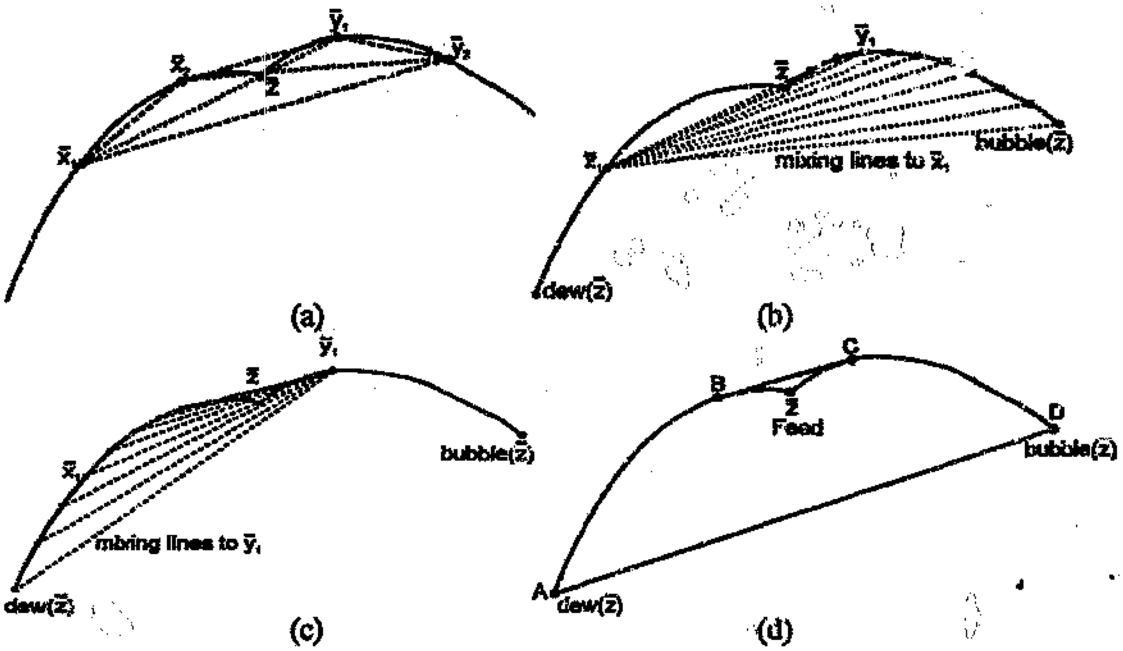


Fig. 3.13 The feasible products of two flash stages arranged in parallel. (a) ϕ_1 and ϕ_2 are fixed. The region of feasible products is bounded by the mixing lines between $\bar{x}_1$, $\bar{x}_2$, $\bar{y}_1$ and $\bar{y}_2$. (b) The fan of mixing lines from $\bar{x}_1$ to points on the vapour-product locus. (d) The fan of mixing lines from $\bar{y}_1$ to points on the liquid-product locus. (c) The convex region of feasible products, *ABCDA*.

For each value of ϕ_1 which is specified, similar mixing fans may be constructed. The feasible product region for two flash stages arranged in parallel is the union of all such mixing fans. One of the outermost mixing lines in this union is the line joining *dew($\bar{z}$)* to *bubble($\bar{z}$)*. This is the line *AD* in Fig. 3.13(d). The other outermost mixing line is that which is tangential to both the liquid product arc and the vapour product arc at its end-points. This is the line *BC* in Fig. 3.13(d). The convex region *ABCDA* shown in Fig. 3.13(d) is the feasible product region for two flash stages arranged in parallel with mixing.

3.3.3 Feasible products of two flash stages arranged in series with mixing

When two flash stages are arranged in series, a feasible product from the first flash stage forms the feed to the second flash stage, as shown in Fig. 3.14; that is, the feed to the second flash stage lies within, or on the boundary of, the product region for a single flash stage.

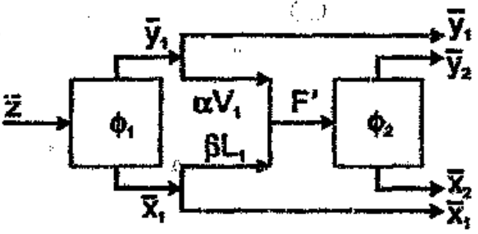


Fig. 3.14 Stream compositions of two flash stages arranged in series. The overall product streams are some mixture of the streams of composition $\bar{x}_1$, $\bar{y}_1$, $\bar{x}_2$ and $\bar{y}_2$.

First it will be shown that only the second-stage feed compositions lying on the boundary of the one-stage product region need be examined. Consider an arbitrary feasible product region, *R*, as shown in Fig. 3.15. If some point *A* in the interior of this region forms the feed to a flash stage, then a product of this flash may lie within *R* (for example, at point *B*), on the boundary of *R* (such as point *C*), or outside of *R* (for example, at point *D*). Only one of the products is considered here; the argument applies equally to either of the products. Point *D* is assumed to be in equilibrium with a point *D'*, which may lie inside, outside, or on the boundary of the region *R*. By mass balance, points *D*, *A* and *D'* lie on a straight line.

Points *B* and *C* lie within the region *R*, and are not of interest, since the feasible product region is not extended by the flash separation of the mixture at *A*. Point *D* lies outside the region, and the line *AD* intersects the boundary of the region *R* at point *E*. Since *D* and *D'* are an equilibrium product pair, and *E* lies on the straight line between these points, it follows that *D* and *D'* are feasible products for a flash stage with feed composition *E*. That is, any products, such as *D*, which extend the product region, may be obtained as flash products of feeds lying on the boundary of the product region *R*. It may be concluded that only compositions on the boundary of the product region for one flash stage need be considered as feeds to a second flash stage arranged in series.

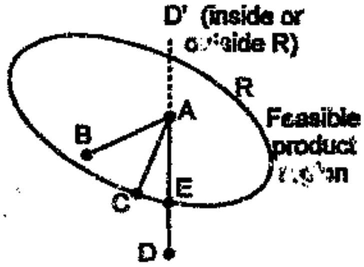
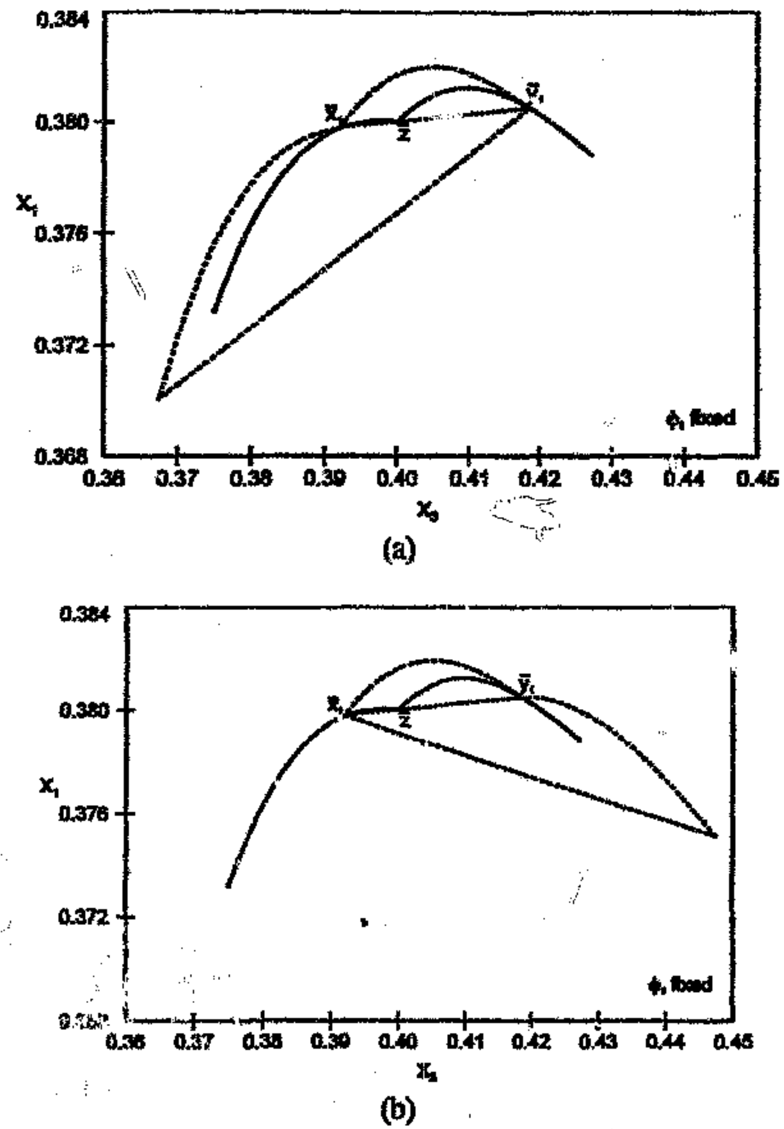


Fig. 3.15 An arbitrary region of feasible products, *R*. A flash with feed composition at *A* may have products lying inside, outside or on the boundary of *R*.

In order to construct the product region for two flash stages arranged in series, feeds lying on the product arcs of a single flash stage, where there is no mixing after the first flash stage, and feeds lying on the lines $\overline{z}$–*dew*($\overline{z}$) and $\overline{z}$–***bubble***($\overline{z}$) will be considered separately.

First consider the case where the feed to the second flash stage lies on the first stage liquid product locus, and is of composition $\overline{x}_1$, and the products of the second flash stage are of compositions $\overline{x}_2$ and $\overline{y}_2$. The remaining product from the first flash stage, of composition $\overline{y}_1$, may be mixed with the second stage products. Fig. 3.16(a) shows a particular first-stage product pair $\overline{x}_1$, $\overline{y}_1$, and the locus of second-stage products where the composition of the second-stage feed is $\overline{x}_1$. A fan of mixing lines may be constructed from $\overline{y}_1$ to points on the second-stage product locus. The region of feasible products for this process is bounded by the second-stage product arcs and the line joining *dew*($\overline{x}_1$) to ***bubble***($\overline{x}_1$), where ***bubble***($\overline{x}_1$) = $\overline{y}_1$. Similarly, Fig. 3.16(b) shows the region of feasible products where the feed to the second flash stage is of composition $\overline{y}_1$.



(a)

(b)

Fig. 3.16 The feasible products for the second of two flash stages arranged in series with mixing. (a) The products for a feed of composition $\bar{y}_1$ mixed with the stream of composition $\bar{x}_1$. (b) The products for a feed of composition $\bar{x}_1$ mixed with the stream of composition $\bar{y}_1$.

The region of feasible products for two flash stages arranged in series, where the second-stage feed lies on the curved boundaries of the single flash stage product region, is given in Fig. 3.17(a).

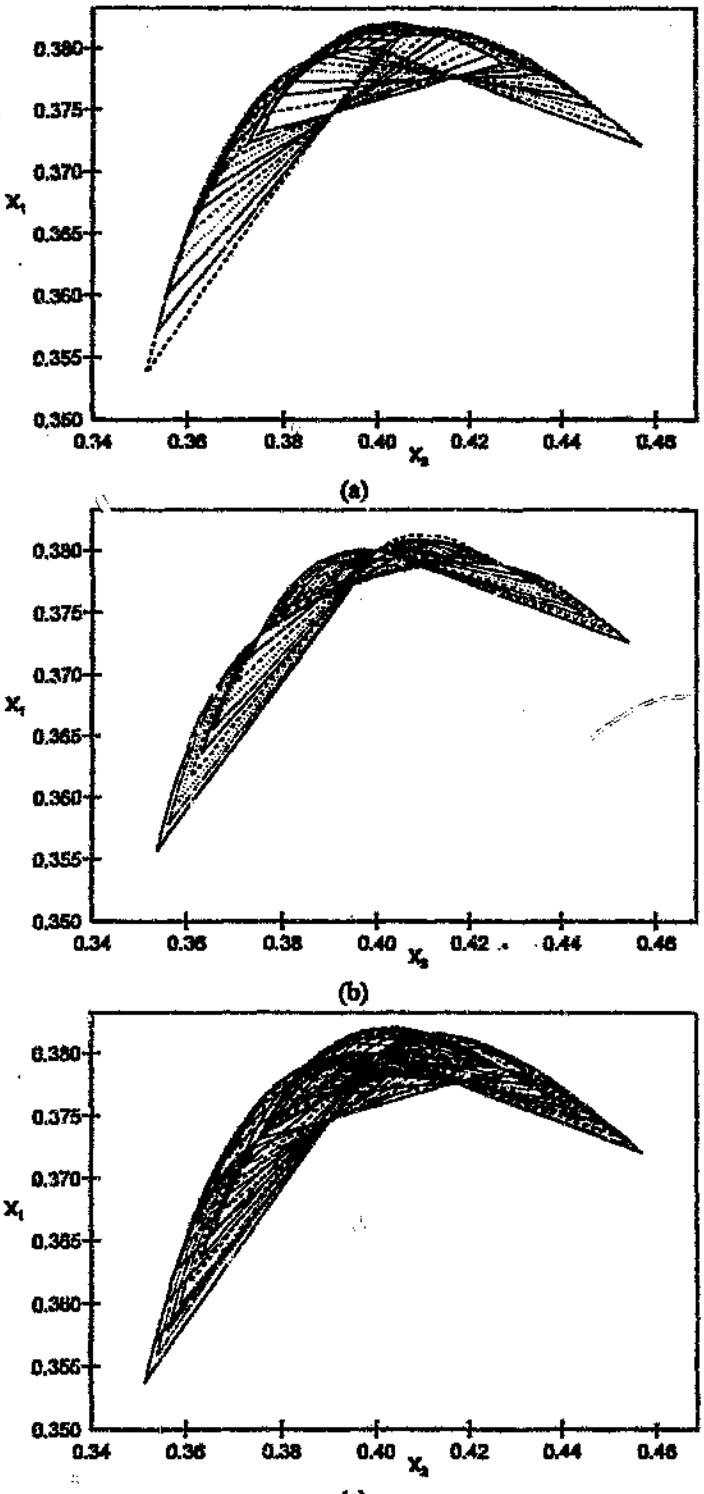


Fig. 3.17 The feasible products of two flash stages arranged in series with mixing. $\overline{z}$: (0.38, 0.22, 0.4). (a) Second-stage feed compositions lying on the first stage product arcs. (b) Second-stage feed compositions lying on the lines $\overline{z}$*−dew*($\overline{z}$) and $\overline{z}$*−bubble*($\overline{z}$). (c) Total product region.

One of the boundaries of the product region for the process is an envelope made up of the outermost points which lie on the second stage arcs. Fig. 3.18 shows two adjacent arcs a_1 and a_2 which are, for example, liquid product loci for two adjacent feeds f_1 and f_2. The points p_1 (on a_1) and p_2 (on a_2) lie on the envelope of outermost points if the tangent to a_1 at p_1, the tangent to a_2 at p_2, and the line $p_1 - p_2$ are collinear. The points on the envelope are generally finite quantity solutions, where they are not at arc-tips, and may be vapour or liquid products. The boundary is formed by three such envelopes: that where f_1 and f_2 are both liquids, where they are both vapours, and where one is a vapour and one a liquid, such that a_1 and a_2 are adjacent although f_1 and f_2 are not.

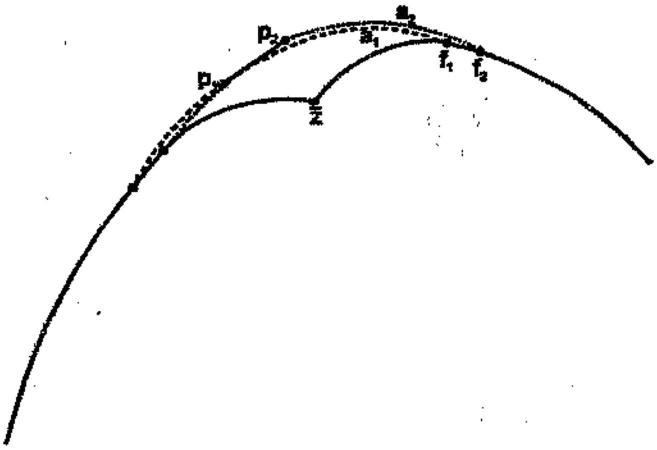


Fig. 3.18 Points p_1 and p_2 on arcs a_1 and a_2 lie on the envelope of boundary points of the region of feasible products for two flash stages arranged in series.

The other boundary of the product region shown in Fig. 3.17(a) is an envelope formed by the lines that join the dew-point and bubble-point compositions of the second-stage feeds. The points on this boundary are zero-quantity solutions. In this example, these lines appear to intersect at just two points, but closer numerical inspection shows that there is not a unique pair of intersection points.

Fig. 3.19 shows the product compositions of the process where the feed to the second flash stage, $\bar{z}_2$, lies on the line $\bar{z} - dew(\bar{z})$. The products of the second flash stage lie on the product arcs of a flash with feed composition $\bar{z}_2$. Since $\bar{z}$, $\bar{z}_2$ and

$dew(\bar{z})$ lie on a straight line, $\bar{z}-dew(\bar{z})$ is also a feasible product pair of the flash with feed $\bar{z}_2$, and the product arcs pass through these three points. The point $bubble(\bar{z}_2)$, incidentally, does not necessarily lie on the line $\bar{z}-bubble(\bar{z})$, since ***"bubble"*** is not a linear transformation, *i.e.*, $bubble(\alpha\,\bar{x} + (1-\alpha)\,\bar{y}) \neq \alpha\, bubble(\bar{x}) + (1-\alpha)\, bubble(\bar{y})$ for some scalar α such that $0 \leq \alpha \leq 1$.

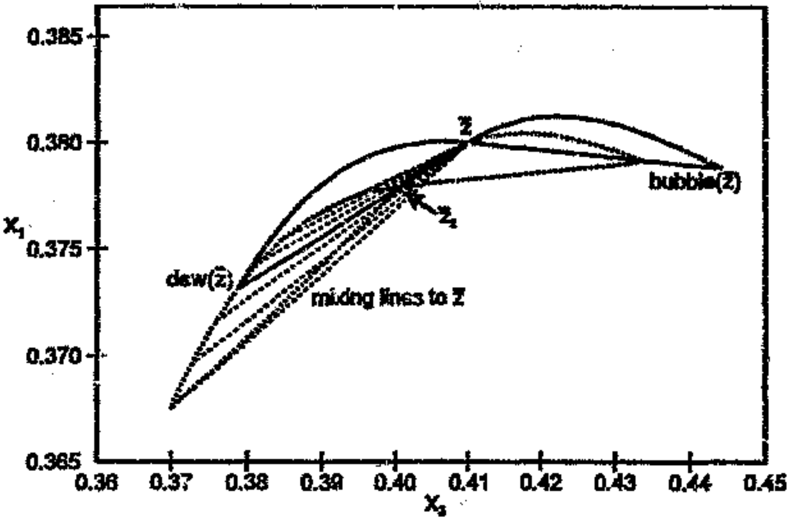


Fig. 3.19 The feasible products for the second of two flash stages arranged in series. The feed to the second flash stage lies on the line $\bar{z}-dew(\bar{z})$, and the feed to the first stage is at (0.38, 0.22, 0.40).

Points on the line $\bar{z}-dew(\bar{z})$ and $\bar{z}-bubble(\bar{z})$ are of zero quantity. Therefore the other first-stage product is identical to the feed in composition and quantity. A fan may be constructed containing mixing lines between $\bar{z}$ and points on the second-stage product locus, as shown in Fig. 3.19. Some of the second stage feed may be bypassed and mixed with second-stage products. Therefore a mixing fan may be constructed between $\bar{z}_2$ and points on the second-stage product arcs, as shown in Fig. 3.19. The union of these two mixing fans constitutes the product region for a fixed $\bar{z}_2$ composition.

The point $\bar{z}_2$ may lie anywhere on the lines $\bar{z}-dew(\bar{z})$ and $\bar{z}-bubble(\bar{z})$. Therefore the region of feasible products, shown in Fig. 3.17(b), is the union of all product regions such as that shown in Fig. 3.19.

The total feasible product region for two flash stages arranged in series is given in Fig. 3.17(c); it is the union of the regions shown in Fig. 3.17(a) and 3.17(b).

3.3.4 Feasible products of two flash stages arranged in series with reflux

In the process comprised of two flash stages arranged in series with reflux, one product from each flash stage forms a feed to the other flash stage, as shown in Fig. 3.20. The feed to the process may be added to either stage I or stage II. Mixing, other than internal recycle, is restricted to forward mixing. In a distillation column, each stage is an equilibrium flash stage, and both products from each stage form feeds to adjacent stages. Essentially, the processes shown in Fig. 3.20 are two-stage distillation columns.

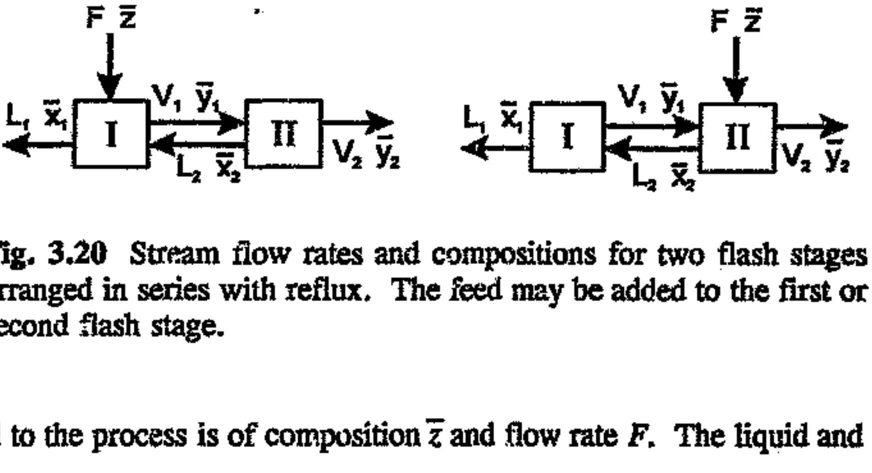


Fig. 3.20 Stream flow rates and compositions for two flash stages arranged in series with reflux. The feed may be added to the first or second flash stage.

The feed to the process is of composition $\bar{z}$ and flow rate F. The liquid and vapour products from stage I are of composition $\bar{x}_1$ and $\bar{y}_1$, and flow rates L_1 and V_1, respectively. Those from stage II are of composition $\bar{x}_2$ and $\bar{y}_2$ and flow rates L_2 and V_2, respectively. The streams L_1 and V_2 are removed as products of the process. There are two symmetrical arrangements of this process, since the feed to the process may be added to the first stage or to the second stage. The mixture between the process feed and the reflux forms a nett feed to one of the flash stages of quantity F^* and composition $\bar{z}^*$. The fractions of the nett feed to the first and second stages which are vaporized are ϕ_1 and ϕ_2, respectively.

The product region of the process with the feed added to the second stage is discussed in detail. When the feed is added to stage II, the feed, of composition $\vec{z}$ and flow rate F, and the first-stage vapour product, of composition $\vec{y}_1$ and flow rate V_1, mix to form a nett feed to the second stage of composition $\vec{z}^*$ and flow rate F^*. The fractions of feed which are vaporized in each stage are given by $\phi_1 = V_1/L_2$ and $\phi_2 = V_2/F^*$.

For a given feed, and some feasible liquid product composition $\vec{x}_1$, a range of feasible vapour-product compositions, $\vec{y}_2$, exist, where x_2, $\vec{z}$ and $\vec{y}_2$ lie on a straight line. Each feasible $\vec{y}_2$ composition is associated with a different ϕ_1, ϕ_2 pair. It appears that the extreme $\vec{y}_2$ compositions arise where there is total reflux (the feed flow rate is effectively zero) and where ϕ_1 or ϕ_2 is minimized or maximized (that is, ϕ_1 or ϕ_2 equals zero or one). (This observation has not been proved, either generally or for the thermodynamics used here.) The product loci for total reflux and extreme values of ϕ_1 and ϕ_2, therefore, form boundary candidates for the product region. These product loci are examined in some detail.

At total reflux, the feed flow rate, F, and therefore, the product flow rates, L_1 and V_2, are all zero. The internal streams, V_1 and L_2, are equal, in both quantity and composition, so $\vec{y}_1 = \vec{x}_2$. Since $\vec{x}_1 = dew(\vec{y}_1)$, and $\vec{x}_2 = dew(\vec{y}_2)$, it follows that $\vec{x}_1 = dew(dew(\vec{y}_2))$. The locus of points for which this property holds and for which the mass balance holds — $\vec{x}_1$, $\vec{z}$ and $\vec{y}_2$ lie on a straight line — is the product locus at total reflux. These curves are labelled *A* in Fig. 3.21 and Table 3.2.

When ϕ_1 equals zero (and the feed flow rate is non-zero), V_1 is zero, so L_2 equals L_1 in both quantity and composition, and $\vec{x}_2 = \vec{x}_1$. It follows that $\vec{y} = bubble(\vec{x}_1)$; that is, $\vec{x}_1$ and $\vec{y}_2$ are an equilibrium product pair of a flash with feed composition $\vec{z}$. The product locus, labelled *B* in Fig. 3.21, is the product pair of a single flash stage with feed composition $\vec{z}$.

When ϕ_1 equals one (and $F \neq 0$), then L_1 is zero. Therefore V_2 equals F and L_2 equals V_1 in quantity and composition (and $\bar{z} = \bar{y}_2$ and $\bar{y}_1' = \bar{x}_2$). It follows that $\bar{x}_1$ = *dew(dew($\bar{z}$))*. A unique pair of points satisfies the condition that $\phi_1 = 1$.

If ϕ_2 equals zero (and $F \neq 0$), V_2 is zero. Therefore L_1 equals F in composition and quantity: $\bar{x}_1 = \bar{z}$. The feed to the second stage is a mixture of the process feed, of composition $\bar{z}$, and the vapour product of the first stage, of composition $\bar{y}_1$ = *bubble($\bar{z}$)*. The composition of the nett feed to the second stage, $\bar{z}^*$, lies anywhere on the line $\bar{z}$–*bubble($\bar{z}$)*. The composition of the vapour product of the process, $\bar{y}_2$, is the bubble-point composition of $\bar{z}^*$, since $\phi_2 = 0$. The curve labelled *C($\bar{y}$)* in Fig. 3.21 is the locus of all such points, that is, the set of all $\bar{y}_2$ such that $\bar{y}_2$ = *bubble($\alpha\bar{z}$ + ($1-\alpha$) bubble($\bar{z}$))* where $0 \leq \alpha \leq 1$. Because there is not a linear relationship between equilibrium liquid and vapour compositions, the locus *C($\bar{y}$)*, mapping a line of points to their bubble-point compositions, is not necessarily a straight line.

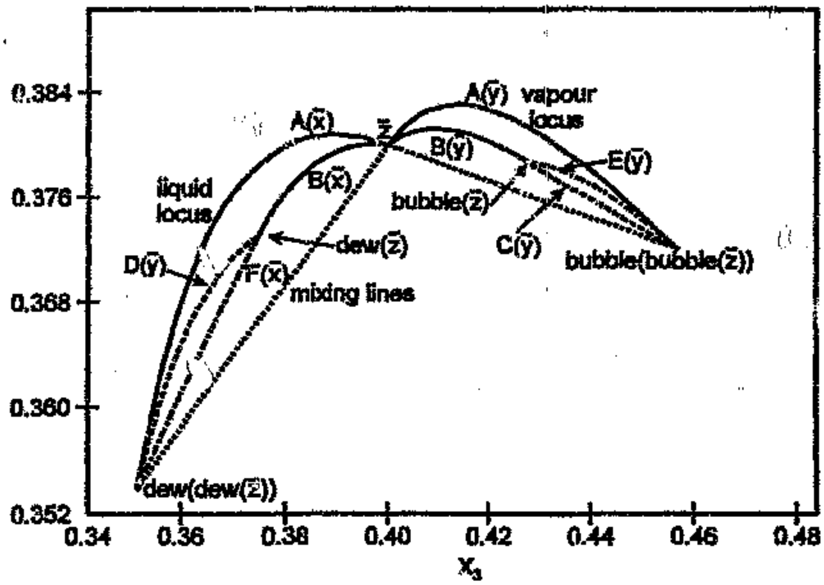


Fig. 3.21 Product region and boundary candidates for two refluxed flash stages and mixing. $\bar{z}$: (0.38, 0.22, 0.4).

Boundary candidates of the region of feasible products

The curves *A*, *B*, *C* and *D* are boundary candidates for the refluxed configuration of two flash stages, where the feed is added to t[illegible]ond stage. Curve *A* is a total reflux product locus, and is therefore associated with a zero-quantity feed; the other product curves (except for curve *B*) are associated with the zero-quantity product, while the co-product is identical to the feed.

A symmetrical set of boundary candidates (curves *A*, *B*, *E* and *F*) may be derived for the case where the feed is added to the first [illegible] the two flash stages arranged in series with reflux. Table 3.2 summarizes these results.

Table 3.2 Boundary candidates for the feasible product region of two flash stages with reflux.

Feed	Case [Curve]	$\bar{x}_1$ composition	$\bar{y}_2$ composition	Product quantity
Stage I or II	Total reflux [*A*]	*dew(dew($\bar{y}_2$))*	$\bar{z}$, $\bar{y}_2$ and $\bar{x}_1$ lie on a straight line	zero
Stage II	$\phi_1 = 0$ [*B*]	liqud product of flash with feed $\bar{z}$	vapour product of flash with feed $\bar{z}$	finite
	$\phi_1 = 1$	*dew(dew($\bar{z}$))*	$\bar{z}$	$L_1=0,\ V_2=F$
	$\phi_2 = 0$ [*C*]	$\bar{z}$	*bubble($\bar{x}_2$)* where $\bar{x}_2$ lies on line $\bar{z}$–*bubble($\bar{z}$)*	$L_1=F,\ V_2=0$
	$\phi_2 = 1$ [*D*]	liquid flash product of feed *dew($\bar{z}$))*	$\bar{z}$	$L_1=0,\ V_2=F$
Stage I	$\phi_1 = 0$ [*E*]	$\bar{z}$	vapour product of flash with feed *bubble($\bar{z}$)*	$L_1=F,\ V_2=0$
	$\phi_1 = 1$ [*F*]	*dew($\bar{y}_1$)*, where $\bar{y}_1$ lies on the line $\bar{z}$-*dew($\bar{z}$)*	$\bar{z}$	$L_1=0,\ V_2=F$
	$\phi_2 = 0$	$\bar{z}$	*bubble(bubble($\bar{z}$))*	$L_1=F,\ V_2=0$
	$\phi_2 = 1$ [*B*]	liquid product of flash with feed $\bar{z}$	vapour product of flash with feed $\bar{z}$	finite

Geometry of boundary candidate curves

A number of features of the geometry of these boundary candidates have been observed and are noted below.

- Curves *B($\bar{x}$)* and *B($\bar{y}$)* are the product loci of a flash with feed $\bar{z}$. Therefore at $\bar{z}$ the tangent to *B($\bar{x}$)* is the line $\bar{z}$–*bubble($\bar{z}$)* and the tangent to *B($\bar{y}$)* at $\bar{z}$

is the line $\bar{z}-\mathit{dew}(\bar{z})$.

- Curves $E(\bar{y})$ and $D(\bar{x})$ are also product loci for a single flash stage and therefore at $\mathit{dew}(\bar{z})$ the tangent to $D(\bar{x})$ is $\bar{z}-\mathit{dew}(\bar{z})$ and at $\mathit{bubble}(\bar{z})$ the tangent to $E(\bar{y})$ is $\bar{z}-\mathit{bubble}(\bar{z})$.
- Curves $A(\bar{x})$ and $A(\bar{y})$ are the total reflux product loci. It is shown below that at $\bar{z}$ the tangent to $A(\bar{x})$ is $\bar{z}-\mathit{bubble}(\mathit{bubble}(\bar{z}))$ and the tangent to $E(\bar{y})$ at $\bar{z}$ is $\bar{z}-\mathit{dew}(\mathit{dew}(\bar{z}))$.
- Curves $D(\bar{x})$ and $F(\bar{x})$ both have $\mathit{dew}(\bar{z})$ and $\mathit{dew}(\mathit{dew}(\bar{z}))$ as end-points. It is shown below that these curves may not intersect. Similarly, $E(\bar{y})$ and $C(\bar{y})$ may not intersect. Which curve is "interior" depends on the system thermodynamics and the feed composition.
- Curve $F(\bar{x})$ is the locus of $\mathit{dew}(\bar{y}_1)$, where $\bar{y}_1$ lies on the straight line between $\bar{z}$ and $\mathit{dew}(\bar{z})$. It appears that at $\mathit{dew}(\bar{z})$, the tangent to $F(\bar{x})$ is equal to the tangent to $B(\bar{x})$. Similarly, at $\mathit{bubble}(\bar{z})$, the tangent to $C(\bar{y})$ appears to be equal to that of curve $D(\bar{y})$.

The geometry of the process requires that $\bar{z}$, $\bar{x}_1$ and $\bar{y}_2$ lie on a straight line (from the overall mass balance) as do $\bar{x}_2$, $\bar{x}_1$ and $\bar{y}_1$; $\bar{z}$, $\bar{y}_1$ and $\bar{z}^*$; $\bar{y}_2$, $\bar{x}_2$ and $\bar{z}^*$. The lengths of the line segments of these straight lines must also satisfy the mass balance. Furthermore, $\bar{x}_1-\bar{y}_1$ and $\bar{x}_2-\bar{y}_2$ are equilibrium pairs. Various iterative calculational methods may be used to find product compositions $\bar{x}_1$ and $\bar{y}_2$ for a given feed of composition $\bar{z}$ and quantity F.

On the total reflux product loci the points $\bar{x}_1$, $\mathit{bubble}(\mathit{bubble}(\bar{x}_1))$ (which is equal to $\bar{y}_2$) and $\bar{z}$ lie on a straight line. Hence:

$$\bar{z} = \alpha\,\bar{x}_1 + (1-\alpha)\,\mathit{bubble}^2(\bar{x}_1) \tag{3.10}$$

where $\mathit{bubble}^2(\bar{z}) = \mathit{bubble}(\mathit{bubble}(\bar{z}))$.

This equation may be differentiated with respect to α to obtain:

$$\frac{d\bar{z}}{d\alpha} = \bar{0} = \bar{x}_1 + \alpha\frac{d\bar{x}_1}{d\alpha} - bubble^2(\bar{x}_1) + (1-\alpha)\frac{d}{d\alpha}(bubble^2(\bar{x}_1)) \tag{3.11}$$

As α approaches unity, and $\bar{x}$ approaches $\bar{z}$, the $\bar{x}_1$ locus is described by:

$$\frac{d\bar{x}_1}{d\alpha}\Big|_{\alpha=1} = bubble^2(\bar{x}_1) - \bar{x}_1 = bubble^2(\bar{z}) - \bar{z} \tag{3.12}$$

Similarly, as α approaches zero, and $\bar{y}_2$ moves towards $\bar{z}$, the $\bar{y}_2$ locus is described by:

$$\frac{d\bar{y}_2}{d\alpha}\Big|_{\alpha=0} = bubble^2(\bar{x}_1) - \bar{x}_1 = \bar{z} - dew(dew(\bar{z})) \tag{3.13}$$

that is, the $\bar{x}_1$ and $\bar{y}_2$ loci near $\bar{z}$ have tangents *bubble(bubble*$(\bar{z})$*))*$-\bar{z}$ and *dew(dew*$(\bar{z})$*))*$-\bar{z}$ respectively.

Another property of the boundary candidates is that curves $D(\bar{x})$ and $F(\bar{x})$ may not intersect. The justification for this statement follows:

$D(\bar{x})$ is the liquid product of a feed of composition *dew*$(\bar{z})$. The locus of bubble-point compositions of points lying on $D(\bar{x})$, which shall be denoted by $D(\bar{y})$, may also be constructed. The curves $D(\bar{x})$ and $D(\bar{y})$ are the product loci of a flash with feed *dew*$(\bar{z})$. The curve $F(\bar{x})$ is the locus of the dew-point compositions of points lying on the line $\bar{z}$*−dew*$(\bar{z})$. If curves $D(\bar{x})$ and $F(\bar{x})$ intersect, and the line $\bar{z}$*−dew*$(\bar{z})$ and the curve $D(\bar{y})$ do not intersect, then this implies that the liquid of composition $\bar{x}_1$ has in equilibrium with it vapours of compositions $\bar{y}_1$ (on $D(\bar{y})$) and $\bar{y}_2$ on the line $\bar{z}$*−dew*$(\bar{z})$, which is not possible. But the line $\bar{z}$*−dew*$(\bar{z})$ and the vapour locus $D(\bar{y})$ may not intersect, without $D(\bar{y})$ containing concavities, and these are not possible, as discussed in Section 3.3.1. An analogous argument may be constructed to show that the loci $C(\bar{y})$ and $E(\bar{y})$ do not intersect.

Conclusions: Feasible products of two refluxed flash stages

Fig. 3.21 illustrates the extremal product loci for the refluxed configuration of two flash stages. The region of feasible products, when forward mixing is considered, contains straight lines representing the mixing of feasible $\overline{x}_1-\overline{y}_2$ product pairs. For the case illustrated in Fig. 3.21, the outermost mixing lines are those joining $\overline{z}$ and *dew(dew($\overline{z}$))* and joining $\overline{z}$ and *bubble(bubble($\overline{z}$))*. The total reflux arc pair (curve *A*) forms the other boundary of the region. The other "boundary candidate" curves (curves *B* to *F*) all lie within the product region, as do all the other mixing lines.

In the case shown in Fig. 3.22, in which a different feed composition is used, part of the *F($\overline{x}$)* and *D($\overline{x}$)* product loci lie beyond the mixing line $\overline{z}-$*dew(dew($\overline{z}$))*. The vapour co-product for both these loci has the same composition and quantity as the feed. The product region may be extended by mixing between $\overline{z}$ and the extreme liquid product of composition $\overline{p}$ on *D($\overline{x}$)*. At $\overline{p}$, the tangent to the *F($\overline{x}$)* locus and the mixing line $\overline{p}-\overline{z}$ (which is not shown) are collinear. Since the liquid products represented by *F($\overline{x}$)* are of zero quantity, so are the products on the line $\overline{p}-\overline{z}$. Whether the mixing lines $\overline{z}-$*dew(dew($\overline{z}$))* and $\overline{z}-$*bubble(bubble($\overline{z}$))* form boundaries to the product region would appear to depend on the curvature in that vicinity. It appears that the total reflux product locus is always a boundary to the product region of this process, and that the other boundaries are formed by mixing lines and the boundary candidates presented in Table 3.2, or portions of these curves and mixing lines.

In the process comprised of two refluxed flash stages, only external products — streams which enter or leave the process as a whole — are considered feasible. For example, for some feasible liquid-product composition, $\overline{x}_1$, the equilibrium vapour stream of composition $\overline{y}_1$ may lie outside the region of feasible products. A stream of this composition cannot be removed from within the process, since the composition $\overline{y}_1$ is only attainable because none of that stream has been removed. Fig. 3.23 shows a set of $\overline{y}_1$ compositions which may occur under total reflux conditions, part of which lies outside the region of feasible products. Van Dongen and Doherty (1985b) also showed how compositions may be achieved within a distillation column which lie outside the feasible product region for that column.

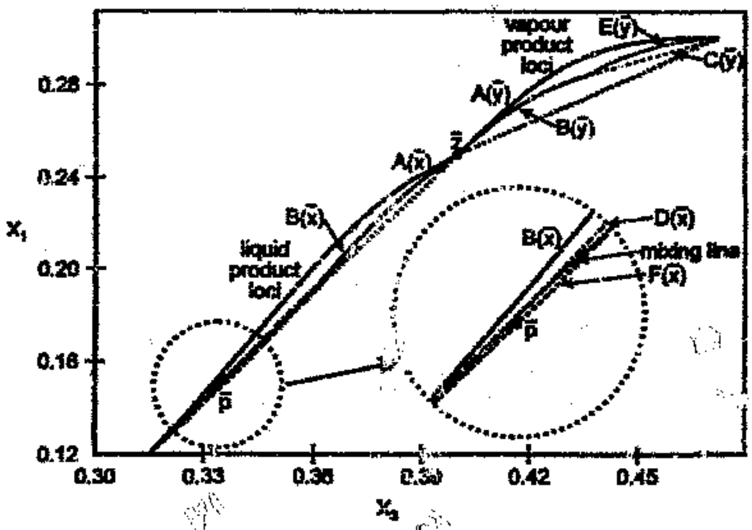


Fig. 3.22 Product region and boundary candidates for two refluxed flash stages and mixing. $\bar{z}$: (0.25, 0.35, 0.4).

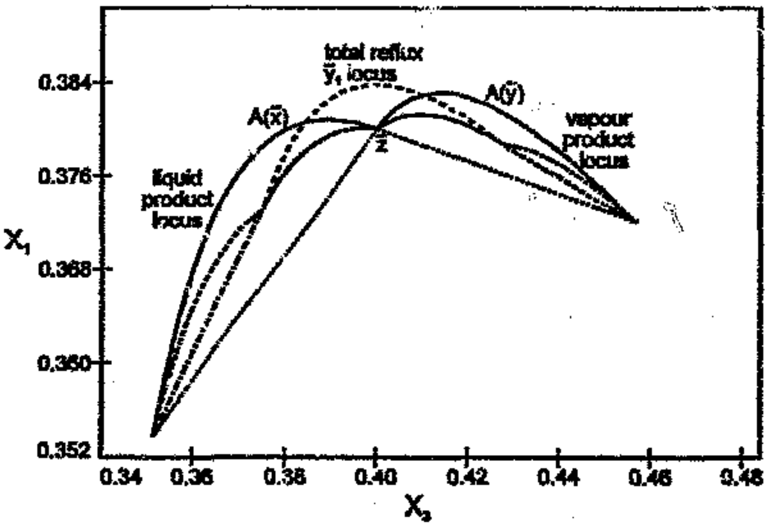


Fig. 3.23 The compositions of internal streams may lie outside the region of feasible products of two refluxed flash stages. $\bar{z}$: (0.38, 0.22, 0.4).

Points on the mixing lines $\bar{z}$–*dew(dew($\bar{z}$))* and $\bar{z}$–*bubble(bubble($\bar{z}$))* are all associated with zero-quantity products, since the co-product from these processes is identical to the feed. Points on the total reflux product arcs represent zero-quantity products, since, at total reflux, the feed flow rate is effectively zero. Therefore all the boundaries of the product region represent impractical solutions: in order to achieve finite amounts of product, infinite amounts of feed, infinite equipment sizes, and an infinite amount of heating or condensing would be required. Once again, composition space is found to produce answers of limited applicability.

The "two-stage distillation column"

The refluxed arrangement of two flash stages is effectively a two-stage distillation column, or a distillation column containing only a partial reboiler, partial condenser and a feed stream. Since this process is less complex than the column distillation process, it is relatively easy to determine the region of feasible products.

The conditions of total reflux were found to give rise to the boundary of the region of feasible products by Stichlmair *et al.* (1989) and Koehler *et al.* (1991). Wahnschafft *et al.* (1992) found that the boundaries are associated with feed pinch point curves, and therefore reversible operation of the distillation column.

Similarly, for the "two-stage column", total reflux conditions appear to give rise to a boundary of the product region. Conditions similar to those of reversible operation occur when the compositions of the passing streams, $\bar{x}_2$ and $\bar{y}_1$ are an equilibrium pair. Therefore no further separation takes place in one of the flash stages and the locus of feasible products is the curve *B*, which is the product locus of a single flash stage. In Section 6.4.4 it is shown that conditions of zero reflux are found to form a boundary to column profile regions. Zero reflux, which is taken to be the case where the flow rate of the stream which is returned to the feed stage is zero, gives rise to the same product locus, curve *B*. Curve *B* is a boundary candidate to the product region for two refluxed flash stages. The other boundary candidates, curves *C* to *F*, do not appear to correspond to limits of the column distillation process.

Like the boundaries of the product region for distillation, all the boundary candidates are associated with the limiting conditions of zero-quantity feed (at total reflux) or a zero-quantity product (when the co-product is identical to the feed). Therefore, one would expect costs to be infinite on the boundaries of the region of feasible products for both the two refluxed flash stages and a distillation column.

It is difficult to make a meaningful extrapolation of the results of the two-stage distillation column to distillation columns generally. The mixing lines between $\bar{z}$, the feed composition, and *dew(dew(*$\bar{z}$*))* and *bubble(bubble(*$\bar{z}$*)* may or may not intersect the boundary candidates, but it is not clear under what conditions this will take place. It is not yet possible to infer the rules for the boundary of a two-stage distillation column. Clearly, distillation is a complex process, which may not be described well by simple rules.

3.3.5 Feasible products of two flash stages: Comparisons and conclusions

The regions of feasible products for three different configurations of two flash stages have been determined, and are illustrated, for a particular feed composition and thermodynamic system, in Fig. 3.13(d), 3.17(c), and 3.21. The three product regions are superimposed in Fig. 3.24, which permits their comparison.

When two flash units are arranged in parallel, the region obtained (the white region containing E, F and G) is convex. Both zero-volume and finite-quantity solutions are found on the boundary. The span of the product region is from *dew(*$\bar{z}$*)* (at E) to *bubble(*$\bar{z}$*)* (at G). For two flash units arranged in series, the span of the product region (the region of dark shading) is *dew(dew(*$\bar{z}$*))* (at A) to *bubble(bubble(*$\bar{z}$*))* (at D). The region is not convex, and the boundary contains both zero-volume ($A-E-D$) and finite-volume ($A-B-C-D$) solutions. For the refluxed configuration of two flash stages, the span of the product region is also *dew(dew(*$\bar{z}$*))* to *bubble(bubble(*$\bar{z}$*))*. The region (which is lightly shaded) is not convex, and the boundaries are in all cases zero-quantity solutions, as was shown in Fig. 3.23. The boundaries $A-H-B-F$ and $F-C-J-D$ are obtained under conditions of total reflux. Internal flows may have compositions which lie outside the product region.

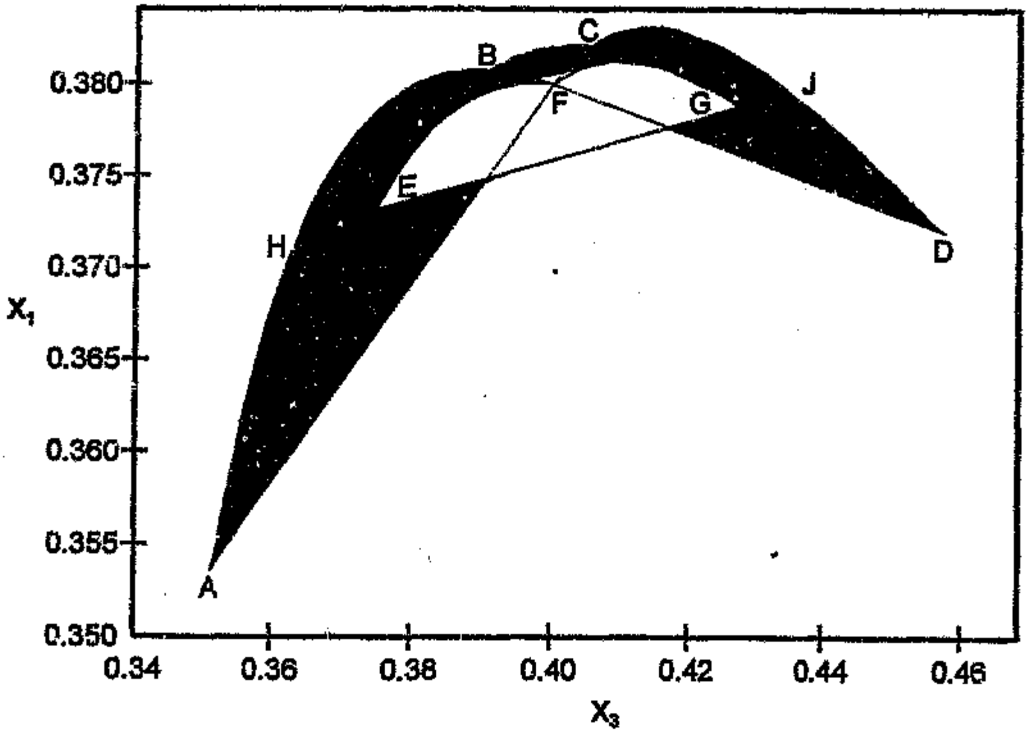


Fig. 3.24 The product regions for two flash stages arranged in parallel (white), in series (dark shading) and in series with reflux (light shading). $\overline{z}$: (0.38, 0.22, 0.4).

When these three product regions are compared, it is found that all the products for the configuration of two flash units in parallel may be obtained by serial arrangement of two flash units. However, the regions for two flash units in series and two flash units in parallel do not completely contain the region for two flash units with reflux, nor *vice versa*. When using two flash stages in series or in parallel, it is possible to obtain some products (in the region of *B*, *C* and *F*) which cannot be obtained using reflux. Similarly, the refluxed process can achieve some products near the boundaries *A*−*H*−*B* and *C*−*J*−*D* which cannot be obtained without reflux. Some products which can be achieved by both two stages in series and two stages with reflux (for example between *B* and *F* and between *C* and *F*) use finite flows in the first configuration and total reflux in the second configuration. This implies that, by the first method, the costs are finite and, by the second, in order to obtain a finite product flow, costs are infinite. Although cost has not been studied here, it can be seen that the serial configuration may be more cost-effective than the refluxed configuration.

These findings are not complete and it is not yet possible to develop rules concerning feasible products for any number of equilibrium-stage processes and any number of components. However, it is interesting to note that the distillation-column-like process does not always surpass other configurations of two equilibrium flash stages. In the literature, the product regions of distillation columns are generally investigated. Perhaps there is an implicit assumption that distillation columns are better than any other VLE separation unit. The results presented here lead one to question the automatic choice of column distillation for separation processes. A more flexible approach, in which the type of equipment to be used is not specified, may allow product regions to be extended. Furthermore, costs may be reduced by using configurations other than distillation columns.

3.4 Conclusions

The feasible product region for simple distillation, simple condensation and forward mixing has been investigated. It is found that, for these processes, the feasible product region is the entire composition space. Constrained separation processes, comprised of one or two equilibrium flash stages and mixing, have been presented. Although the study is limited to two-flash configurations, a surprising result emerges. A distillation-column-like configuration may be less than optimal, both in terms of attainable products and in terms of the cost of obtaining that product. It appears that it would be beneficial to use a flexible approach in the synthesis of separation processes and not limit the equipment used to distillation columns.

As with previous investigations of feasible product regions in the literature, many of the extremal products are of zero quantity and will never be optimal solutions. Objective functions can never be functions of product and feed compositions only, since infinite flow rates, equipment sizes and heating requirements must be accounted for. It is clearly necessary to formulate separation problems in terms of process variables which are relevant to the objective function. A pair of such variables will be developed in Chapter 5.

Chapter 4

Review of the Literature on Process Synthesis and Separation Process Optimization

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4.1 Introduction

It is the objective of process synthesis to generate process flowsheets which can achieve the required product flows and to find from the set of all feasible flowsheets those flowsheets which are cost-effective. In this chapter, some of the literature pertaining to process synthesis and optimization is examined, with particular attention to the optimization of the separation component of the process.

4.2 Process synthesis

4.2.1 Objectives of process synthesis

The object of process synthesis is the preliminary design of a feasible and cost-effective process to obtain a certain product from some given feedstock. This preliminary design includes selecting the optimal type and design of processing units and selecting the best interconnections between these units. A large number of alternative processes may be able to meet the process requirements, and generally the information which is available is incomplete (Nishida *et al.*, 1981). Usually, a set of feasible alternative processes is assessed and the unattractive alternatives are discarded. This preliminary screening process need not be rigorous (Linnhoff *et al.*, 1983; Fisher *et al.*, 1985a; Malone *et al.*, 1985). More detailed calculations are carried out as the design process progresses.

4.2.2 Criteria for process screening

The feasible process alternatives are assessed according to some criteria. The total annual cost (TAC) of the process is frequently used as the basis for comparison. Other criteria used are total annual profit (Mizsey and Fonyo, 1990) or product recovery (Fisher *et al.*, 1985b; Yamada *et al.*, 1987). This work focuses on the TAC of the process.

Alternative processes may be meaningfully compared at their optimum operation, that is, using the operating parameters which minimize the objective function, and not at some arbitrary set of operating conditions (Knight and Doherty, 1989). Tedder and Rudd (1978a) found that, at their optimum operating conditions, alternative designs of distillation sequences tend to have the same utility requirements, so costs vary only due to different equipment costs.

Calculating the TAC of a process includes calculating, in detail, the capital investment requirements of the process. To do this requires a detailed knowledge of the process, but in the early stages of process design, these details are not known. A detailed costing of the process is therefore neither possible nor appropriate to the process screening stage, and is also time-consuming. Instead, it is common practice to use an objective function which correlates well with the TAC of the process for comparing various process alternatives.

4.2.3 Interactions between units

Processes will generally be comprised of a number of different units, for example, a reactor, a separation sequence and heat exchangers. The interactions between the separation sequence and the reactor, between the reactor and the heat-exchange network, and between the separators and heat exchangers may be significant (Douglas, 1988; Novak *et al.*, 1994). In particular, in a reactor-separator network, there are interactions between the conversion achieved in the reactor and the load on the separation process (Mizsey and Fonyo, 1990). Therefore the whole process, rather than just the constituent units, must be optimized. However, it is computationally very demanding to optimize a whole process, as has been illustrated for a simple reactor-separation system by Kokossis and Floudas (1990). Therefore the optimization of individual separation units, or a sequence of distillation columns, still receives much attention.

It is necessary to optimize a process or unit in order to make comparisons to fulfil the process synthesis objectives. In this review, the optimization of individual distillation columns in particular is examined.

4.3 Separation process optimization

4.3.1 Criteria for comparison of flowsheet alternatives

Researchers have used a range of different criteria upon which to compare individual distillation columns or sequences of distillation columns. Some of these are presented in Table 4.1. Many of the cases presented in Table 4.1 (Cases *a-m*) incorporate both the capital and operating costs of the units. The operating costs arise from the utility requirements of the process, usually steam and cooling water or refrigerants.

Modi and Westerberg (1992, case *n*) investigated three different cost criteria, including the TAC, and energy requirements only, for which there is no cost penalty associated with infinitely many stages in a column, and minimum energy requirements, which is the same criterion as was used in cases *r* and *s*. Petlyuk *et al.* (1965, case *o*) aimed to maximize the thermodynamic efficiency of the process, so the objective functions which they used considered only energy expenditure and work of separation in order to compare column alternatives, and did not consider capital costs. For Fonyo (1974, case *p*), similarly, the goal was to minimize production of entropy, while considering also such issues as capital costs, product composition and operating flexibility. Flower and Jackson (1964, case *q*) focused on utility costs and costs of heat pumping, heat exchange and compressing equipment, rather than the column capital cost.

Table 4.1 The cost criteria used in the literature for separation processes.

Case	Authors	Cost criteria
a	McCabe and Smith (1956)	Capital costs and energy costs
b	Nishimura and Hiraizumi (1971)	
c	Doukas and Luyben (1978)	
d	Tedder and Rudd (1978b)	
e	Fisher *et al.* (1985a)	
f	Malone *et al.* (1985)	
g	Ho and Keller (1987)	
h	Fair (1987)	
i	Douglas (1988)	
j	Cheng and Liu (1988)	
k	Knight and Doherty (1989)	
l	Dhole and Linnhoff (1993)	
m	Malek and Glavic (1994)	
n	Modi and Westerberg (1992)	Capital and energy costs *or* energy costs *or* minimum energy costs.
o	Petlyuk *et al.* (1965)	Energy required; work of separation
p	Fonyo (1974)	Minimize entropy and consider capital costs.
q	Flower and Jackson (1964)	Total energy costs, heat pumping and compression costs.
r	Koehler *et al.* (1991)	Minimum energy costs.
s	Fidkowski and Krolikowski (1990)	
t	Lucia and Kumar (1988)	Energy costs and internal flows of certain components.
u	Fisher *et al.* (1985b)	Product loss and column cost.
v	Yamada *et al.* (1987)	Maximize recovery of products.

Koehler *et al.* (1991, case *r*) and Fidkowski and Krolikowski (1990, case *s*) asserted that only minimum energy cost is a significant optimization criterion. This criterion is not adequate because it does not allow one to optimize columns with respect to reflux ratio. The cost criteria used by Lucia and Kumar (1988, case *i*) were condenser and reboiler heat duties and flow rates of light or heavy key compounds in the column. These criteria apparently consider utility requirements and column diameter only. Fisher *et al.* (1985b, case *ii*) incorporated the product composition into their cost function, as well as tray costs in either the rectifying or stripping section of the column. They assumed that the product composition is approximately independent of internal flow rates, and therefore excluded energy costs from the objective function. Yamada *et al.* (1987, case *v*) considered only product compositions in order to assess column performance.

4.3.2 Capital and operating costs of distillation columns

Many researchers have worked on the assumption that utility costs dominate the TAC (see, for example, Fidkowski and Krolikowski, 1990 and Koehler *et al.*, 1991). Others, including Flower and Jackson (1964), Ho and Keller (1987), Fair (1987), and Dhole and Linnhoff (1993), while acknowledging the impact of capital cost on overall process costs, tended to focus on the energy requirements of columns to be optimized.

Doukas and Luyben (1978) attempted to quantify the relative contribution of capital and operating costs to a sequence of distillation columns and found that energy costs dominated the total process cost. Only 10 to 20 % of the TAC calculated was due to fixed costs of equipment; this amount included heat exchange equipment and column costs. A number of different cases, including a range of mixtures, feed compositions and column sequences, were studied in detail, but the effect of reflux ratio on process costs was not explored.

On the other hand, Ho and Keller (1987) illustrated a case in which the capital costs of the process amounted to 47% of the total process costs. When the capital costs for steam production were included, capital costs amounted to 80% of the TAC. In this work, it is assumed that both capital costs and operating costs contribute significantly to the TAC of a process.

Tedder and Rudd (1978a) examined and optimized a number of column configurations and found that their results corresponded closely with some other researchers' results. They concluded that "the economic differences between designs are relatively insensitive to the underlying, common price structure and the form of the objective function, so long as operating costs and capital investment requirements are both considered".

4.3.3 Objective functions for distillation processes

A number of objective functions and column cost functions have been used which incorporate both capital and operating costs of a distillation column. Some of these functions are presented in Table 4.2. The costs functions are all presented in terms of the internal vapour flow rate in the column, V, and the number of stages in the column, N. In Appendix A, the original forms of the cost functions proposed are transformed into the forms presented in Table 4.2.

Table 4.2 Form of cost functions for TAC (C) or column cost (C_{col}) expressed in terms of number of theoretical stages, N, and vapour flow rate, V. (dia = diameter). Transformations of the original expressions are derived in Appendix A.

Authors	**Form of cost function or objective function used.**
Colburn (1936, cited by Malone *et al.*, 1985)	$C = a + bNV + cV$; ($dia \propto V^{1/2}$)
McCabe and Smith (1956)	$C_{col} \propto NV$; $dia \propto V^{1/2}$
Nishimura and Hiraizumi (1971)	$C \propto [aN + b]\, V$; $dia \propto V^{1/2}$
Malone *et al.* (1985)	$C \propto aN^{0.82}V^{0.53} + bV^{0.65} + cV$ or $C = a + bN + cV$; $dia \propto V^{1/2}$
Fisher *et al.* (1985a)	$C = aN^{0.802}V^{0.53} + bV^{0.65} + cV$; $dia \propto V^{1/2}$
Cheng and Liu (1988)	$C = [aN + b]\, V^{1.13} + cV^{0.65} + dV$; $dia \propto V$
Knight and Doherty (1989)	$C = aV^{0.27}N^{0.82} + bV^{0.39}N + cV^{0.65} + dV$; $dia \propto V^{1/2}$; column height $\propto N$
Remer and Chai (1990)	$C_{col} \propto V^{0.35}N$ or $V^{1/2}N^{0.7}$; $dia \propto V^{1/2}$; height $\propto N$

The cost functions presented in Table 4.2 are based on empirical correlations (such as Guthrie, 1969) or on more theoretical considerations (for example, Nishimura and Hiraizumi, 1971). The constants *a, b, c, etc.* of Table 4.2 are explicitly related to process costs, including some of the following: specific steam costs, inflation, pay-back period, heat transfer coefficients of heat exchangers, tray efficiencies, liquid density, materials of construction and heats of vaporization.

The column diameter and the internal vapour flow rate of the column are clearly related. A number of different relationships are assumed in Table 4.2. While McCabe and Smith (1956), Nishimura and Hiraizumi (1971), Malone *et al.* (1985) and Fisher *et al.* (1985a) take the column diameter to be proportional to the square root of the vapour flow rate, Cheng and Liu (1988) assume direct proportionality between the diameter and vapour flow rate, and the derivation of Knight and Doherty (1989) implies that the diameter is proportional to $V^{1/4}$, as shown in Appendix A.

4.3.4 Rank order functions for distillation processes

Tedder and Rudd (1978b) assessed a number of functions against a particular cost function (which they did not give). The success of the function, or rank order function, is its ability to rank in the correct order the costs of a number of similar distillation columns in a limited range of column configurations. These rank order functions are presented in Table 4.3 in decreasing order of this ability. Most of these functions are comprised of the minimum vapour flow rate, the minimum number of stages and the temperature drop across the column. These functions cannot be used to compare columns using different reflux ratios for the same product specifications.

The minimum vapour flow rate in a column is found to perform fourth best of the rank order functions, and Tedder and Rudd (1978b) therefore concluded that the minimum vapour flow rate, which is closely related to the minimum energy requirements of the process, is a satisfactory objective function for assessing distillation columns.

The constants and power indices of the second, third and fifth functions appearing in Table 4.3 are not discussed by Tedder and Rudd (1978b). Presumably they are best-fit empirical constants, unlike the constants of Table 4.2 which are explicitly linked to process costs. It is not clear whether these functions are still applicable, since the assumptions about pay-back period, utility costs, *etc.*, are not made explicit.

Table 4.3 Objective functions presented in order of decreasing ability to rank costs of alternative column sequences. (Tedder and Rudd, 1978b)

Objective function	**Rank**
$V_m^{0.648} N_m^{0.184} \delta T^{0.144}$	1
$90.22 V_m + 153.9 N_m + 344.2 \delta T$	2
$107.7 V_m + 203.3 \delta T$	3
V_m	4
$88.34 V_m + 912.1 N_m$	5
$0.2996\ CAP_j + 0.52\ OP_j$	6
$V_m N_m \delta T$	7
$V_m N_m$	8
Feed rate/boiling-point difference of components to be separated	9
$V_m \delta T$	10

V_m: minimum vapour flow rate in the rectifying section; N_m: minimum number of stages; δT: temperature drop across column. CAP_j, capital cost, OP_j, operating cost, using V_m and theoretical number of trays.

4.3.5 Time and place constraints of cost functions

The actual costs predicted by a cost function change with time (Remer and Chai, 1990), not only due to inflation, but also due to non-uniformity in inflation. For example, rising energy costs and relatively stable capital costs need to be reflected in the cost function. Similarly, different locations or countries will be subjected to quite different utility costs, labour costs, investment costs, transport costs, insurance costs, *etc.* (Plasvic, 1993). Pay-back period is affected by both the location of the process and the time at which the process was evaluated, and strongly influences the capital cost portion of the process costs.

4.4 Heuristic rules for the optimization of distillation processes

A large amount of research has gone into developing heuristics for optimizing individual distillation columns and sequences of columns. The work which concerns itself with sequences of columns will not be discussed here. Other work has focused on finding optimal operating conditions for an individual column with specified feed and product compositions. The most important operating parameters include the internal reflux ratio and the column pressure.

4.4.1 Optimum column pressure

A study by Tedder and Rudd (1978b) found that the column operating pressure is an important optimization variable. The optimum pressure was found to vary widely from feed to feed, and the total process cost was found to be particularly sensitive to low pressures where refrigerants were required.

4.4.2 Optimum reflux ratio

In binary distillation, it is well known that as the reflux ratio increases, for a given product pair, the number of stages required decreases from infinitely many at the minimum reflux ratio, to a minimum number of stages at infinite reflux. As the reflux ratio increases, the utility requirements of the column increase from a minimum value, as do the utility capital costs and the diameter of the column. As the number of stages decreases, the cost of the column decreases. These two effects result in a minimum in the overall cost curve; the corresponding reflux ratio is the optimum reflux ratio.

The value of the optimum reflux ratio has been found empirically to lie in the range

1.03 to 1.3 times the minimum reflux ratio, R_{min}. This heuristic, which is often taken as 1.2 times the minimum reflux ratio, has become widely accepted. It may not be applicable, for example, to heat integrated columns, where a different reflux ratio may lead to greater cost-saving opportunities than would the heuristically determined optimum reflux ratio (Linnhoff et al., 1983) precisely because of the interactions between processing units. It would also not be applicable to processes where the minimum reflux ratio is zero or less than zero. Such processes are easiest to visualize using a McCabe-Thiele construction, where, for example, the operating line of the rectification section at minimum reflux is horizontal or has a negative slope.

It would appear that the total process cost has a relatively flat optimum with respect to the reflux ratio (McCabe and Smith, 1956; Linnhoff *et al.*, 1983). Knight and Doherty (1989) found that the TAC was relatively insensitive to the reflux ratio for the ternary case they studied. They concluded that it is sufficient to use the heuristic reflux ratio of 1.2 times the minimum reflux ratio. However, Tedder and Rudd (1978b) illustrated a case in which the utility costs are relatively expensive, and the TAC is quite sensitive to the reflux ratio, indicating that it is important to optimize with respect to the reflux ratio, and not merely rely on the optimum reflux ratio heuristic.

A number of researchers studied ternary distillation processes and optimized them with respect to reflux ratio, using one of the objective functions presented in Table 4.2. The values of the ratio of the optimum reflux ratio to the minimum reflux ratio evaluated by these researchers are presented in Table 4.4. These results show that the heuristic that the optimum reflux ratio is 1.03 to 1.3 times the minimum reflux ratio still applies to the ternary systems studied.

These researchers did not all use the same objective functions. In particular, Fisher *et al.* (1985a) used a different criterion for optimization from Fisher *et al.* (1985b) as shown in Table 4.1 for cases *e* and *u*. The results of Table 4.4 indicate that the optimum reflux ratio is not very sensitive to the objective function used, which is essentially the conclusion reached by Tedder and Rudd (1978a).

Table 4.4 Optimum ratios of reflux ratio to minimum reflux ratio evaluated for ternary distillation processes.

Authors	Case*	Optimization criteria	R_{opt}/R_{min} evaluated
Doukas and Luyben (1978)	*c*	Capital and Energy costs	1.1
Tedder and Rudd (1978b)	*d*	"	1.03-1.11
Fisher *et al.* (1985a)	*c*	"	1.07, 1.09
Fisher *et al.* (1985b)	*u*	Columns costs and product loss	1.29

* See Table 4.1.

However, ternary distillation processes exhibit behaviour which is quite different to that of binary distillation processes (Laroche *et al.*, 1992a; Fien and Liu, 1994). For example, even for an ideal mixture of hexane, heptane and nonane, for which relative volatilities are assumed constant, the minimum reflux ratio may actually decrease as the purity of the distillate increases (Levy *et al.*, 1985). Similarly, for a fixed reflux ratio, increasing the number of stages does not always increase product separation (Laroche *et al.*, 1992a). The phenomenon of maximum reflux ratio (Fien and Liu, 1994) which occurs in ternary distillation processes also implies that the relationship between reflux ratio and number of stages required is different to that for binary distillation processes. How the TAC function changes with reflux ratio and product purity may therefore be quite different for binary and ternary distillation processes.

4.5 Conclusions

A process synthesis exercise requires the optimization of individual columns and sequences of columns. A range of optimization criteria have been adopted in the literature. The most commonly used criterion is to minimize the sum of the capital investment requirements and the utility costs of the process; that is, the total annual cost of the process.

A number of cost functions have been presented for calculating the TAC of distillation processes. These functions are based on various empirical correlations or theoretical relationships. The operating pressure is an important operating parameter for distillation optimization where refrigerants are used for the cooling utility. The most important optimization variable is the internal reflux ratio in the column.

The heuristic rule specifying that the optimum reflux ratio is 1.03 to 1.3 times the minimum reflux ratio is well established for binary distillation processes. It has been confirmed for a number of ternary separation processes. The TAC is found to vary relatively little in the region of the optimum reflux ratio. However, a case was reported by Tedder and Rudd (1978b) in which the TAC was relatively sensitive to the reflux ratio. Because of the difference between distillation column behaviour for binary and ternary mixtures, it is not clear that the heuristic rule for the optimum reflux ratio is always applicable to multicomponent systems.

The subject of optimization of separation processes has been dealt with extensively for distillation columns. Research into the optimization of other VLE separation alternatives is not known to have been conducted. The objective functions for the optimization of distillation columns are specific to distillation processes, and cannot be meaningfully extrapolated to other VLE separation processes. There is thus no simple procedure available for the comparison of a broad range of VLE separation processes.

Chapter 5

Introducing the Capacity Variables

5.1 Introduction

It is clear from the work presented in Chapter 3 that composition space alone cannot be used for comparing alternative VLE separation sequences in process synthesis exercises. A product of a certain composition may be obtained through a number of different equipment configurations, but the cost effectiveness of the various options may differ widely. It is necessary to have a cost indicator which will allow the selection of economically attractive flowsheet configurations. At the flowsheet generation stage, it should not be necessary to conduct full cost estimates on the various alternatives.

The criteria for this cost indicator are that it should:

- incorporate both capital and operating costs
- consider both boiling and condensing requirements
- be applicable to a wide range of VLE separation equipment.

Both capital and operating costs should be considered, since both of these have been shown to contribute significantly to the total annual costs of a separation process. There are utility and equipment costs associated with both vaporization and condensation, so the cost of both these processes should be incorporated by the cost indicator. Distillation columns are widely used for VLE separation processes; they are not the only possible equipment, and it should be possible to consider various alternatives when generating a flowsheet. A common basis from which to compare the alternatives is therefore needed.

In this chapter a pair of cost indicators has been defined, one related to vaporization and one related to condensation. These cost indicators have been called *capacity variables*. A boiling capacity variable and a condensing capacity variable are defined in Section 5.2. These capacity variables are associated with particular streams within a process, of which there may be many. In Section 5.3 the definition is extended and a pair of *overall capacity variables* are defined; these serve as cost indicators for an entire process. The definitions are applied to a wide range of VLE separation processes in Section 5.4. The results are summarized and the conclusions to this chapter are presented in Section 5.5.

5.2 Definition and linear mixing property of capacity variables

5.2.1 Definition of capacity variables

The boiling capacity, κ, is defined for an equilibrium stage in the following way:

$$\kappa = \kappa_{feed} + \frac{\text{molar amount of vapour produced in equilibrium stage}}{\text{molar amount fed to equilibrium stage}} \tag{5.1}$$

The condensing capacity, λ, is defined for an equilibrium stage in an analogous manner:

$$\lambda = \lambda_{feed} + \frac{\text{molar amount of liquid produced in equilibrium stage}}{\text{molar amount fed to equilibrium stage}} \tag{5.2}$$

For a steady-state process, the right-hand term is the ratio of the molar rate of vaporization (or condensation) in the equilibrium stage to the molar feed flow rate to the stage, irrespective of the phase of the feed.

Each stream is associated with a capacity pair. In particular, the feed stream to a stage is associated with the capacity pair (κ_{feed}, λ_{feed}). Any streams leaving a particular equilibrium stage are associated with an identical capacity pair. (There are two streams, the equilibrium vapour and liquid product, leaving an equilibrium stage.) The feed capacity terms, κ_{feed} and λ_{feed}, accommodate feed streams which are products from another part of the process. The capacity variables thus provide a cumulative measure of the amount of vaporization and condensation experienced upstream in the process.

5.2.2 Extension to non-steady state processes

Eqs. (5.1) and (5.2) define the capacity variables for steady-state (flow) processes. These definitions may be extended to non-steady state processes by defining suitably the concept of an equilibrium stage and the following terms: κ_{feed}, λ_{feed}, the "amount of liquid (or vapour) produced", and the "amount fed" to the stage.

During a differential time-slice, the vapour and liquid phases are in equilibrium. An "equilibrium stage" is taken to be the process over a differential time period, Δt. The nett "feed" to the stage is the amount of material in the process at the start of the time period being considered, as well as any material added to the process during that time period. The feed capacity pair, (κ_{feed}, λ_{feed}), is the capacity pair associated with the nett feed to the process. The product capacity pair is associated with the material in the process at time $t + \Delta t$ and with any material leaving during the time period Δt.

The amount of liquid (or vapour) produced may be taken alternately as the amount of liquid (or vapour) *leaving* the process during Δt, or as the amount of liquid (or vapour, respectively) *in the process* at the end of the time period under consideration.

The definitions of eq. (5.1) and (5.2) may thus be extended to non-steady state processes in terms of quantities leaving the process:

$$\kappa = \kappa_{feed} + \frac{\text{moles of vapour leaving during } \Delta t}{\text{nett molar amount fed to equilibrium stage}} \qquad (5.1a)$$

$$\lambda = \lambda_{feed} + \frac{\text{moles of liquid leaving during } \Delta t}{\text{nett molar amount fed to equilibrium stage}} \qquad (5.2a)$$

In terms of quantities "produced" (*i.e.*, in the process at the end of a differential time period), the definitions of κ and λ extend to the following, for non-steady state processes:

$$\kappa = \kappa_{feed} + \frac{\text{moles of vapour produced during } \Delta t}{\text{nett molar amount fed to equilibrium stage}} \qquad (5.1b)$$

$$\lambda = \lambda_{feed} + \frac{\text{moles of liquid produced during } \Delta t}{\text{nett molar amount fed to equilibrium stage}} \qquad (5.2b)$$

These two interpretations of the amounts of vapour and liquid produced give rise to quite different results, as discussed in Section 5.4.1 and Section B.1.1 of Appendix B. Only results arising from eqs. (5.1a) and (5.2a) are presented in this chapter.

5.2.3 Linear mixing of capacity variables

The capacity variables obey the linear mixing rule. For example, if two streams, of flow rates F_1 and F_2 and boiling capacities κ_1 and κ_2 respectively, are mixed, the mixed stream will have flow rate $F_1 + F_2$ and capacity κ^*, where:

$$\kappa^* = \frac{F_1}{F_1+F_2}\kappa_1 + \frac{F_2}{F_1+F_2}\kappa_2 \qquad (5.3)$$

that is:

$$\kappa^* = \alpha\,\kappa_1 + (1 - \alpha)\,\kappa_2 \qquad (5.4)$$

where $0 \leq \alpha \leq 1$, since $\alpha = F_1/(F_1 + F_2)$.

5.3 Definition of the overall capacity variables of a process

A separation process may be comprised of any number of equilibrium stages, each of which has two product streams. The process therefore may have several output streams, each of which is associated with a pair of capacity variables. It is useful to characterize a process comprised of N product streams by the overall boiling capacity of the process, κ_{ov}, and the overall condensing capacity of the process, λ_{ov}, which are defined as follows:

$$\kappa_{ov} = \frac{\sum_{i=1}^{N} F_i \kappa_i}{\sum_{i=1}^{N} F_i} \tag{5.5}$$

$$\lambda_{ov} = \frac{\sum_{i=1}^{N} F_i \lambda_i}{\sum_{i=1}^{N} F_i} \tag{5.6}$$

where the i^{th} product stream is of flow rate F_i and associated with capacity pair (κ_i, λ_i).

The process then has a single capacity pair associated with it: (κ_{ov}, λ_{ov}). It is convenient to talk about the change in overall capacity of a process, which is simply the difference between the value of the capacity of the input (feed) stream and the capacity of the process, namely, $\kappa_{ov} - \kappa_{feed}$ and $\lambda_{ov} - \lambda_{feed}$.

5.4 Application of the definitions of capacity variables to VLE separation processes

In this section the definitions of the capacity variables will be applied to a range of simple VLE separation processes. The definitions of capacity and overall capacity, the linear mixing rule and the process mass balance are combined to obtain the results which follow. Results for non-steady state processes are presented in Sections 5.4.1 to 5.4.4 using only the definitions of κ and λ given by eq. (5.1a) and (5.2a). These derivations are included in some detail in Appendix B; the results are presented below with little explanation. The focus of this section is on the overall capacity of the processes considered.

5.4.1 Simple distillation

In this process, a liquid, of initial quantity L_o, and associated with capacity pair (κ_o, λ_o), is gradually boiled. The vapour, which is in equilibrium with the liquid, is removed as it is formed. After some time, the quantity of liquid remaining in the still is L and the capacity pair of the residual liquid is (κ, λ). The vapour which is removed is accumulated to form a vapour product of quantity V^*, associated with capacity pair (κ^*, λ^*).

The following results are derived in Section B.1.1:

$$\kappa = \kappa_o - \ln\left[\frac{L}{L_o}\right] \tag{5.7}$$

$$\lambda = \lambda_o \tag{5.8a}$$

for $t < t_{final}$, by applying eq. (5.2a).

$$\lambda = \lambda_o + 1 \tag{5.8b}$$

for $t = t_{final}$, by applying eq. (5.2a).

$$d\lambda = 1 - \frac{\dot{V}}{L}\,dt \tag{5.8c}$$

by applying eq. (5.2b).

$$\kappa^* = \frac{L_o\kappa_o - L\kappa + V^*}{V^*} \tag{5.9}$$

$$\lambda^* = \lambda_o \tag{5.10}$$

$$\kappa_{ov} = \kappa_o + \frac{V^*}{L_o} \tag{5.11}$$

$$\lambda_{ov} = \lambda_o + \frac{L}{L_o} \tag{5.12}$$

The change in the overall boiling capacity of the process, $\kappa_{ov}-\kappa_o$, is the ratio of the total amount of vapour leaving the process to the total amount fed to the process. Similarly, the change in the overall condensing capacity, using the definition of eq. (5.2a), is the ratio of the amount of liquid removed at the end of the process to the total amount fed to the process.

Using eq. (5.2b) to define λ of an equilibrium stage results in eq. (5.8c). This means that λ increases infinitely with time, since in each equilibrium stage, the amount L of residual liquid is "produced". Eq. (5.2a) defining λ in terms of quantities leaving the stage gives a result which is consistent with the other results presented in this chapter. The contradictions of these two results have not been resolved. However, it is argued that it is not possible to make a meaningful analysis of the condensing requirements of a pure boiling process. Eqs. (5.1b) and (5.2b) give similar results for the other non-steady state processes presented in this chapter, and will not be explored further.

5.4.2 Simple condensation

In this process, a vapour, of initial quantity V_o and associated with capacity pair (κ_o, λ_o), is gradually condensed and the liquid which is in equilibrium with it is removed as it is formed. At the end of the process, the residual vapour, of amount V, is removed; the vapour is associated with the capacity pair (κ, λ). The condensed liquid is collected into a product of quantity L^*, the capacity pair of which is given by (κ^*, λ^*).

The following results are obtained in Section B.1.2 by applying the definitions of capacity and overall capacity to this process:

$$\kappa = \kappa_o \tag{5.13a}$$

for $t < t_{final}$.

$$\kappa = \kappa_o + 1 \tag{5.13b}$$

for $t = t_{final}$.

$$\lambda = \lambda_o - \ln\left[\frac{V}{V_o}\right] \tag{5.14}$$

$$\kappa^* = \kappa_o \tag{5.15}$$

$$\lambda^* = \frac{V_o\lambda_o - V\lambda + L^*}{L^*} \tag{5.16}$$

$$\kappa_{ov} = \kappa_o + \frac{V}{V_o} \tag{5.17}$$

$$\lambda_{ov} = \lambda_o + \frac{L^*}{V_o} \tag{5.18}$$

The change in the overall boiling capacity of this process is the ratio of the amount of residual vapour to the total feed to the process. The change in the overall condensing capacity of the process is the ratio of the total amount of liquid formed in (and leaving) the process to the total feed to the process.

5.4.3 Simple distillation with continuous addition of material

Consider a boiling process to which material is added continuously at a non-zero rate of $\dot{s}$ moles per unit time. The capacity pair of the material added is (κ', λ'). The vapour formed is in equilibrium with this mixture. The rate of vaporization is $\dot{v}$ moles per unit time. The feed mixture is of quantity L_o and is associated with the capacity pair (κ_o, λ_o).

The definitions of capacity and overall capacity are applied to this process. It is assumed that the rates of vaporization, $\dot{v}$, and feed addition, $\dot{s}$, are constant and non-zero, that the capacity values of the additional feed material, κ' and λ', are constant with time, that $\dot{v} \neq \dot{s}$, and that $\lambda' \neq \lambda$. The following results are obtained in Section B.1.3:

$$\kappa = \kappa' + \frac{\dot{v}}{\dot{s}} - (\kappa' - \kappa_o + \frac{\dot{v}}{\dot{s}}) \left[\frac{L}{L_o}\right]^{\frac{-\dot{s}}{\dot{s}-\dot{v}}} \tag{5.19}$$

$$\lambda = \lambda' - (\lambda' - \lambda_o) \left[\frac{L}{L_o}\right]^{\frac{-\dot{s}}{\dot{s}-\dot{v}}} \tag{5.20a}$$

for $t < t_{final}$.

$$\lambda = \lambda' - (\lambda' - \lambda_o) \left[\frac{L}{L_o}\right]^{\frac{-\dot{s}}{\dot{s}-\dot{v}}} + 1 \tag{5.20b}$$

for $t = t_{final}$.

$$\kappa^* = \left[\dot{v}t(\kappa' + \frac{\dot{v}}{\dot{s}}) + (\kappa' - \kappa_o + \frac{\dot{v}}{\dot{s}})(L_o^{\frac{\dot{s}}{\dot{s}-\dot{v}}} L^{\frac{-\dot{v}}{\dot{s}-\dot{v}}} - L_o)\right] \frac{1}{V^*} \tag{5.21}$$

$$\lambda^* = \left[\dot{v}t\lambda' + (\lambda' - \lambda_o)(L_o^{\frac{\dot{s}}{\dot{s}-\dot{v}}} L^{\frac{-\dot{v}}{\dot{s}-\dot{v}}} - L_o)\right] \frac{1}{V^*} \tag{5.22}$$

$$\kappa_{ov} = \bar{\kappa}_o + \frac{\dot{v}t}{L_o + \dot{s}t} \tag{5.23}$$

$$\lambda_{ov} = \bar{\lambda}_o + \frac{L}{L_o + \dot{s}t} \tag{5.24}$$

where $\bar{\kappa}_o$ and $\bar{\lambda}_o$ are the mean boiling and condensing capacity, respectively, of the nett feed, given by:

$$\bar{\kappa}_o = \frac{L_o \kappa_o + \dot{s} t \kappa'}{L_o + \dot{s} t} \tag{5.25}$$

$$\bar{\lambda}_o = \frac{L_o \lambda_o + \dot{s} t \lambda'}{L_o + \dot{s} t} \tag{5.26}$$

The change in the overall boiling capacity of the process is the ratio of the total amount of vapour produced within (*i.e.*, leaving) the process to the total feed to the process. The change in the overall condensing capacity of the process is the ratio of the amount of liquid removed from the process to the nett feed to the process.

5.4.4 Simple condensation with continuous addition of material

A vapour of quantity V is condensed at a constant rate of $\dot{c}$ moles per unit time. Material is continuously added to the process at a constant rate of $\dot{a}$ moles per unit time. This material is associated with capacity pair (κ', λ'). The feed to the process is of quantity V_o and is associated with capacity pair (κ_o, λ_o).

It is assumed that the rates of condensation, $\dot{c}$, and feed addition, $\dot{a}$, are constant and non-zero, that the capacity values of the additional feed material, κ' and λ', are constant with time, that $\dot{c} \neq \dot{a}$, and that $\kappa' \neq \kappa$. The following results are obtained in Section B.1.4:

$$\kappa = \kappa' - (\kappa' - \kappa_o)\left[\frac{V}{V_o}\right]^{\frac{-\dot{a}}{\dot{a}-\dot{c}}} \tag{5.27a}$$

for $t < t_{final}$.

$$\kappa = \kappa' - (\kappa' - \kappa_o)\left[\frac{V}{V_o}\right]^{\frac{-\dot{a}}{\dot{a}-\dot{c}}} + 1 \tag{5.27b}$$

for $t = t_{final}$.

$$\lambda = \lambda' + \frac{\dot{c}}{\dot{a}} - (\lambda' - \lambda_o + \frac{\dot{c}}{\dot{a}})(\frac{V}{V_o})^{\frac{-\dot{a}}{\dot{a}-\dot{c}}} \tag{5.28}$$

$$\kappa^* = \left[\dot{c}\kappa' t + (\kappa' - \kappa_o)(V_o^{\frac{\dot{a}}{\dot{a}-\dot{c}}} V^{\frac{-\dot{c}}{\dot{a}-\dot{c}}} - V_o)\right] \frac{1}{L^*} \tag{5.29}$$

$$\lambda^* = \left[\dot{c}t(\lambda' + \frac{\dot{c}}{\dot{a}}) + (\lambda' - \lambda_o + \frac{\dot{c}}{\dot{a}})(V_o^{\frac{\dot{a}}{\dot{a}-\dot{c}}} V^{\frac{-\dot{c}}{\dot{a}-\dot{c}}} - V_o)\right] \frac{1}{L^*} \tag{5.30}$$

$$\kappa_{ov} = \bar{\kappa}_o + \frac{V}{V_o + \dot{a}t} \tag{5.31}$$

$$\lambda_{ov} = \bar{\lambda}_o + \frac{L^*}{V_o + \dot{a}t} \tag{5.32}$$

where $\bar{\kappa}_o$ and $\bar{\lambda}_o$ are the weighted averages of the mean boiling and condensing capacity, respectively, of the feed streams to the process, given by:

$$\bar{\kappa}_o = \frac{V_o\kappa_o + \dot{a}t\kappa'}{V_o + \dot{a}t} \tag{5.33}$$

$$\bar{\lambda}_o = \frac{V_o\lambda_o + \dot{a}t\lambda'}{V_o + \dot{a}t} \tag{5.34}$$

The change in the overall boiling capacity of this process is the ratio of the quantity of vapour removed from the process to the nett feed to the process. The change in the overall condensing capacity of the process is the ratio of the total amount of liquid formed within the process to the total feed to the process.

5.4.5 Single flash stage

A single flash stage, with a feed of molar flow rate F and associated with capacity pair (κ_F, λ_F), is partially vaporized in a single flash stage into a liquid product of flow rate L and a vapour product of flow rate V. The flash stage is an equilibrium separation stage. The definitions of κ and λ may be applied as follows:

$$\kappa = \kappa_F + \frac{V}{F} \tag{5.35}$$

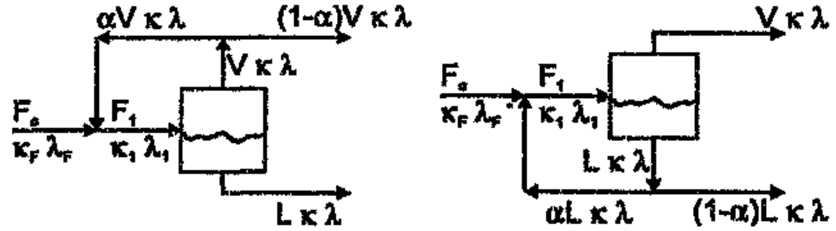
$$\lambda = \lambda_F + \frac{L}{V} \tag{5.36}$$

The capacity values of the vapour and liquid streams are identical, as they are the equilibrium products from the same stage.

The overall capacity pair of the process is the weighted average of the capacity pair of the two product streams; it follows that $\kappa_{ov} = \kappa$ and $\lambda_{ov} = \lambda$.

5.4.6 Single flash stage with recycle

Consider the processes shown in Fig. 5.1, in which a portion of one the products from a single flash stage is recycled and mixed with the feed to the process.



(a) (b)

Fig. 5.1 Capacity variables of a single flash stage with recycle. (a) Vapour recycled. (b) Liquid recycled.

For these processes, the capacity pairs of the two product streams are identical and equal to the overall capacity pair of the process.

The definitions of capacity and overall capacity are applied to this process in Section

B.2.2 to obtain the following results:

$$\kappa_{ov} = \kappa_F + \frac{V}{F_o} \tag{5.37}$$

$$\lambda_{ov} = \lambda_F + \frac{L}{F_o} \tag{5.38}$$

The change in the overall boiling (or condensing) capacity of the process is the ratio of the total rate of formation of vapour *within* the process to the nett feed flow rate of the feed to the process. This result is obtained by applying the definition of capacity of the equilibrium stage, in which the nett feed rate to the stage and the rate of formation of vapour and liquid product are considered. The boiling capacity of the process is related to the vaporization rate *within* the process, V, and not simply to the nett flow rate of vapour product from the process, for example, $(1 - \alpha)V$, in the process depicted in Fig. 5.1(a).

5.4.7 Two flash stages arranged in series

The product of a flash stage may form the feed to a second flash stage, as shown in Fig. 5.2.

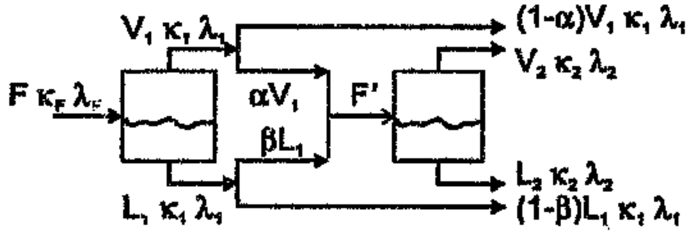


Fig. 5.2 Capacity variables of two flash stages arranged in series.

The feed to the second stage, of flow rate F', is the mixture of some portion of the two products of the first flash stage; that is:

$$F' = \alpha V_1 + \beta L_1 \tag{5.39}$$

where $0 \leq \alpha \leq 1$ and $0 \leq \beta \leq 1$, and V_1 and L_1 are the vapour and liquid product flow rates, respectively, of the first flash stage.

The following results are derived in Section B.2.3:

$$\kappa_{ov} = \kappa_F + \frac{V_1 + V_2}{F} \tag{5.40}$$

$$\lambda_{ov} = \lambda_F + \frac{L_1 + L_2}{F} \tag{5.41}$$

The change in the overall boiling (or condensing) capacity of the process is the ratio of the total rate of formation of vapour (or liquid, respectively) *within* the process to the nett feed flow rate to the process. As was seen in Section 5.4.2, the total vaporization rate is not directly related to the vapour product flow rate, and thus the overall boiling capacity is not directly related to the nett rate of vapour production.

5.4.8 Two flash stages arranged in parallel

A feed may be split into two portions, of flow rates αF and $(1 - \alpha)F$, where $0 \leq \alpha \leq 1$. These two streams are fed into two flash stages arranged in parallel, as shown in Fig. 5.3.

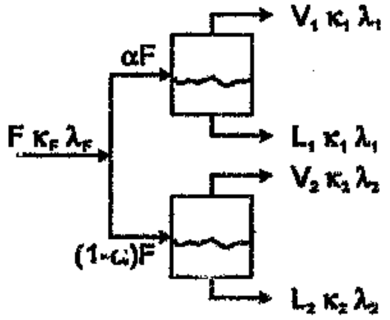


Fig. 5.3 Capacity variables of two flash stages arranged in parallel.

The definition of the capacity variables may be applied to each of the equilibrium stages, and the definition of overall process capacity may be applied to the four products of this process. It is shown in Section B.2.4 that:

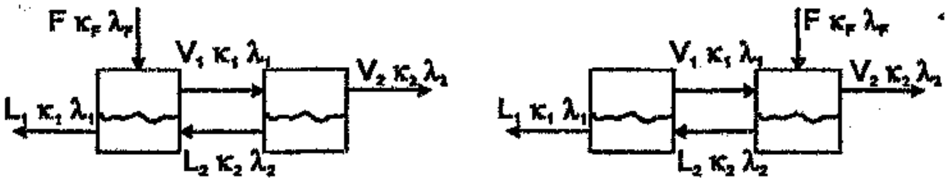
$$\kappa_{ov} = \kappa_F + \frac{V_1 + V_2}{F} \tag{5.42}$$

$$\lambda_{ov} = \lambda_F + \frac{L_1 + L_2}{F} \tag{5.43}$$

The change in the overall boiling (or condensing) capacity of the process is the ratio of the flow rate of vapour (or liquid, respectively) produced within the process to the flow rate of feed flow rate to the process.

5.4.5 Two flash stages arranged in series with reflux

Consider the process illustrated in Fig. 5.4(a), in which the feed, of flow rate F, is added to the first flash stage of two flash stages arranged in series with reflux. The vapour and liquid products of the first stage are of flow rate V_1 and L_1, respectively, associated with capacity pair (κ_1, λ_1). The second stage products are of flow rates V_2 and L_2, associated with capacity pair (κ_2, λ_2). The nett feed to the first stage is of flow rate F^*, where $F^* = F + L_2$.



(a) (b)

Fig. 5.4 Capacity variables of two flash stages arranged in series with reflux. (a) Feed added to the first flash stage. (b) Feed added to the second flash stage.

The definitions of capacity and overall capacity are applied to the two equilibrium flash stages in Section B.2.5 to give the following results:

$$\kappa_{ov} = \kappa_F + \frac{V_1 + V_2}{F} \tag{5.44}$$

$$\lambda_{av} = \lambda_F + \frac{L_1 + L_2}{F} \tag{5.45}$$

The change in the overall boiling (or condensing) capacity of the process is the ratio of the total rate of vapour (or liquid, respectively) production within the process to the flow rate of the feed to the process. The same result is obtained for a process in which the feed is added to the second flash stage, as shown in Fig. 5.4(b).

5.4.10 Distillation column

Consider the simple distillation column shown in Fig. 5.5. The feed, distillate and bottoms flow rates of the column are F, D and B, respectively. The capacity pairs associated with these streams are (κ_F, λ_F); (κ_D, λ_D) and (κ_B, λ_B) respectively. It is assumed that the feed and products are saturated liquids and that there is constant molar overflow in the column. The reflux ratio, r, is the ratio of the liquid flow rate in the rectification section, L, to the flow rate of the distillate product, D. The reboil ratio, s, which is not independent of the reflux ratio, is defined as the ratio of the vapour flow rate in the column, V, to the bottoms product rate, B. The liquid flow rate in the stripping section of the column, L', is the sum of the feed flow rate and the liquid flow rate in the rectification section, *i.e.* $L' = F + L$.

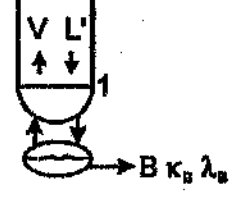


Fig. 5.5 Capacity variables of a distillation column.

Each stage of the column is treated as an ideal stage, and is simply an equilibrium flash separation. Except for the condenser and reboiler, the nett feed to a stage is the sum of the liquid from the previous stage and the vapour from the following stage. The capacity of the nett feed to the stage is obtained using the mixing rule. The overall capacity variables of the process are determined for a column with N stages in the rectification section and M stages in the stripping section. The following results for the distillation column are obtained by applying the definition of capacity to each equilibrium stage in the column. The stage-to-stage calculations are generalized using inductive proofs, as shown in Section B.3 of Appendix B.

The total rate of vaporization in the column is V on each of N+M stages plus V in the reboiler. The overall boiling capacity of the process is found to be:

$$\kappa_{ov} = \kappa_F + \frac{V(N + M + 1)}{F} \tag{5.46}$$

The change in overall boiling capacity of the process is thus the ratio of the total vaporization rate within the process to the feed flow rate to the process.

The total rate of condensation in the column is a rate L on each of N stages in the rectification section, plus a rate L' on each of M stages of the stripping section, plus a rate V in the total condenser, plus a rate B in the reboiler. The overall condensing capacity of the process is:

$$\lambda_{ov} = \lambda_F + \frac{LN + L'M + V + B}{F} \tag{5.47}$$

The change in the overall condensing capacity of the process is thus the ratio of the total rate of liquid production within the process to the feed flow rate to the process.

5.5 Summary of results and conclusions

In the previous section, the definitions of the capacity and overall capacity variables have been applied to the following VLE separation processes: one flash stage, with and without product recycle; two flash stages configured in series, in parallel and in series with reflux; simple distillation and condensing, with and without the continuous addition of feed material (the rate of addition of material and the capacity of this material were assumed constant for these processes); and a simple distillation column.

The fundamental definitions of the capacity variables are applicable to individual equilibrium separation stages. The stage-wise definitions and the mixing rules were applied to a range of VLE separation processes to obtain overall capacity variables, which are of a similar form to the equilibrium-stage capacity variables. The overall capacity pair is a measure of the internal vaporization and condensation requirements of the process. Thus, for a wide range of VLE separation processes, consistent and elegant results have been obtained for the overall boiling and condensing capacity of the process. It is proposed, but it has not been proved, that these results are generally true, at least for steady state VLE separation processes.

In the light of the results of Chapter 3, in which regions of feasible products for a range of VLE separation processes were determined in composition space, it was concluded that a cost indicator is required for the synthesis of such processes. The criteria for the cost indicator were that it should incorporate both capital and energy costs, that both boiling and condensing should be considered, and that the cost indicator should be applicable to a wide range of VLE separation equipment. The success of the overall capacity variables to fulfil these criteria is discussed below.

The overall capacity variables are related to internal vaporization or condensation requirements. The utility requirements of a process in which there is heat exchange to every equilibrium stage are therefore directly related to the overall capacity variables. (All the processes considered, except column distillation, fall into this category.) Similarly, in these processes, the physical size, and therefore cost, of the equipment and ancillaries will be related to the flow rates of material into and out of each stage of the process, and therefore to the overall capacity variables.

In the distillation column, eqs. (5.46) and (5.47) show explicitly how the overall capacity variables are related to the vapour or liquid flow rates in the column, which determine the utility requirements and column diameter, and to the number of stages in the column, which determines the height of the column. Therefore both energy requirements and capital costs are incorporated by the overall capacity variables. The overall capacity variables are evaluated for a range of separation processes in the following chapter, where this theme will be further developed.

In order to accommodate both boiling and condensing costs, two separate and independent capacity variables were defined. Therefore costs of a process due to both boiling and condensing may be assessed. It is anticipated that one of these variables will dominate, either because boiling or heat costs are far greater than condensing costs, or *vice versa*, or because the internal vaporization requirements of the process are far greater than the internal condensing requirements, or *vice versa*.

Consistent results are obtained for the overall capacity variables for a wide range of VLE separation processes. This fulfils the third criterion for a cost indicator for separation processes. As a result, alternative processes which may achieve some specified separation may be compared on a common basis. A full costing of the alternative processes would also allow such a comparison, but is time consuming and inappropriate to the initial stages of process synthesis, and a common basis for comparison is still not guaranteed.

The overall capacity variables are therefore found to fulfil the requirements of cost indicators for VLE separation processes. In addition, these variables arise naturally out of the material balance equations of a separation process, and thus are not computationally demanding. That a physical interpretation exists for the capacity variables permits the integration of engineering intuition and engineering science in the synthesis and optimization of VLE separation processes.

Chapter 6

Case Studies: Applying the Capacity Variables to VLE Separation Processes

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6.1 Introduction

Two of the questions which must be answered as part of process synthesis are:

- Are the specified products of a given process feasible?
- What are the costs associated with this process?

In Chapter 3, in which only product compositions were considered, it was concluded that both feasible compositions and process costs must be taken into account. In this chapter, the capacity variables which were introduced in Chapter 5 are used to examine simultaneously the product compositions and process costs for a range of processes.

The capacity variables were defined for single equilibrium stages. The definitions were extended to overall capacity variables; which may be used to characterize whole processes. These have been derived for a number of processes in Section 5.4. The composition and the overall capacity variables of the products of some of these processes are presented in this chapter for a range of simple thermodynamic models. Distillation is given particular attention. In all cases, the feed to the process is assumed to be associated with boiling and condensing capacity values of zero.

Most of these results were calculated using SPARCompiler Fortran 2.0.1 and Numerical Algorithms Group Fortran library routines Mark 16 (D02BBF for integrating differential equations, C05PCF for solving non-linear equations simultaneously, C05ADF for root-finding and E04ABF for minimizing objective functions). Some of the constant relative volatility results were calculated using the spreadsheet package Quattro Pro V.

6.2 Simple distillation

In the simple distillation process, a mixture is gradually boiled, and the vapour that is formed is removed continuously. The overall capacity variables for this process are given by eqs. (5.11) and (5.12).

Fig. 6.1 illustrates the composition-boiling capacity trajectories of the residual liquid (capacity and overall capacity *vs.* composition) and the accumulated vapour (capacity *vs.* composition) for the simple distillation of an ideal binary mixture. The overall boiling capacity of the process is limited to 1, as can be seen from eq. (5.11), but the capacity of the residual liquid is not constrained, as can be seen from eq. (5.7). The product regions for processes comprised of simple distillation and forward mixing have not been presented in this discussion.

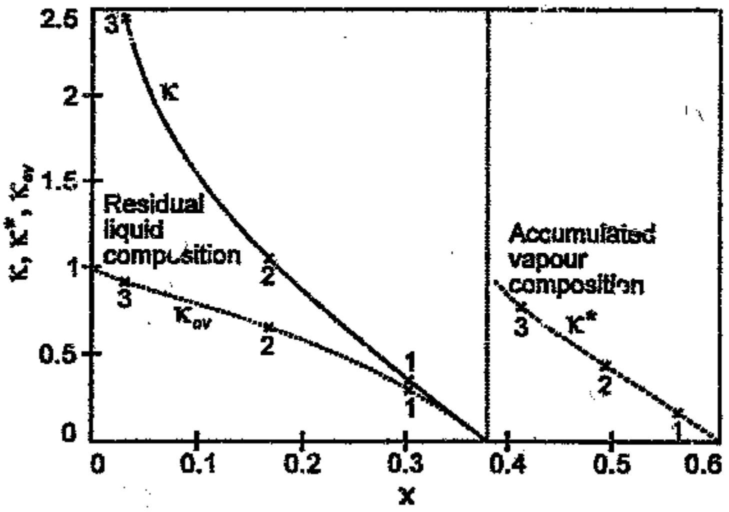


Fig. 6.1 Compositions and stream capacity variables for the simple distillation of an ideal binary mixture. κ and κ_{ov} are plotted for the liquid residue and κ^* is given for the accumulated vapour product. Points 1, 2 and 3 mark corresponding (x, κ), (x, κ_{ov}) and (y, κ^*) pairs at three arbitrary times.

6.3 Processes comprised of one or two equilibrium flash stages

Chapter 3 examined the feasible products of one or two equilibrium flash stages. The product regions were generated in composition space for processes comprised of flash separation and forward mixing, that is, mixing (without recycle) of achievable streams. The feasible products of flash processes with mixing of products (*i.e.*, without recycle or feed bypass) are presented in composition-overall capacity space in this section.

6.3.1 A single flash stage

A mixture may be separated in a single flash stage. The capacity pair is identical for both products from this process; the capacity variables are given by eqs. (5.35) and (5.36). The locus of feasible product compositions and the associated capacity variables of an ideal binary mixture separated in a single flash stage are plotted in Fig. 6.2. The vapour and liquid product compositions and the associated overall capacity variables are noted for an arbitrary product pair, $x{-}y$.

The liquid product compositions, for a particular feed, range between the feed composition and the dew-point composition of the feed. At extreme operation, an infinitesimal amount of liquid at the dew-point composition is obtained when all the feed is vaporized, that is, $\kappa_{ov} = 1$ and $\lambda_{ov} = 0$. The liquid product has the same composition as the feed when a zero-quantity vapour product is formed, thus $\kappa_{ov} = 0$ and $\lambda_{ov} = 1$. The vapour product composition, similarly, lies between the feed composition ($\kappa_{ov} = 1$, $\lambda_{ov} = 0$) and the bubble-point composition of the feed ($\kappa_{ov} = 0$, $\lambda_{ov} = 1$). Fig. 6.2 illustrates the relationships between the capacity variables and product composition. It does not show explicitly quantities of products.

A region of feasible products may be constructed in composition-κ_{ov} space for a process comprised of a single flash stage and mixing of products. The region *ABCDA* in Fig. 6.2(a) is such a region for the separation of an ideal binary mixture. Feasible products pairs may be mixed; therefore all points on all horizontal lines joining feasible product points may be obtained. A feasible product region in composition-λ_{ov} space, *EFGHE*, may be similarly constructed, and is shown in Fig. 6.2(b).

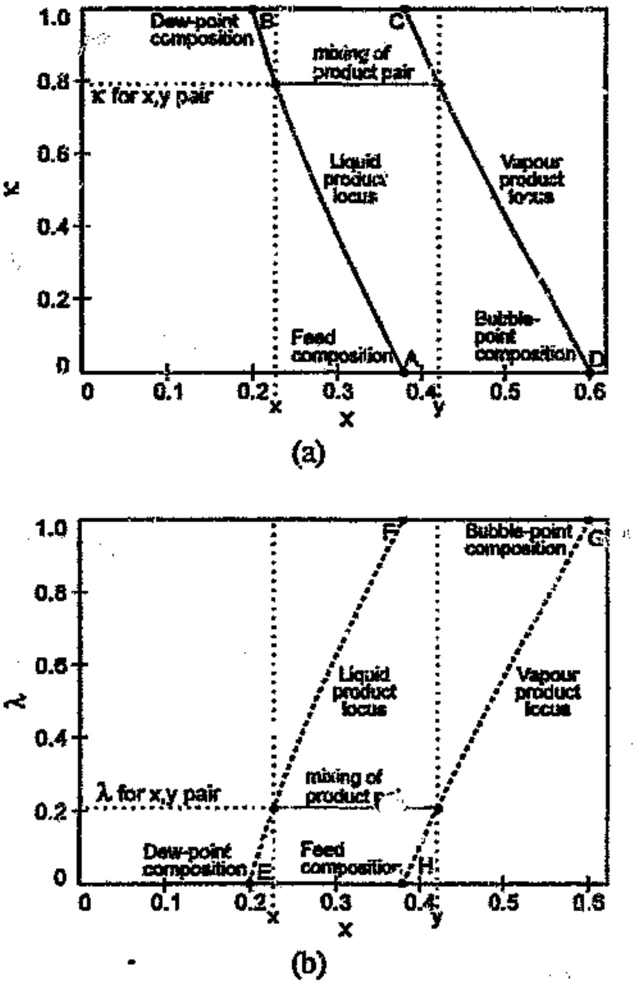


Fig. 6.2 Product compositions and capacity variables for the separation of an ideal binary mixture in a single flash stage. x_F: 0.38. (a) κ, which is equal to κ_{ov}. (b) λ, which is equal to λ_{ov}.

The feasible products of a ternary system separated in a single flash stage may be plotted in three-dimensional composition-κ_{ov} space, as shown in Fig. 6.3. The projection of these points in the composition plane is the single flash stage arc-pair shown in Fig. 3.6. For a process comprised of a single flash stage and mixing of products, the feasible product region is the surface formed by all constant-κ_{ov} mixing lines between feasible product pairs. This feasible product region is not illustrated.

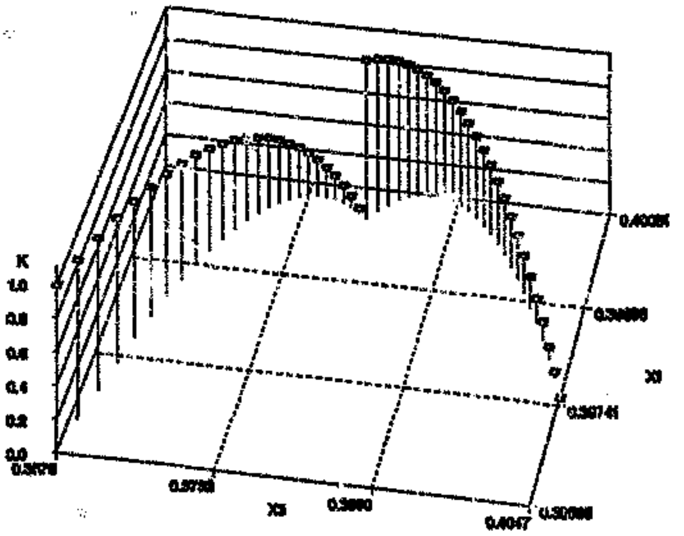


Fig. 6.3 Product compositions and κ_{ov} for the separation of a ternary mixture using a single flash stage. $\overline{x}_F$: (0.40, 0.22, 0.38).

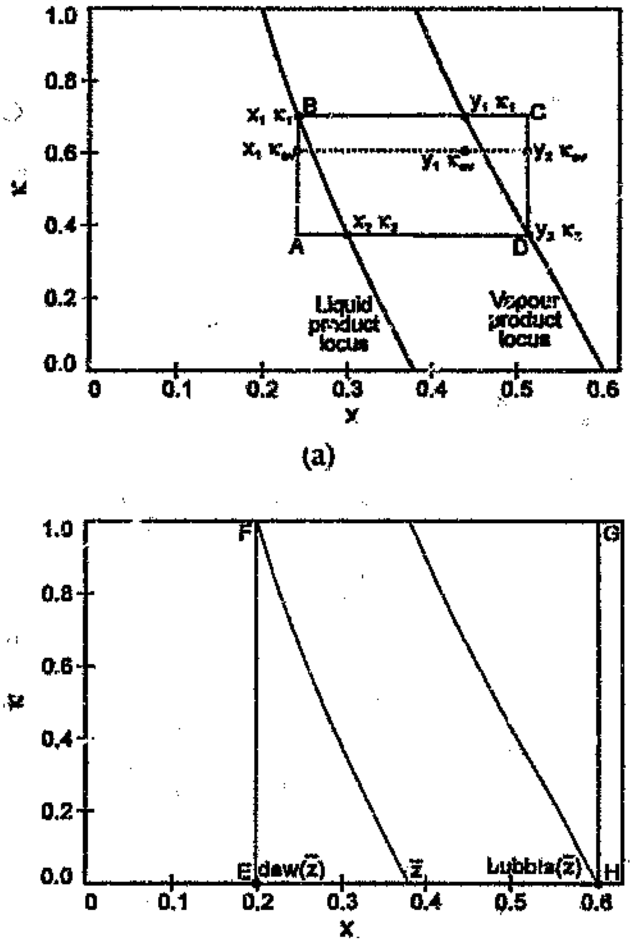
6.3.2 Two flash stages in parallel

Two flash stages may be arranged in parallel, as shown in Fig. 3.11. The overall capacity variables are given by eqs. (5.42) and (5.43). The total rate of vaporization or condensation within the process is some fraction of the feed to the process, so the overall capacity values both lie between zero and unity.

Fig. 6.4(a) shows two product pairs (x_1-y_1 and x_2-y_2) and the stream capacity variables (κ_1 and κ_2) of such a process. The overall boiling capacity of this process is the weighted average of κ_1 and κ_2. Since the flow rate of feed to the first stage, αF, may range between zero and F, κ_{ov} may lie anywhere between κ_1 and κ_2. The compositions of feasible products lie between x_1 and y_2. Therefore all products in the rectangle *ABCD* are feasible. Composition-capacity space does not make explicit what quantities are involved. Some of the feasible products, for example, point *A*, are achievable only in infinitely small quantities.

The region of feasible products of two flash stages arranged in parallel may be found by extending this argument for all such x_1-y_1 and x_2-y_2 product pairs. The rectangle

EFGH in Fig. 6.4(b), ranging from the dew-point composition of the feed to the bubble-point composition of the feed, is this product region for a binary system.



(a)

(b)

Fig. 6.4 Product composition and boiling capacity variables for the separation of an ideal binary mixture in two flash stages arranged in parallel. (a) Product pairs $x_1 - y_1$ and $x_2 - y_2$ are fixed. (b) All possible products.

The feasible products of a ternary system separated by two flash stages arranged in parallel are, similarly, any mixture of any feasible products of a single flash stage. A convex volume, with the base given by the product region in the composition plane (Fig. 3.13(d)), and a height of one, represents all possible composition-κ_{ov} combinations for this process. This volume is not illustrated.

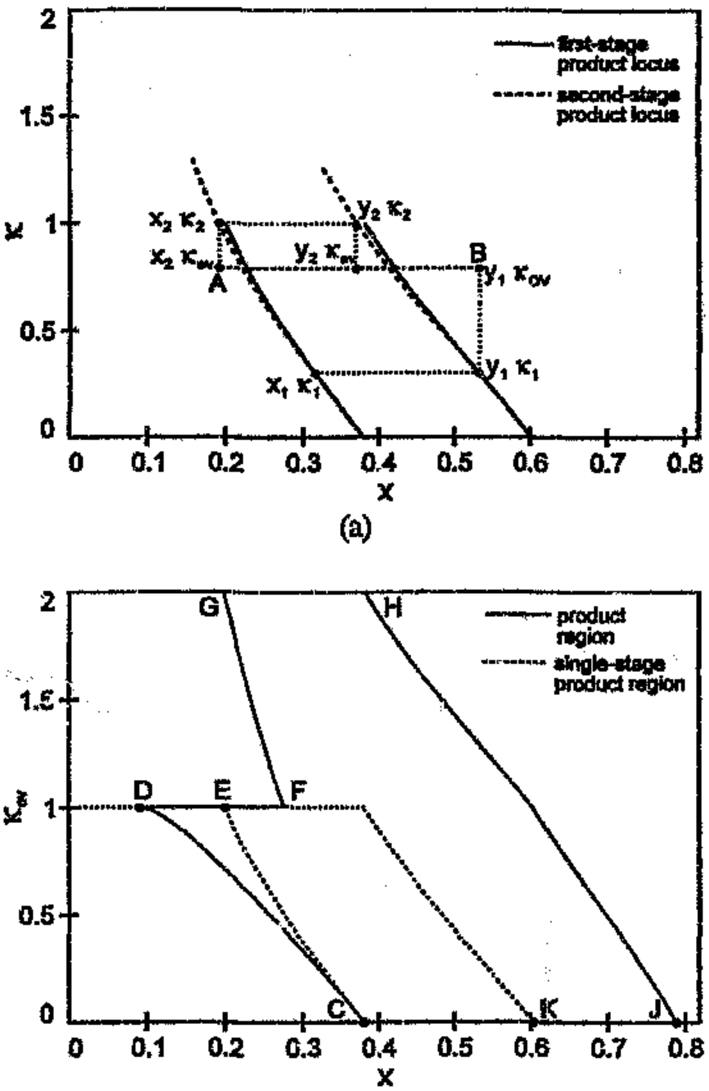
6.3.3 Two flash stages arranged in series

Two flash stages may be operated in series, as shown in Fig. 3.14. The total amount of vapour or liquid formed in the process is limited to twice the feed flow rate; this results in an upper bound of two on the overall capacity variables, as given by eqs. (5.40) and (5.41).

The product region in composition-overall capacity space, for the separation of an ideal binary mixture of composition $\bar{z}$ in a single flash stage, is illustrated in Fig. 6.3. One of the products of the first flash stage forms the feed to the second flash stage. Each product is associated with a pair of capacity variables. The feed to the second stage is then associated with a pair of capacity variables, while the capacity variables of the feed to the first stage were both assumed to be zero.

For example, a liquid of composition x_1, flowrate L_1 and boiling capacity κ_1 may form the feed to the second flash stage, the products of which are of quantity L_2 and V_2 and compositions x_2 and y_2, respectively, and are associated with boiling capacity κ_2. The other product of the first stage is of quantity V_1 and composition y_1. The weighted average of the boiling capacity variables of these three products is κ_{ov}. Fig. 6.5(a) shows the stream and overall boiling capacity variables of a binary mixture separated in this process.

Mixing between attainable products allows any point on the line *AB* between (x_2, κ_{ov}) and (y_1, κ_{ov}) in Fig. 6.5(a) to be obtained. For a fixed second-stage feed, each possible second-stage product pair will produce a similar line. The union of all such lines for all possible second-stage feed compositions, is the region of feasible products of two flash stages arranged in series. Such a region is the region bounded by *C-D-E-F-G-H-J-K-C* shown in Fig. 6.5(b). The compositions of points *J*, *K*, *E* and *D* are *bubble(bubble($\bar{z}$))*, *bubble($\bar{z}$)*, *dew($\bar{z}$)* and *dew(dew($\bar{z}$)*, respectively.



(a)

(b)

Fig. 6.5 Product compositions and boiling capacity variables for the separation of an ideal binary mixture in two flash stages arranged in series. (a) Product pairs $x_1 - y_1$ and $x_2 - y_2$ are specified. (b) All possible products.

The region of feasible products in ternary composition space for two flash stages arranged in series is shown in Fig. 3.16(a), where, for simplicity, it is assumed that feasible products of the first flash stage were not mixed, but fed directly into the second flash stage. The product region in composition-κ_{ov} space is plotted in Fig. 6.6. The extremal products of this process are associated with finite capacity variables.

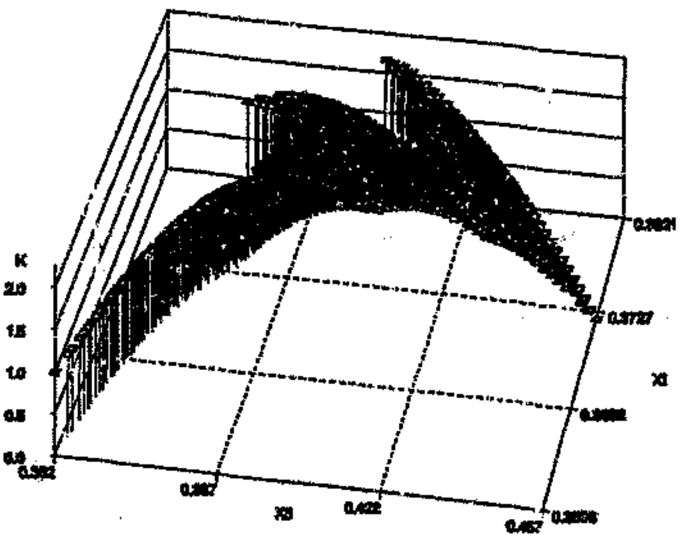
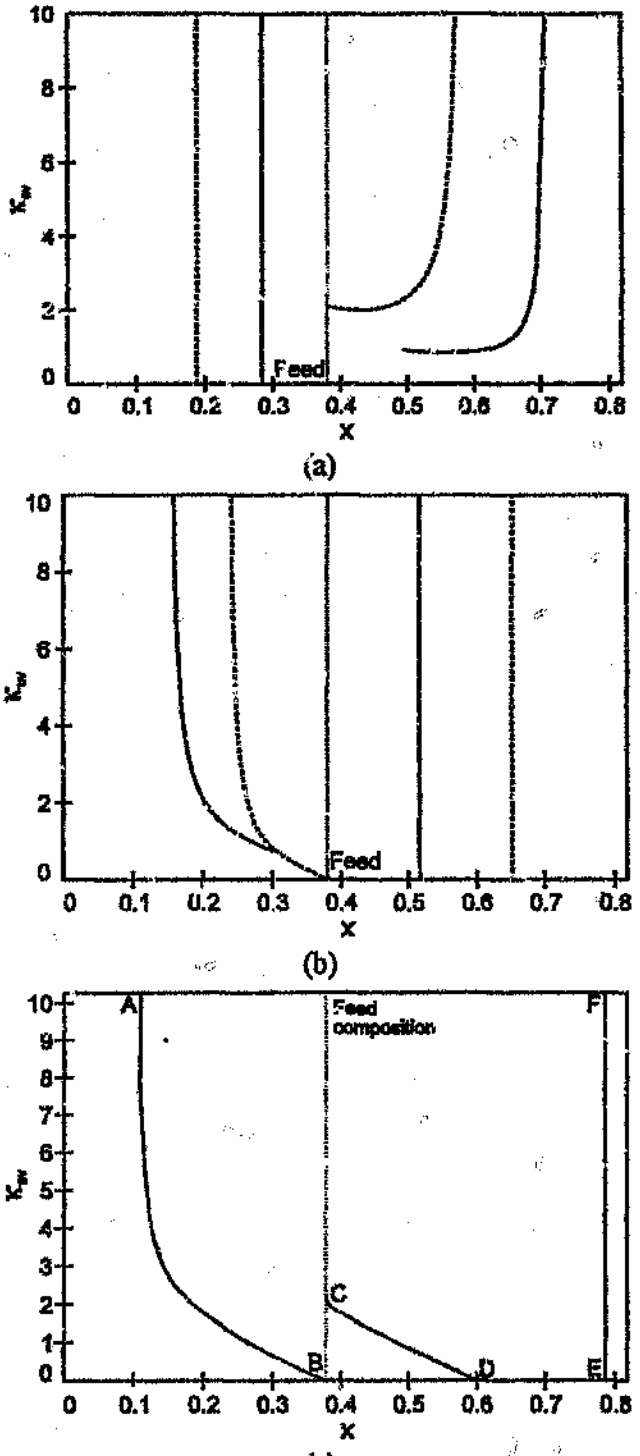


Fig. 6.6 Feasible products and κ_{ov} for the separation of a ternary mixture in two flash stages arranged in series. $\overline{x}_F$: (0.38, 0.22, 0.40).

6.3.4 Two flash stages arranged in series with reflux

Two flash stages may be arranged in series with reflux, as shown in Fig. 3.20. The composition of the feed and one of the products, for example, the liquid product, of composition $\overline{x}_1$, may be specified and the range of feasible co-product compositions and overall capacity variables may be calculated using eqs. (5.44) and (5.45). When the extremal co-product is obtained at total reflux, the products are associated with infinite overall capacity variables. It has been assumed that there is no external mixing in this process, that is, the feasible products are not mixed with each other to form the final products of the process.

This process, with feed addition to the first stage, is examined for an ideal binary mixture. Fig. 6.7(a) shows the range of feasible vapour products in composition-κ_{ov} space for a given feed and two specified liquid products. The vapour products lie between the feed composition and *bubble(bubble(*$\overline{x}_1$*))* or between *bubble(*$\overline{x}_1$*)* and *bubble(bubble(*$\overline{x}_1$*))*, where $\overline{x}_1$ is the composition of the specified liquid product. The product *bubble(bubble(*$\overline{x}_1$*))* is obtained at total reflux and is associated with infinite overall capacity variables.



(a)

(b)

(c)

Fig. 6.7 Product compositions and κ_{ov} for the separation of an ideal binary mixture in two flash stages arranged in series with reflux. (a) Vapour products of two specified liquid co-products. (b) Liquid products of two specified vapour co-products. (c) All feasible liquid and vapour products. x_F: 0.38.

The range of liquid products which may be obtained for two specified vapour products and a given feed are shown in Fig. 6.7(b). The extreme liquid product compositions which may be obtained are *dew(dew($\overline{y}_2$))*, where $\overline{y}_2$ is the composition of the specified vapour product, and are associated with infinite overall capacity variables. Fig. 6.7(c) shows feasible vapour and liquid products, in composition-κ_{ov} space, for all feasible co-products of this process.

The product region in composition space is shown in Fig. 3.21 for a ternary system. The total reflux products of this region are associated with infinitely large capacity variables, because of the infinitely large internal flow rates. The product region for this process (without external mixing) in composition-capacity space is the surface illustrated in Fig. 6.8. It may be noted that points on the total reflux boundary are associated with high values of κ_{ov}.

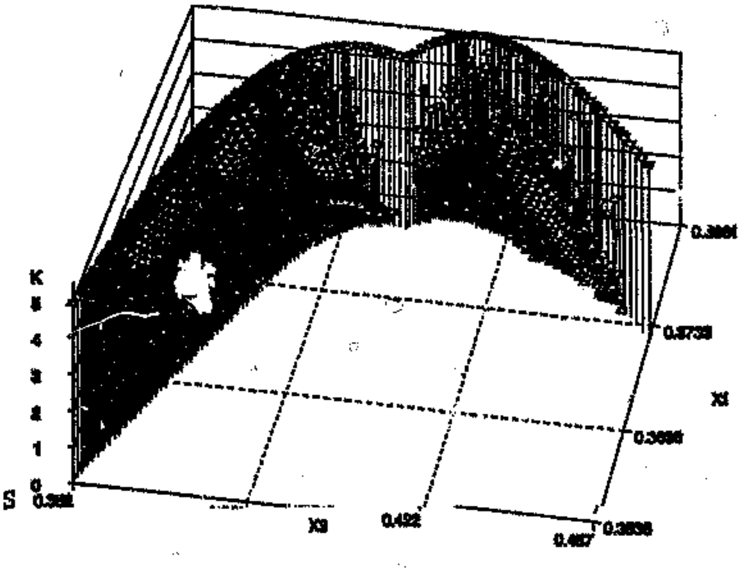


Fig. 6.8 Product compositions and κ_{ov} for the separation of a ternary mixture in two flash stages arranged in series with reflux. $\overline{x}_F$: (0.38, 0.22, 0.40).

6.3.5 Comparison of product regions for configurations of two flash stages

The product regions of three configurations of two equilibrium flash stages were investigated in composition-space for a ternary mixture in Section 3.3 of Chapter 3. It was seen that two stages in series can obtain all products obtained by two stages arranged in parallel. For the binary example studied, all the products which may be obtained by two flash stages arranged in parallel may be obtained at the same or smaller capacity variables in a single flash stage or in two flash stages arranged in series.

It was also observed that some products which are attainable by two ternary flash stages with reflux cannot be obtained by two flash stages in series, and *vice versa.* Fig. 3.24 shows that some subset of product compositions can be obtained by both the serial and the refluxed configurations of two flash stages. For example, a range of products which may be obtained at total reflux for the refluxed arrangement may also be obtained by the serial arrangement. A qualitative comparison of the capacity variables of the products of a ternary mixture, which are illustrated in Figures 6.6 and 6.8, confirms that the serial arrangement is associated with lower capacity values than the refluxed arrangement for some range of products, and that the opposite is also true for some products.

In particular, a subset of the ternary products on the total reflux boundary of the product region for the refluxed arrangement (which are associated with infinite capacity variables), can also be obtained at finite reflux ratios (where they are associated with finite capacity variables). The costs of these products were discussed qualitatively in Chapter 3. The products obtained at total reflux are associated with infinite costs, since infinitely large internal flow rates result in large equipment sizes and high energy requirements. The products obtained in the serial configuration of two flash stages are associated with finite costs, because the internal flow rates and energy requirements of the process are bounded. It has thus been qualitatively demonstrated that the capacity variables follow the same trends as cost for these two processes. This demonstrates that the overall capacity variables are effective as cost indicators and allow the comparison of different VLE separation processes.

This analysis could be extended to configurations of three and more flash stages. For the serial arrangement of a finite number of stages, with forward mixing only, the capacity variables will always have a finite bound, while the refluxed arrangement (the distillation-column-like configuration) will always be associated with infinitely high capacity variables at total reflux. This suggests that, for larger problems, it may be useful to compare the product regions and process costs of distillation columns and configurations of flash stages (in series, parallel, and complex series-parallel-recycle configurations). The capacity variables would permit this comparison to be made without a full process costing being required.

6.4 Column distillation

Column distillation is the most widely used VLE separation process. It is a complex process, and not as well understood as it might be, as was discussed in Chapters 2 and 4. The capacity variables for a simple distillation column, such as that represented in Fig. 5.5, were evaluated and are presented in this section. Constant molar overflow and ideal equilibrium stages, saturated liquid feed and saturated liquid products were assumed. A constant pressure in the column of 100 kPa was assumed. The results for some binary and ternary, ideal and non-ideal mixtures are presented.

6.4.1 Distillation of an ideal binary mixture

The separation of an ideal binary mixture in a simple distillation column was simulated using the assumptions given above. A constant relative volatility of 2.47 was assumed, and both the liquid and vapour phases were assumed to show ideal behaviour. The overall capacity for the process was calculated as follows: The feed, distillate and bottoms compositions were fixed, and a reflux ratio was specified. The mass balance difference equations and equilibrium relationships were solved simultaneously for the rectification and stripping sections of the column using the boundary value approach of Section 2.4.1. The number of stages required in each section were calculated, using an algebraic McCabe-Thiele algorithm. The overall capacity variables were calculated from eqs. (5.46) and (5.47), since the number of stages required and the internal and feed flow rates were known.

Fractional stages were counted. Column operating lines for a binary system may be drawn on x-y axes, as shown in Fig. 6.9. Horizontal lines joining the compositions of a pair of passing streams and an equilibrium vapour-liquid pair may be constructed. For example, in the rectification section the passing streams (x_n, y_{n+1}) and the equilibrium pair (x_{n+1}, y_{n+1}) may be joined, as shown in Fig. 6.10. This line intersects the vertical line representing the saturated liquid feed. The ratio of the length of the line $x_F - x_n$ to the length of the line $x_{n+1} - x_n$ is taken to be the fraction of a stage which is required to reach the feed line. The fraction of a stage required in the stripping section is similarly calculated. It is not clear what the physical meaning of a fraction of a stage is. It is assumed that the capacity variables may be calculated for fractional stages, using eqs. (5.46) and (5.47), exactly as if there were an integral number of stages.

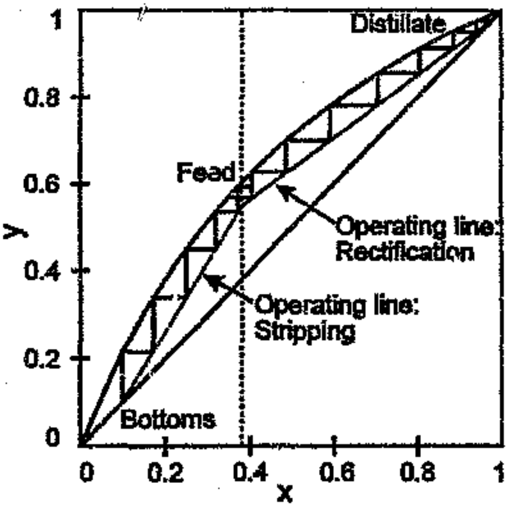


Fig. 6.9 McCabe-Thiele construction for the separation of an ideal binary mixture using a distillation column. x_F: 0.38, x_D: 0.975, x_B: 0.10. $R = 2.5$.

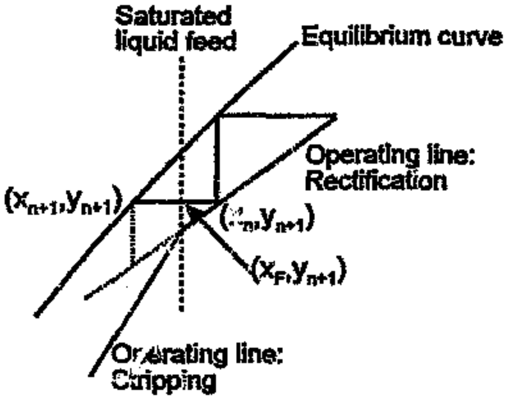


Fig. 6.10 Construction showing how fractional stages are calculated from where the operating line intersects the feed line.

In Fig. 6.11, the overall process capacity variables are plotted against reflux ratio for specified feed and product compositions. It may be seen that:

(i) The values of κ_{ov} and λ_{ov} are large for small reflux ratios, *i.e.*, for reflux ratios just larger than the minimum reflux ratio.

(ii) The values of κ_{ov} and λ_{ov} increase with reflux ratio for reflux ratios greater than the optimum reflux ratio.

(iii) The capacity variables show minima with respect to reflux ratio; the optimum reflux ratios are at 1.43 and 1.55 times the minimum reflux ratio for κ_{ov} and λ_{ov}, respectively.

(iv) The minima of κ_{ov} and λ_{ov} are not coincident.

These observations shall be examined in the light of well-known binary column performance.

Point (i) above notes that the capacity variables are large for low reflux ratios. At low reflux ratios, large numbers of stages are required. From eqs. (5.46) and (5.47) it is clear that the overall capacity variables are large for large numbers of stages. Distillation at low reflux ratios increases capital costs since large numbers of stages are required, and column height is related to the number of stages. Although the energy requirements are low at low reflux ratios, capital costs dominate the total annual costs.

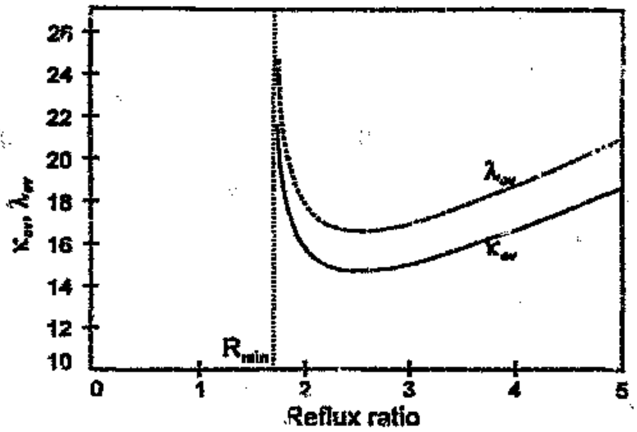


Fig. 6.11 Overall capacity variables as a function of reflux ratio for the distillation of an ideal binary mixture. x_F: 0.38, x_D: 0.98, x_B: 0.10.

Point (ii) above indicates that κ_{ov} and λ_{ov} increase for large internal flow rates, associated with high reflux ratios. The annual costs of binary distillation columns follow closely these trends; capital costs are related to column diameter, which in turn depends on internal flow rates, and operating costs are related to internal flow rates.

Point (iii) highlights the minima in the capacity curves. Typical total annual costs *vs.* reflux ratio curves also show minima, usually at reflux ratios between 1.03 and 1.3 times the minimum reflux ratio. These typical annual cost curves apply to both ideal and non-ideal mixtures. The capacity variables can thus be seen to follow the same trends with respect to reflux ratio as annual costs. The overall capacity curves are relatively flat, indicating that the overall capacity variables are not very sensitive to reflux ratio near to the optimum reflux ratio. Total annual costs have also been reported not to be very sensitive to the reflux ratio near to optimum operation (McCabe and Smith, 1956; Linnhoff *et al.*, 1983).

The optimum reflux ratios lie at 1.43 and 1.55 times the minimum reflux ratio for κ_{ov} and λ_{ov}, respectively. These values are close to the heuristic optimum of 1.03 to 1.3 times R_{min}. The two minima in the capacity curves occur at different optimum reflux ratios, as noted in point (iv) above. The two objective functions, namely the capacity variables, were determined and minimized independently with respect to reflux ratio, and there is no particular reason why the two optimum reflux ratios should be identical.

The overall capacity variables were calculated for a range of reflux ratios for four different distillate composition specifications. The capacity curves are plotted in Fig. 6.12. The following may be observed:

(i) Each curve has a similar shape to the curves in Fig. 6.11.
(ii) The minimum capacity values increase with increasing product purity.
(iii) The optimum reflux ratios increase with increasing product purity.

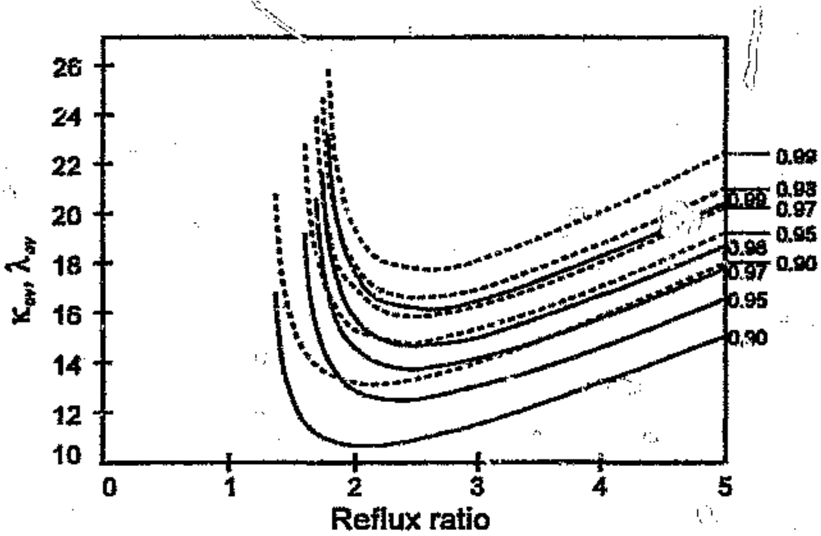


Fig. 6.12 Overall capacity variables (— κ_{ov}, -- λ_{ov}) for the distillation of an ideal binary mixture, for a range of distillate compositions. x_F: 0.38, x_B: 0.10. Distillate compositions shown.

These observations, once again, correlate with what is known about the cost and operation of binary distillation columns. Point (i) generalizes the observations which were made about the results presented in Fig. 6.11, that the capacity variables follow the trends in cost for binary distillation columns.

It may be seen in Fig. 6.13 that the minimum reflux ratio increases as the product purity increases. It would seem to follow that, for optimum operation, higher operating reflux ratios would be used for higher product purities. This would be the case, for example, if the heuristic rule of using a multiple of the minimum reflux ratio were adopted. The increasing operating reflux ratios contribute to the increase, with product purity, in the operating-costs component of the total annual costs.

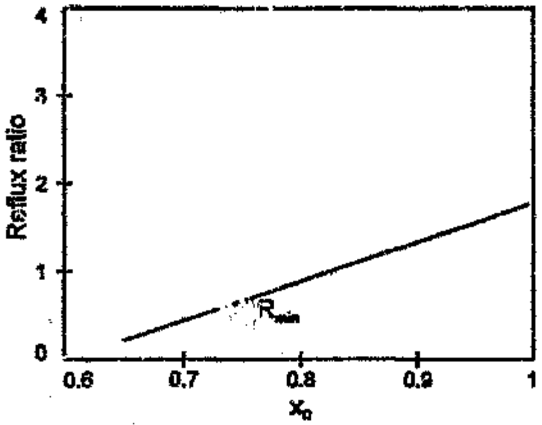


Fig. 6.13 Minimum reflux ratio for the distillation of an ideal binary mixture. x_F: 0.38, x_B: 0.10.

The number of stages required for a given reflux ratio, and for a given multiple of the minimum reflux ratio, are plotted in Fig. 6.14 and may be seen to increase with product purity. The capital costs of the column thus increase with product purity, both because of the higher minimum internal flow rates, and because of the larger number of stages required.

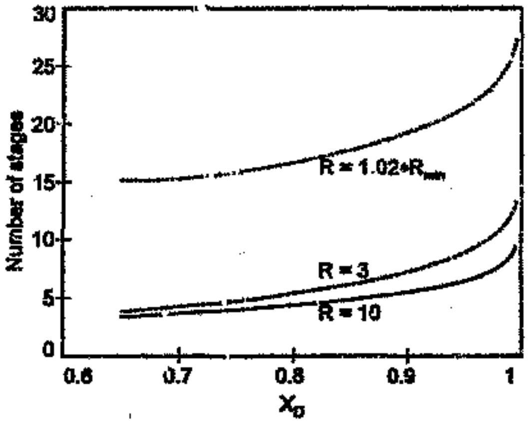


Fig. 6.14 Number of stages required for the distillation of an ideal binary mixture using three different reflux ratios. x_F: 0.38, x_B: 0.10.

A smooth curve is obtained in Fig. 6.14 when the number of stages required is plotted against product composition. It thus appears that using fractional stages is not inappropriate. It may also be observed in Fig. 6.14 that a change in reflux ratio from 3 to 10 for impure products generally gives rise to a small increase in the number of stages required, but for pure products, the number of stages required is far more sensitive to the reflux ratio used.

Two effects have been observed: the minimum reflux ratio increases with product purity, and the number of stages required increases with increasing product purity, causing both capital and operating costs to increase for a typical binary column.

Point (ii) above notes that the capacity variables follow the same trends as costs, since higher product purities are associated with higher total annual costs. Point (iii) also shows that the capacity variables follow the same trend as costs, since for optimum column operation, higher reflux ratios are required for higher product purities. Thus the capacity variables are shown to be effective cost indicators with respect to product purity.

The minimum overall capacity variables for a range of distillate compositions were obtained by minimizing the overall capacity variables with respect to reflux ratio for specified product compositions. These values are plotted in Fig. 6.15. The following is observed:

(i) The minimum overall capacity variables increase with increasing product purity.

(ii) For distillation products approaching pure component 1, which is the more volatile component, the minimum overall capacity variables increase sharply.

The first of these observations reiterates that the capacity variables follow the same trends as costs, with respect to product purity. As shown in Fig. 6.14, the number of stages required increases sharply as the product composition approaches pure component 1, leading to a sharp increase in cost. The capacity variables, which also increase sharply for nearly pure products, as noted in point (ii) above, may be seen to follow the trends in annual costs as the product purity increases.

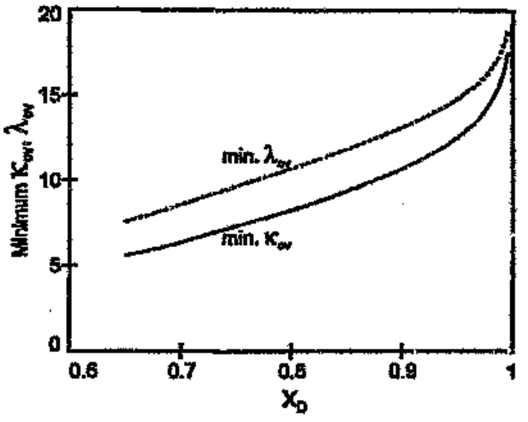


Fig. 6.15 Overall capacity variables as a function of product purity for the distillation of an ideal binary mixture. x_F: 0.38, x_B: 0.10.

The optimum reflux ratio (R_{opt}) and the ratio of the optimum reflux ratio to the minimum reflux ratio (R_{opt}/R_{min}) are plotted in Fig. 6.16 for a range of distillate product compositions. The general trend is that the optimum reflux ratio increases with product purity. The trend is not smooth, however, especially for purer products. The ratio R_{opt}/R_{min} decreases from around 3 at low product purities to values of around 1.5 for purer products. The ratio R_{opt}/R_{min} changes relatively little for purer products, but does fluctuate within this small range, especially for products approaching pure component 1.

The irregularities in the curves of optimum reflux ratio curves *vs.* product purity in Fig. 6.16 may stem from several sources. Firstly, the relationship between the number of stages required and the reflux ratio is non-linear, as it is governed by the simultaneous solution of the mass balance equations and equilibrium relationships. Secondly, it has been noted (and illustrated in Fig. 6.14) that the number of stages is more sensitive to reflux ratio at higher product purities. Thirdly, the definition of fractional stages is somewhat arbitrary, and its physical meaning is not clear; this definition may give rise to mathematical anomalies. It is not clear what causes the erratic behaviour shown in the reflux ratio curves of Fig. 6.16, but it is noteworthy that this behaviour arises even for the most ideal of distillation processes: a binary, constant relative volatility system.

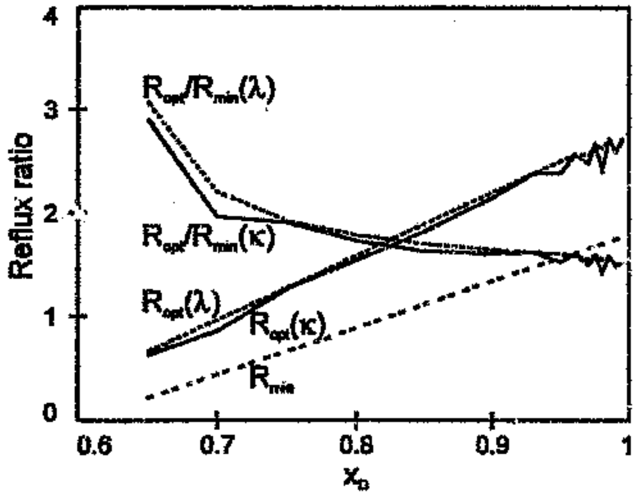


Fig. 6.16 Minimum reflux ratio, optimum reflux ratio, and R_{opt}/R_{min} as a function of product purity for the distillation of an ideal binary mixture. x_F: 0.38, x_B: 0.10.

The first of these three points will be examined in some more detail. The reflux ratio and number of stages required, for a given product and feed specification, are not independent. The number of stages required may be calculated by the simultaneous solution of the mass balance and equilibrium relationships for a given reflux ratio. As shown in Fig. 6.14, there is a smooth relationship between the number of stages, N, and the reflux ratio, R. The expressions for κ_{ov} and λ_{ov} also depend on both the reflux ratio and the number of stages required. For example, the overall boiling capacity is proportional to $(R+1)(N+1)$ for a fixed product pair. The curve of κ_{ov} *vs.* R is smooth for any particular product composition; it is the curves of the optimum reflux ratio and the associated number of stages required as a function of product purity which are not smooth. Also, the optimum reflux ratios for minimum values of κ_{ov} and λ_{ov} are sometimes identical and sometimes different from each other; the reasons for this must be similar to the reasons for the irregularities in the curves of the optimum reflux ratio *vs.* product purity.

The minimum capacity variables, optimum reflux ratios, and the numbers of stages required for a range of distillate product compositions are presented in Table C.1 in

Appendix C. It is interesting to note that the number of stages required in either the rectification or stripping section, for minimum κ_{ov} or λ_{ov}, is frequently, but not always, an integer. This result was generated by the minimization routine, for which the optimization variable was the reflux ratio and was checked using a range of methods. It is thought that the non-smooth behaviour shown in Fig. 6.16 and the occurrence of an integral number of stages in one column section are due to complex interactions between the mass balance equations and the equilibrium relationships. The underlying mathematics, which is based on the difference equations describing the column mass balance, lies outside the area of expertise of the author, so this result cannot be fully explained. This phenomenon is seen to occur for the simplest case studied -- namely, the distillation of an ideal binary mixture — as well as for all the other distillation columns studied in this chapter.

Summary

The capacity variables have been shown to follow known trends in costs associated with binary distillation processes for an ideal binary mixture, for which constant relative volatilities were assumed. The minimum overall capacity variables are seen to increase with increasing product purity, following the trends in cost for a binary distillation column. An optimum in the capacity curves, with respect to reflux ratio, was observed, which is also observed in the total annual cost curves for distillation processes. The optimum reflux ratios, with respect to capacity variables, were, in this case, approximately 1.5 times the minimum reflux ratio, that is, they were close to the heuristic optimum reflux ratio of 1.03 to 1.3 times the minimum reflux ratio. The capacity variables are thus seen to be effective cost indicators.

There are non-linear relationships between the reflux ratio and the number of stages required, both in the simultaneous solution of the mass balance and equilibrium equations, and in the form of the capacity variables. These relationships may give rise to the erratic behaviour of the optimum reflux ratio and number of stages with respect to product purity which was observed. It is noted that this behaviour occurs even for the highly idealized thermodynamics assumed here, namely constant relative volatilities and ideal vapour interactions, and for the relatively simple and well-understood binary distillation system.

6.4.2 Distillation of a non-ideal binary mixture

The distillation of a binary methyl ethyl ketone (MEK)-toluene mixture was simulated. Non-ideal interactions in the liquid phase and ideal vapour phase behaviour were assumed. The vapour pressures were described by Antoine equations, and a two-suffix Margules equation was used to describe the liquid behaviour. No azeotropes are formed by this system at the simulation pressure of 100 kPa. Thermodynamic data for this mixture are given in Table 6.1.

Table 6.1 Thermodynamic data for non-ideal binary and ternary systems.
* Antoine equation: ln([illegible] [kPa]) = $A_i - B_i/(T\,[°\mathrm{C}] + C_i)$
\# A_{12}: 0.372; A_{21}: 0.198 (Smith and Van Ness, 1987)

	A^*	B	C	$\ln\gamma$
MEK	10.736	1412	147.468	$x_2^2(A_{12} + 2(A_{21}-A_{12})x_1)^\#$
Toluene	10.829	1517	133.634	$x_1^2(A_{21} + 2(A_{12}-A_{21})x_2)^\#$
Vinyl acetate	19.076	5781	327.420	0

The overall capacity variables for this process are plotted against reflux ratio in Fig. 6.17 for a specified feed and a range of product compositions. The curves in Fig. 6.17 follow the same trends of those of Figs. 6.11 and 6.12, and of typical total annual cost curves.

The minimum overall capacity variables are plotted against distillate composition in Fig. 6.18. The same trends noted for Fig. 6.13 are observed: the overall capacity variables are seen to follow the trends in cost with respect to product purity, and to increase sharply as the product approaches pure component 1 (MEK). The non-idealities of this mixture do not fundamentally change the behaviour of the binary distillation process, which is as might have been expected.

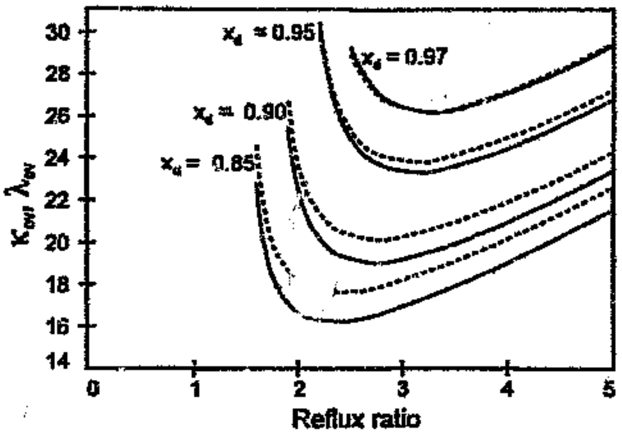


Fig. 6.17 Overall capacity variables for the distillation of a non-ideal binary mixture as a function of reflux ratio for a range of distillate compositions. x_F: 0.38, x_B: 0.05.

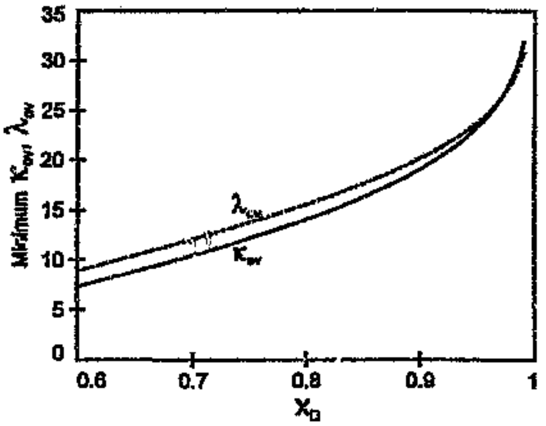


Fig. 6.18 Minimum overall capacity variables for the distillation of a non-ideal binary mixture as a function of product purity. x_F: 0.38, x_B: 0.05.

The minimum and optimum reflux ratios are plotted in Fig. 6.19. For this non-ideal mixture, the minimum reflux ratio increases with product purity, as for the ideal mixture, but the irregularities in the R_{opt} and R_{opt}/R_{min} curves are more pronounced. Possible reasons for this erratic behaviour were presented in Section 6.4.1. In this case, as in the ideal case, the ratio R_{opt}/R_{min} is larger for very impure distillate products (where R_{min} approaches zero) and fluctuates in a narrow range close to 1.5 for the purer products.

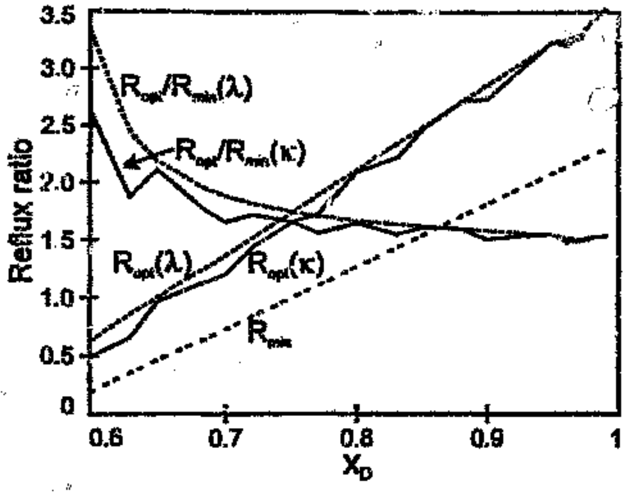


Fig. 6.19 Minimum reflux ratio, optimum reflux ratio and R_{opt}/R_{min} for the distillation of a non-ideal binary mixture. x_F: 0.38, x_B: 0.05.

The minimum overall capacity variables, optimum reflux ratio and required number of stages, for a range of distillate compositions, are given in Table C.2. In many cases, the optimum reflux ratio is associated with an integral number of stages in either the rectification or stripping section of the column. Once again, it is proposed that the non-linear interactions between the reflux ratio and number of stages cause convergence at integral numbers of stages.

Summary

When this non-ideal binary mixture is separated in a distillation column, the capacity variables follow the same trends as for the distillation of an ideal binary mixture. This supports the argument that the capacity variables are effective cost indicators.

6.4.3 Distillation of an ideal ternary mixture

The distillation of a hexane-heptane-nonane mixture was simulated using difference equations and the boundary value method. The overall capacity variables of the distillation process were investigated and are presented in this section. The thermodynamic data is based on that used by Levy *et al.* (1985). The constant relative volatility of hexane and heptane is 2.47, and of hexane and nonane is 12.67. (The value of 2.47 for hexane-heptane is derived from Levy *et al.* (1985) from the values of 2.57 for pentane-hexane and 6.35 for pentane-heptane.) The residue curve map for this system is shown in Fig. 6.20.

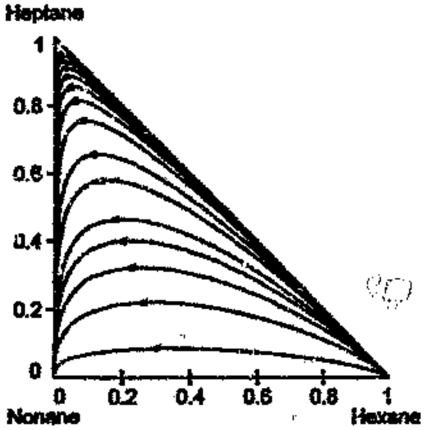


Fig. 6.20 Residue curve map for the ideal hexane-heptane-nonane system.

Using differential equations to describe column distillation, Levy *et al.* (1985) showed the minimum reflux ratio decreasing with increasing distillate purity for this system. The minimum reflux ratio was seen to approach an "absolute minimum" as the amount of nonane in the distillate product approached zero. In this work, difference equations (2.5) and (2.6) were used to model column behaviour. It is shown in Fig. 6.21 that the minimum reflux ratio decreases as the purity of the distillate increases, which agrees with the trends found by Levy *et al.* (1985). The numerical values obtained are different to those obtained by Levy *et al.* (1985), but these differences may be attributed to the slightly different hexane-heptane relative volatility (2.37) used by them, and to discrepancies between using difference equations and differential equations to model column behaviour.

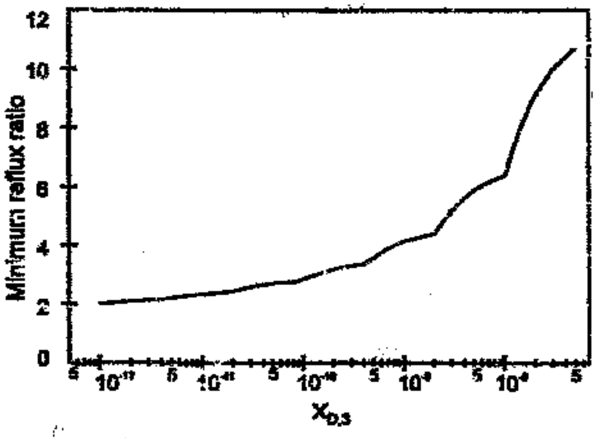
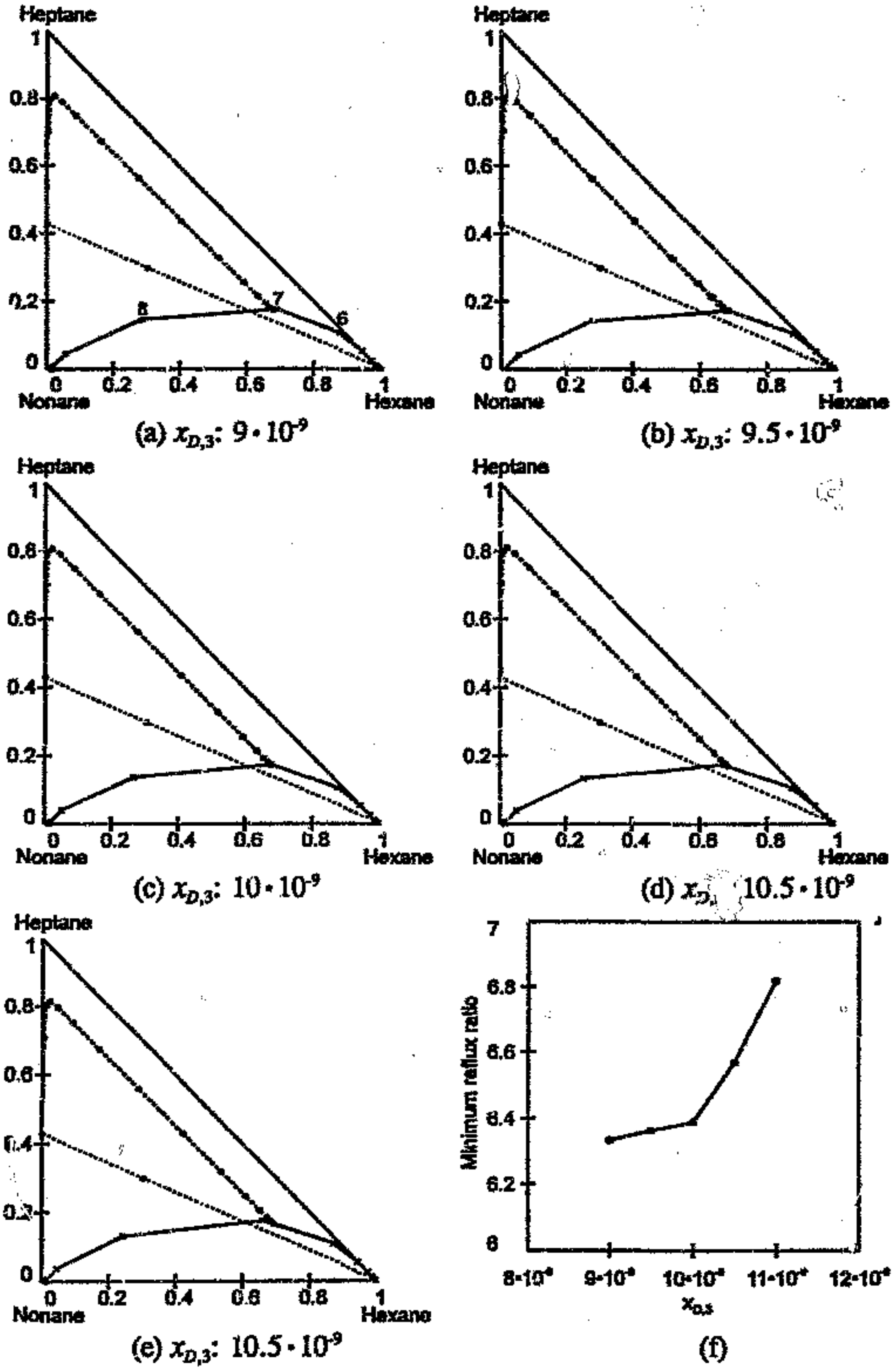


Fig. 6.21 Minimum reflux ratio for the distillation of a hexane-heptane-nonane mixture. $\bar{x}_F$: (0.30, 0.30, 0.40), $x_{B,1}$: 0.001, $x_{D,1}$: 0.999.

The relationship between R_{min} and distillate purity is not smooth. Figs. 6.22(a-e) show the column profiles at the minimum reflux ratio for fixed feed and bottoms compositions and a narrow range of distillate compositions. The stripping profiles may be seen to just touch the rectification profiles at the stripping pinch point. The pinch point of the stripping section moves from after the seventh stage to after the sixth stage of the rectification section as the purity of the distillate increases. This gives rise to a sharp change in the slope of R_{min} *vs.* $x_{D,3}$, as shown in Fig. 6.22(f). Each of the changes in slope in Fig. 6.21 may be attributed to a similar change in position of the stripping profile pinch.

The overall capacity variables were calculated for this system and are shown for some particular product specification in Fig. 6.23(a). The number of stages required in the stripping and rectification sections, as a function of reflux ratio, are shown in Fig. 6.23(b). Near to the intersection of the rectification and stripping profiles, the consecutive liquid composition points on the stripping profile lie increasingly close together as the reflux ratio decreases and approaches the minimum reflux ratio. Therefore the number of stages in the stripping profile increases sharply, as the reflux ratio decreases, until, at the minimum reflux ratio, the profiles just touch at the stripping pinch point. This explains the sharp increase in the number of stripping stages required for low reflux ratios.



(a) $x_{D,3}$: $9 \cdot 10^{-9}$

(b) $x_{D,3}$: $9.5 \cdot 10^{-9}$

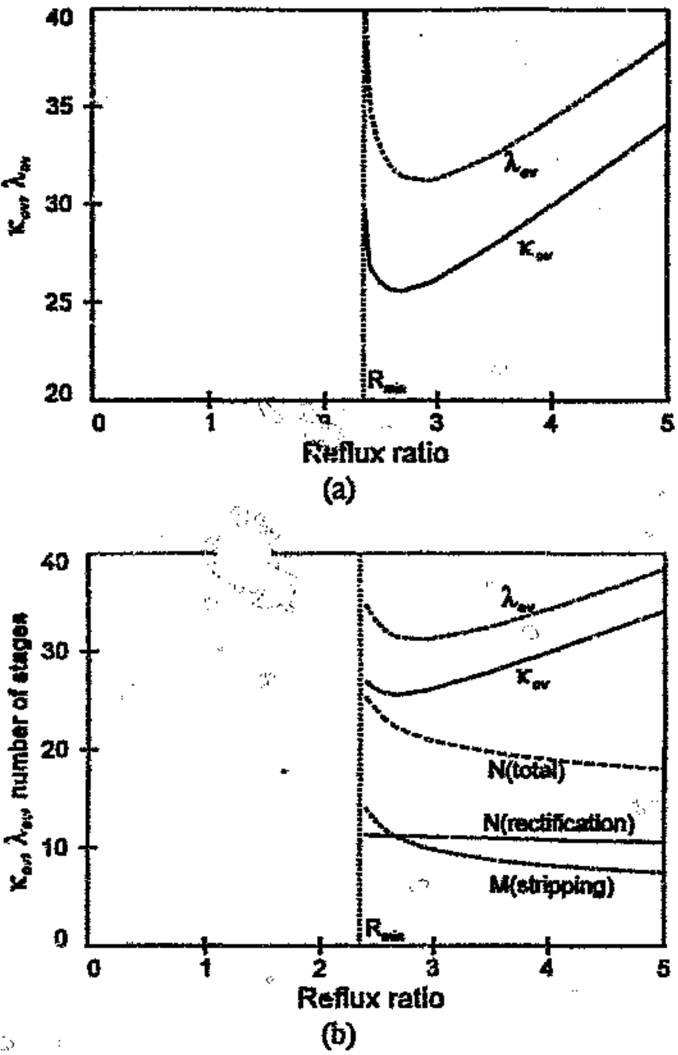
(c) $x_{D,3}$: $10 \cdot 10^{-9}$

(d) $x_{D,3}$: $10.5 \cdot 10^{-9}$

(e) $x_{D,3}$: $10.5 \cdot 10^{-9}$

(f)

Fig. 6.22 (a-e) Column profiles for the distillation of an ideal ternary mixture at the minimum reflux ratio. Stripping profile pinch point moves from after to before the seventh stage of the rectification profile. (f) Minimum reflux ratio changes sharply with product purity as a result of this change. $\overline{x}_F$: (0.3, 0.3, 0.4), $x_{B,1}$: 0.001, $x_{D,1}$: 0.999.



(a)

(b)

Fig. 6.23 (a) Overall capacity variables for the distillation of a hexane-heptane-nonane mixture. $\bar{x}_F$: (0.3, 0.3, 0.4), $x_{B,1}$: 0.001, $x_{D,1}$: $1 \cdot 10^{-11}$. (b) Number of stages required as a function of reflux ratio.

The minimum overall capacity variables were calculated for a range of distillate specifications, and are presented in Fig. 6.24. The minimum overall capacity variables follow closely the trend in R_{min} with distillate composition: minimum κ_{ov} and λ_{ov} decrease with increasing product purity and exhibit changes in slope similar to those of the R_{min} curve. That κ_{ov} and λ_{ov} decrease with product purity is a surprising result, since it suggests that annual costs decrease with product purity.

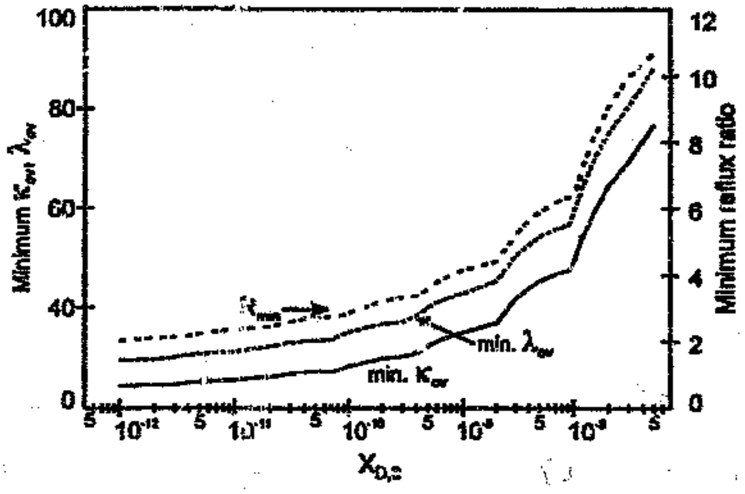


Fig. 6.24 Minimum overall capacity variables and minimum reflux ratio as a function of product purity for the distillation of a hexane-heptane-nonane mixture. $\bar{x}_F$: (0.3, 0.3, 0.4), $x_{B,1}$: 0.001, $x_{D,1}$: 0.999.

Fig. 6.25 shows that the number of stages required generally changes very little with product purity for a fixed reflux ratio. (The upper curve tends to infinity where the product specification is such that the minimum reflux ratio is equal to 3. For product compositions to the right of the asymptote, separation is not feasible at a reflux ratio of 3.) Given that the minimum reflux ratio decreases with increasing product purity and that the number of stages is almost constant with respect to product purity, it follows that costs may well decrease with product purity. The surprising result that κ_{ov} and λ_{ov} decrease with product purity does not therefore imply that the capacity variables are poor cost indicators.

In Fig. 6.24, the minimum overall capacity variables show sharp changes in slope in similar positions to the changes in the R_{min} *vs.* $x_{D,3}$ curve. These sharp changes in slope may arise through geometrical effects similar to those which gave rise to the changes in slope in the graph of minimum reflux ratio *vs.* product purity.

The optimum reflux ratios are plotted in Fig. 6.26 and may be seen to follow the same general trends as R_{min}: the optimum reflux ratios decrease with increasing product purity, but the trend is not smooth. The optimum reflux ratios for κ_{ov} lie in the narrow range of 1.05 to 1.17 times the minimum reflux ratio, and for λ_{ov} they lie in the range 1.06 to 1.28 times R_{min}. Both ranges fall within the heuristic range of 1.03 to 1.3 times R_{min}. In both cases, there is a slight general increase in the ratio R_{opt}/R_{min} with product purity, although this trend is not smooth. These irregularities may be attributed to the non-linear relationship between reflux ratio and number of stages, as discussed previously.

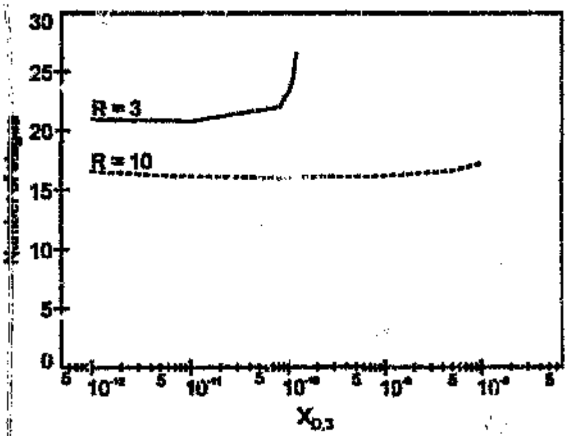


Fig. 6.25 Number of stages required as a function of product purity, for two fixed reflux ratios, for the distillation of a hexane-heptane-nonane mixture. $\overline{x}_F$: (0.3, 0.3, 0.4), $x_{B,1}$: 0.001, $x_{D,1}$: 0.999.

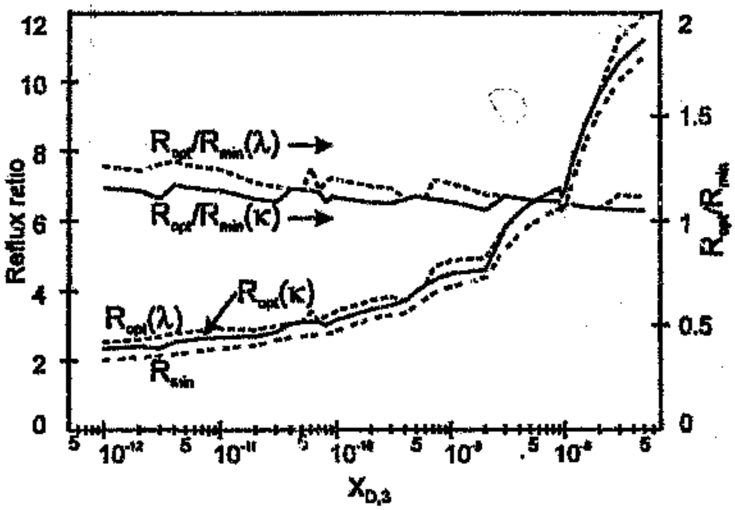


Fig. 6.26 Minimum reflux ratio, optimum reflux ratio and R_{opt}/R_{min} for the distillation of a of a hexane-heptane-nonane mixture. $\overline{x}_F$: (0.3, 0.3, 0.4), $x_{B,1}$: 0.001, $x_{D,1}$: 0.999.

The number of stages which are required for minimum κ_{ov} and λ_{ov} for a range of distillate product compositions are presented in Table C.3. It may be seen that, for every specified distillate composition, optimum column operation requires the use of an integral number of stages in either the stripping section (more usually) or the rectification section of the column. The discrete changes in the number of stages required do not seem to correspond to the discrete changes in the slope of the minimum capacity variables with product purity.

6.4.4 Distillation of a non-ideal ternary mixture

The distillation of the system methyl ethyl ketone (MEK)—toluene—vinyl acetate was simulated, and the behaviour of the overall capacity variables was examined. All three components were assumed to behave ideally in the vapour phase. Vinyl acetate was assumed to show ideal behaviour in the liquid phase, while the behaviour of MEK and toluene was described by a two-suffix Margules equation The residue curve map for this system is given in Fig. 6.27 and the thermodynamic data are given in Table 6.1. Three cases were studied for this mixture, the product specifications for which are given in Table 6.2. The mass balance lines for these cases are shown on the residue curve map in Fig. 6.28.

Table 6.2 Feed and product specifications of the non-ideal ternary distillation processes studied.

	Feed composition	Distillate composition	Bottoms composition
Case A	0.2 0.5 0.3	0.3 0.15 0.55	$x_{B,3} = 0.003 - 0.175$
Case B	0.2 0.5 0.3	0.2 0.05 0.75	$x_{B,3} = 0.01 - 0.29$
Case C	0.2 0.5 0.3	$x_{D,2} = 0.005 - 0.334$	0.2 0.75 0.05

The most volatile component is vinyl acetate. The distillate compositions may be seen to be generally rich in vinyl acetate, and the bottoms compositions are rich in the least volatile component, toluene. In Case A, as the specification of the bottoms changes along the mass-balance line, more vinyl acetate and MEK are introduced into the bottoms. In Cases B and C, the mole fraction of MEK, the intermediate-boiling component, is held constant, and the product composition is varied, so more low-boiling vinyl acetate remains in the bottoms in Case B, and more high-boiling toluene remains in the distillate in Case C.

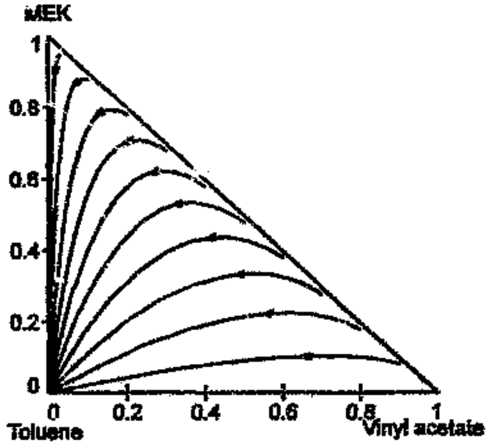


Fig. 6.27 Residue curve map for the MEK—toluene—vinyl acetate system.

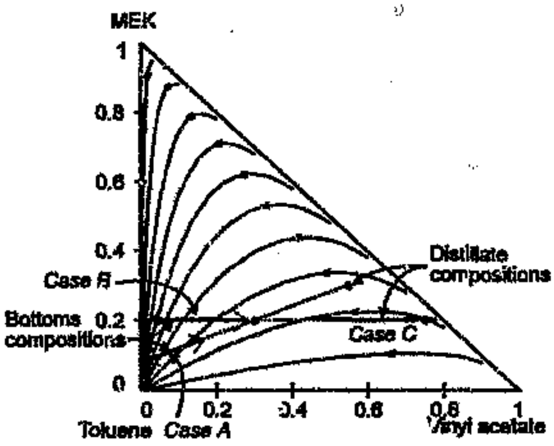


Fig. 6.28 Mass balance lines for the three non-ideal ternary distillation cases studied.

Typical overall capacity-reflux ratio curves are shown in Fig. 6.29 for two different product compositions, where the feed and co-product compositions are fixed. The overall capacity variables follow the trends in total annual costs, as was the case in Figs. 6.11 and 6.12 for the ideal binary distillation example. It may be observed that the minimum values of κ_{ov} and λ_{ov} may increase or decrease with increasing product purity, and that in all three cases the optimum value of the reflux ratio decreases with product purity. These two results seem counter-intuitive, since it would be expected that the optimum reflux ratio and process costs would increase with product purity, as they do in the case of a binary distillation column. These phenomena have been noted previously for the distillation of an ideal ternary mixture in Section 6.4.3. It is also noted that κ_{ov} may be greater or smaller than λ_{ov}.

Fig. 6.30, in which the minimum reflux ratio is presented as a function of product purity, provides some clues to why the optimum reflux ratio may decrease with product purity. In all the cases presented, R_{min} decreases with product purity. In Cases A and C, the relationship is not smooth, and in Case C it is not monotonic. The general shape of the R_{min} curve and the range of R_{min} values differ for the three cases, which is indicative of the counter-intuitive behaviour of ternary distillation systems.

The minimum reflux ratio curves end short of the feed composition in Cases A and C because limitations on product composition occur; there are maximum feasible values of $x_{B,3}$ in Case A and $x_{D,2}$ in Case C. The column profile regions for a bottoms composition close to the limiting product composition, B^*, and a fixed distillate composition are shown in Fig. 6.31(a) for Case A. Bottoms product compositions on the mass balance line closer to the feed than the point B^* are not feasible, but those further from the feed (on the left of point B^* on the same mass balance line) are feasible.

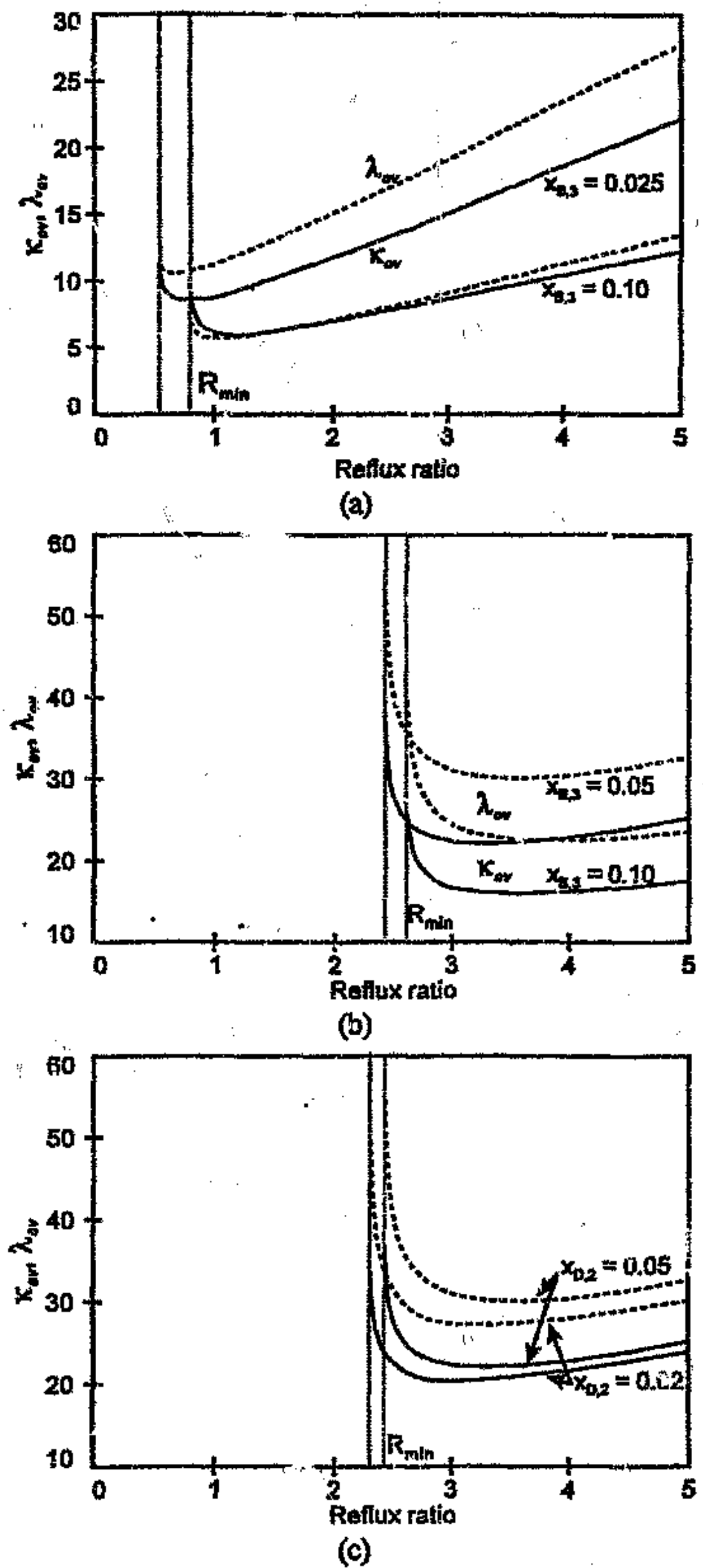
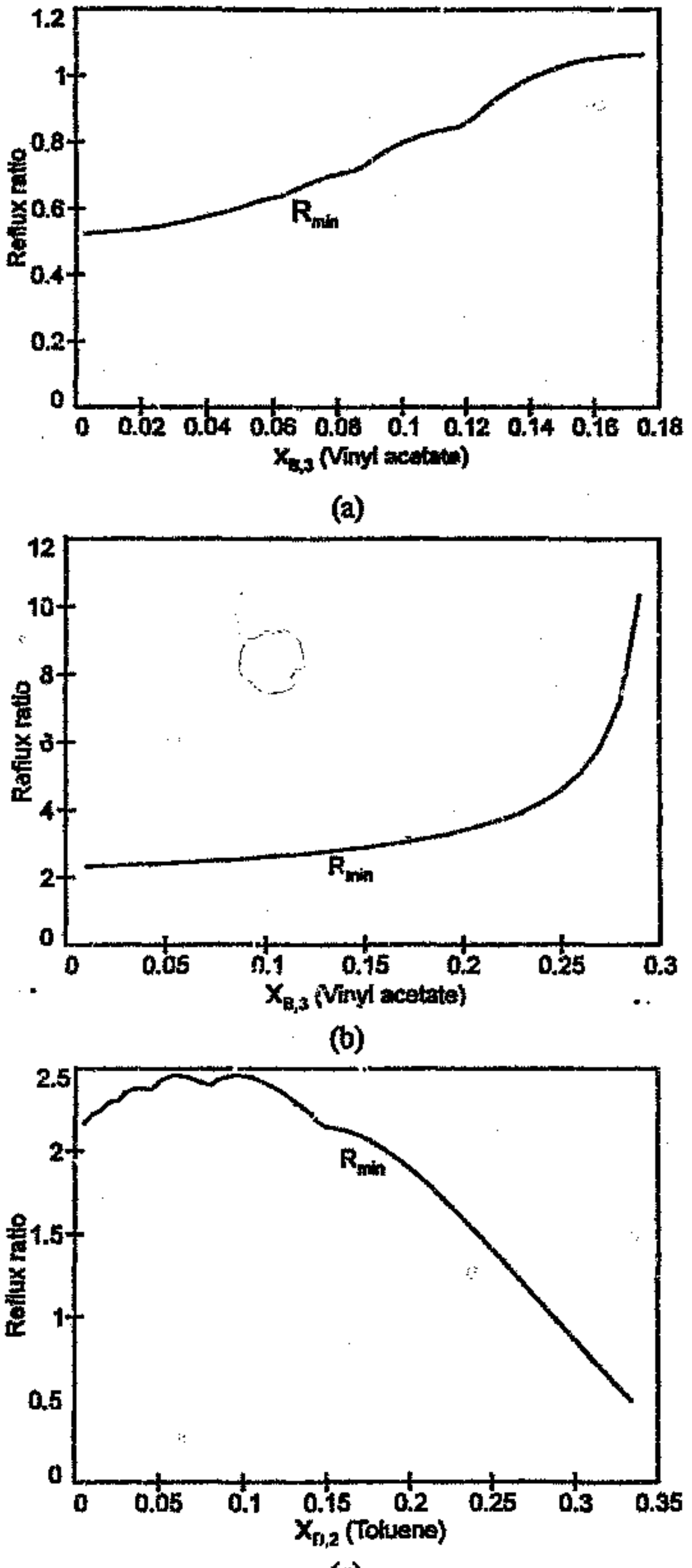


Fig. 6.29 Overall capacity variables for two product compositions, for the distillation of a non-ideal ternary mixture. $\bar{x}_F$: (0.2, 0.5, 0.3). (a) Case A. (b) Case B. (c) Case C.



(a)

(b)

(c)

Fig. 6.30 Minimum reflux ratio as a function of product purity for the distillation of a non-ideal ternary mixture. $\bar{x}_F$: (0.2, 0.5, 0.3). (a) Case A. (b) Case B. (c) Case C.

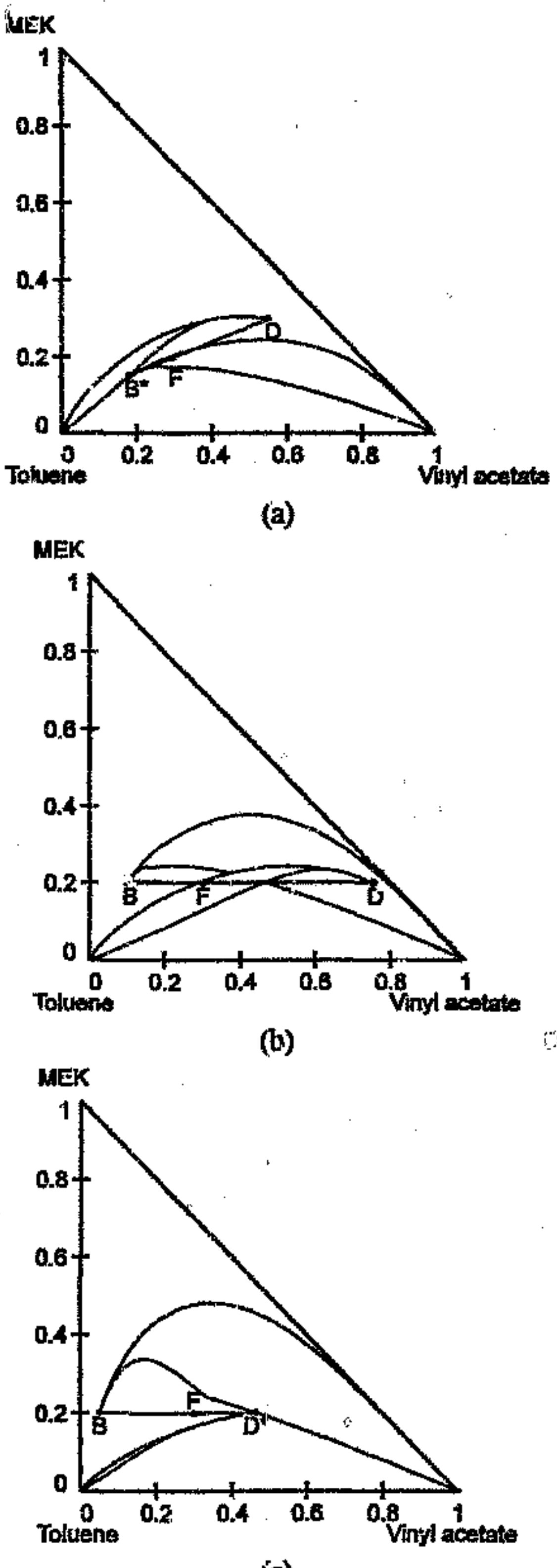
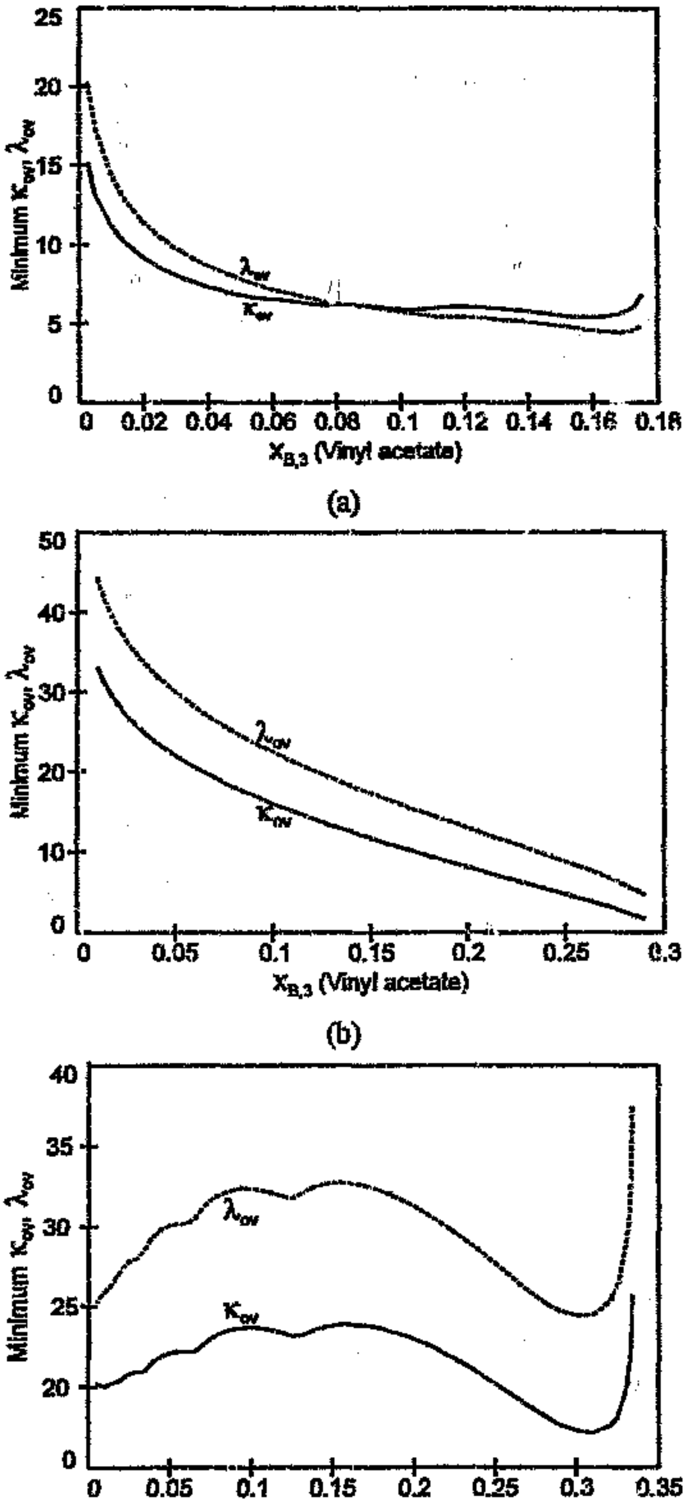


Fig. 6.31 Column profile regions. $\overline{x}_F$: (0.2, 0.5, 0.3). (a) Case A: B^* is just feasible. (b) Case B. (c) Case C: D^* is just feasible.

The boundary of the rectification profile region is given by the total reflux curve (the residue curve through D) and the reversible distillation profile (the pinch point curve through D), as discussed by Wahnschafft *et al.* (1992). The boundary of the stripping profile region is given by the residue curve and the pinch point curve through B^* and the zero-reflux profile initiated at B^*. The last of these three loci is required to close the region, since the only common point of the residue curve and the pinch point curve through B^* is the pure vinyl acetate vertex. The zero-reflux profile was not discussed by Wahnschafft *et al.* (1992). It represents the case where the liquid flowrate in the stripping section is equal to the feed flow rate. When the intersection of the rectification profile region and the stripping profile region is a single point, then the minimum reflux ratio is equal to the maximum reflux ratio, which must also be equal to the optimum reflux ratio.

Similar limitations on the product composition are observed in Case C. Fig. 6.31(c) shows the product profile regions for a distillation product which is just feasible, since the product profile regions just intersect. Distillate products on the mass balance line closer to the feed than the point marked D^* are not feasible, while those to the right of D^* and on the same mass balance line are feasible. The column profile regions for the distillate and an arbitrary bottoms composition are shown in Fig. 6.31(b). These regions may be seen to overlap easily and substantially, so that product limitations do not arise in Case B.

The minimum overall capacity variables are plotted against bottoms product purity in Fig. 6.32. In Case A, they vary smoothly, increasing sharply for very pure products, and increasing slightly for $x_{B,3}$ very close to the maximum feasible value at B^*. The minimum values of κ_{ov} and λ_{ov} vary relatively little for a wide range of bottoms compositions. For purer products, the minimum overall boiling capacity is smaller than the minimum overall boiling capacity, but around $x_{B,3} = 0.085$, the order of these two variables is reversed. The two cases presented in Fig. 6.29(a) also show how the minimum value of κ_{ov} may be greater or smaller than the minimum value of λ_{ov}.



(a)

(b)

(c)

Fig. 6.32 Minimum overall capacity variables for the distillation of a non-ideal ternary mixture. $\overline{x}_F$: (0.2, 0.5, 0.3). (a) Case A. (b) Case B. (c) Case C.

In Case B, Fig. 6.32(b) shows that the minimum values of κ_{ov} and λ_{ov} increase smoothly as the product purity increases, and for very pure distillate products, these variables increase sharply. However, in Case C, the minimum overall capacity variables decrease sharply as the product purity increases from the limiting composition at $D*$, and then generally increase and then decrease with increasing product purity, as shown in Fig. 6.32(c). These general trends are interrupted by local changes in the slopes of the curves. The decrease in the minimum overall capacity variables as the mole fraction of toluene decreases is rather surprising, but was also observed for the ideal ternary distillation process. The sharp increase in κ_{ov} and λ_{ov} for products approaching B^* in Case A ($x_{B,3}$ = 0.176) and D^* in Case C ($x_{D,3}$ = 0.334) will be seen to be the result of operating close to R_{min}.

The minimum and optimum reflux ratios for the feasible range of product compositions are given in Fig. 6.33. In Case A, optimum reflux ratios, corresponding to minimum κ_{ov} and λ_{ov}, vary between 0.64 and 1.45, which is a relatively narrow range. Optimum reflux ratio values generally decrease with increasing product purity, following the general trends in R_{min}, but close to the limiting product composition, $B*$, this trend is reversed. At B^* the optimum reflux ratio is equal to R_{min}.

Therefore the ratio R_{opt}/R_{min}, which is plotted in Fig. 6.33(a), tends towards unity for products approaching $B*$, but otherwise displays no particular trend with product composition. The average of the values of the ratio R_{opt}/R_{min} fall within the heuristic range, but some individual values do not. The irregularities in the R_{opt}/R_{min} curve for κ_{ov} and λ_{ov} are quite different from each other: changes in slope do not occur at similar product compositions, increases in R_{opt}/R_{min} for κ_{ov} may be matched by decreases in R_{opt}/R_{min} for λ_{ov}, and the magnitude of change is generally greater for κ_{ov} than for λ_{ov}.

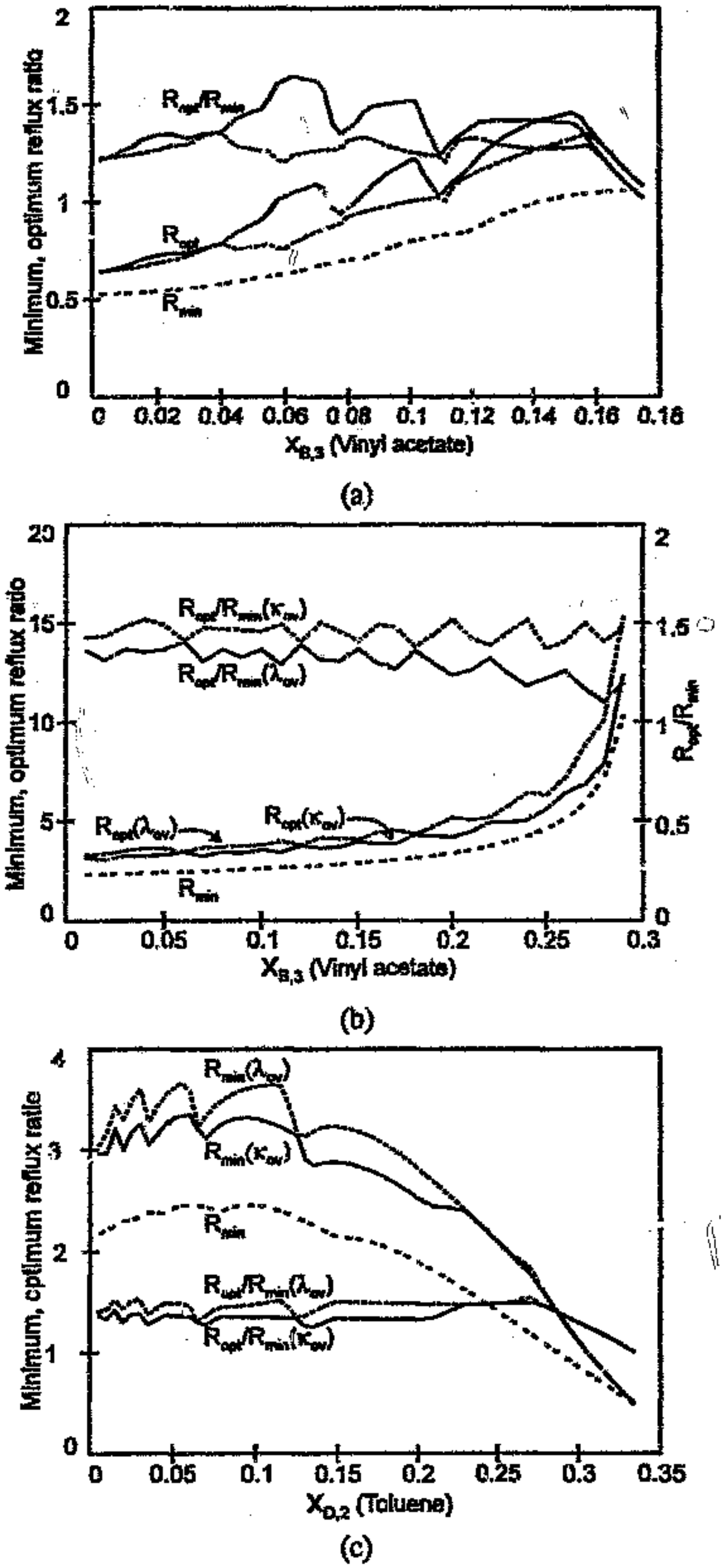


Fig. 6.33 Minimum reflux ratio, optimum reflux ratio and R_{opt}/R_{min} as a function of product purity. (a) Case A. (b) Case B. (c) Case C.

In Case B, as shown in Fig. 6.33(b), the optimum reflux ratios decrease as the product purity increases, following the trend of the minimum reflux ratio. The optimum reflux ratio curves are uniformly not smooth. For both κ_{av} and λ_{av}, the ratio R_{opt}/R_{min} generally fluctuates around the average value of R_{opt}/R_{min} (*i.e.*, in the range of 1.10 to 1.52 times R_{min}) which is close to the heuristic range. The optimum reflux ratios roughly follow the trends in R_{min} as the product purity increases in Case C. R_{opt} generally increases with product purity, and for purer products, the optimum reflux ratios fluctuate within a narrow range. The ratio R_{opt}/R_{min} is generally around 1.3 for κ_{av} and around 1.4 for λ_{av}, except for products approaching D^*, where the ratio decreases and approaches unity.

In all three cases, the optimum reflux ratios for κ_{av} and λ_{av} are independent of each other, as discussed for the ideal binary distillation case in Section 6.4.1. Likewise, in all three cases, the optimum reflux ratio curves exhibit pronounced irregularities similar to those reported for other distillation systems.

The minimum capacity variables, optimum reflux ratios and number of stages required for a range of bottoms product specifications are given in Tables C.4A to C. For some choices of product composition, one or both of the capacity variables are minimised when an integral number of stages is used in either the stripping or the rectifying section of the column. Some of the fluctuations in the optimum reflux ratio appear to be associated with changes in the number and position of the integral stages for minimum κ_{av} or λ_{av}.

In Case A, as shown in Fig. 6.34(a), the relationship between changes in the slope of κ_{av}, particularly, or λ_{av}, and the number and position of the integral stages in the column may be seen. However, not all fluctuations can be linked to changes in the number and position of integral stages in the column. In Case B there is no clear relationship between the change in number and position of the integral stages and the irregularities in the optimum reflux ratio curves. It is shown in Fig. 6.35(b) that in Case C the changes in the optimum reflux ratio for κ_{av} follow closely changes in the number and position of the integral stages. However, only some of the fluctuations in the optimum reflux ratio for λ_{ov} can be loosely linked to the changes in the number and position of integral stages.

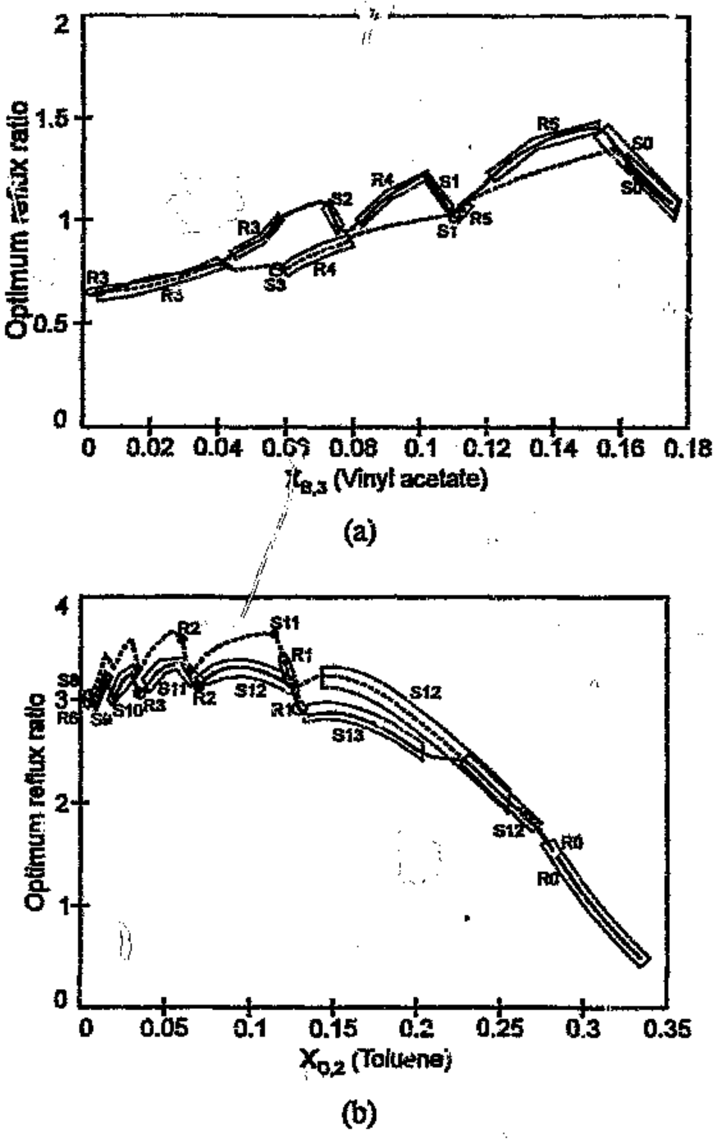


Fig. 6.34 Optimum reflux ratio for the distillation of an non-ideal ternary mixture. Integral number of stages required in the rectification (R) or stripping (S) section are marked. — κ_{ov}, -- λ_{ov}. (a) Case A. (b) Case C.

In Fig. 6.35, the total number of stages required, corresponding to the minimum overall capacity variables, are plotted as a function of product composition. In Case A, the number of stages increases sharply for products close to the extreme feasible compositions: that is, as $x_{B,3}$ approaches 0 and 0.18. For intermediate product compositions, the total number of stages varies relatively little. In Case B, the total number of stages in the column increase as the product purity increases, although this trend is not smooth. In Case C, the number of stages varies little, but not smoothly, for both minimum κ_{ov} and minimum λ_{ov} as the product purity increases. However, as the distillate specification approaches D*, the number of stages required increases sharply. In all cases, the irregularities in these curves are related to those in the optimum reflux ratio curves, illustrated in Fig. 6.33, since the capacity variables relate the reflux ratio and the number of stages required.

Summary

The overall capacity variables for the distillation of a non-ideal ternary mixture were studied for three sets of product specifications. All the overall capacity-reflux ratio curves followed known trends of annual costs as a function of reflux ratio, showing the capacity variables to be useful cost indicators with respect to reflux ratio.

All three cases showed R_{min} decreasing with increasing product purity, not necessarily smoothly. This trend is somewhat unexpected, but is the same as the trend demonstrated for the ideal ternary (constant relative volatility) system. The geometries of the column profiles are responsible for this trend, as well as for the changes of slope in the R_{min} curve. In Case C, R_{min} as a function of product purity is not a monotonic function.

The minimum overall capacity variables increase smoothly and sharply with product purity for very pure products in Cases A and B, but decrease in Case C. Where there are limitations on product composition (in Cases A and C) the minimum overall capacity variables increase as the product composition approaches the limiting composition. In Case A, κ_{ov} and λ_{ov} increase only by a small amount near to the limiting bottoms composition. Cases where κ_{ov} is greater than λ_{ov}, and where κ_{ov} is smaller than λ_{ov}, have been observed.

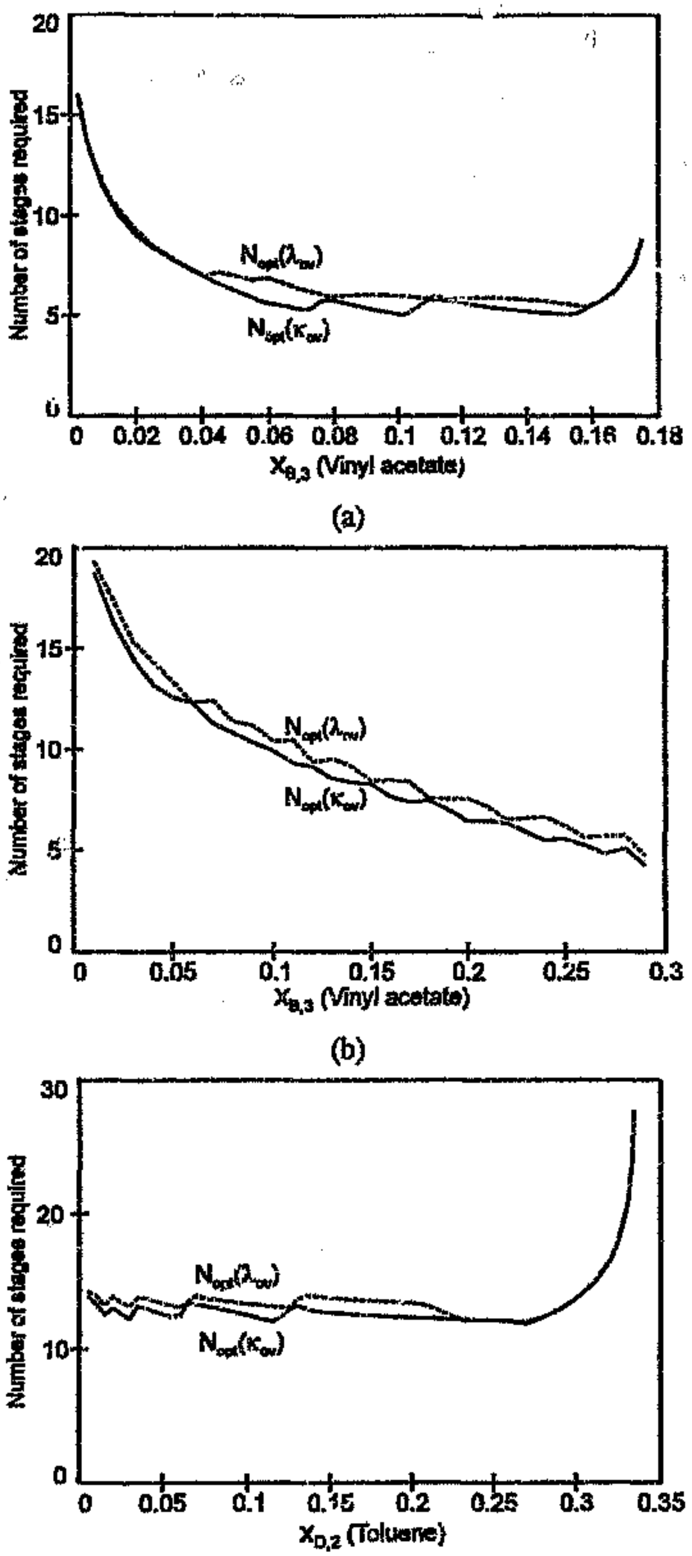


Fig. 6.35 Optimum number of stages required as a function of product purity for the distillation of a non-ideal ternary mixture. (a) Case A. (b) Case B. (c) Case C.

The ratio of the optimum reflux ratio to the minimum reflux ratio, R_{opt}/R_{min}, was plotted in the three non-ideal ternary cases considered. In all cases, the values of R_{opt}/R_{min} lay close to the heuristic range and did not exhibit any distinct general trends. This indicates that κ_{ov} and λ_{ov} agree with distillation experience and optimization heuristics: that the ratio R_{opt}/R_{min}, which lies in a narrow range, is relatively insensitive to feed and product compositions and system thermodynamics. The optimum reflux ratio curves always show some irregularities, as they did for the ideal binary case.

A number of strange and "counter-intuitive" features have been observed for the distillation of a non-ideal ternary mixture. In Chapters 2 and 4, it has been argued that present understanding of distillation is not as developed as it might be. It is asserted that the phenomena which have been observed are features of the distillation process, rather than introduced by the capacity variables.

6.4.5 Summary of results for column distillation

Binary and ternary systems, both ideal and non-ideal, have been investigated regarding the behaviour of their overall capacity variables for distillation processes. A small number of cases have been presented, and few common trends have been observed. It is therefore not possible to draw general conclusions about the overall capacity variables for distillation. Several questions have been raised for which answers are not yet available.

It has been argued that κ_{ov} and λ_{ov} are cost indicators, from the forms of eqs. (5.46) and (5.47). For the binary columns studied, it is clear that these proposed cost indicators do indeed follow the known trends in cost for binary distillation. The costs and feasible products of ternary columns are not as well understood. Some evidence has been used to show that the behaviour of κ_{ov} and λ_{ov} agrees with distillation practice.

The minimum reflux ratios for a range of systems and product specifications have been presented. It is clear from the R_{min} *vs.* product compositions curves that column operation changes with the system thermodynamics and product specifications. Given that the minimum reflux ratio curves change with product specification, it is to be expected that trends in κ_{ov} and λ_{ov} also change with product specification. That the behaviour of the minimum reflux ratio as a function of product composition is often "counter-intuitive" indicates that our intuition may not always be adequately developed. The forms of eqs. (5.46) and (5.47) relate the capacity variables to internal flow rates and number of stages, and thus to both operating and capital costs. The observed anomalies must be introduced by unexpected relationships between flow rate, number of stages and product composition, rather than by the capacity variables.

Limitations in feasible products for a given mass balance line also appear to be associated with increased capacity variables. This is contrary to general expectation: surely it is always cheaper to achieve less separation than more separation? Limiting product compositions most often arise under limiting conditions of distillation (Wahnschafft *et al.*, 1992), for example, total reflux, or operation at a pinch point. These limiting conditions are associated with high costs. This would seem to confirm that it is not necessarily cheaper to relax product specifications.

It has been shown here and previously (for example, by Laroche *et al.*, 1992a) that ternary distillation columns display some "curious" effects. It is proposed that the strange behaviour of the overall capacity variables merely reflects the behaviour of ternary distillation columns. It is likely that more such effects would be displayed by azeotropic systems, which have not been considered in this study.

The irregularities in the curves depicting the optimum reflux ratios and optimum number of stages are not fully explained. The fact that they appear for the simplest possible distillation case — namely, for an ideal (constant relative volatility) binary mixture — would seem to indicate that they are a property of the minimum overall capacity variables for distillation. The algebra involved in the simultaneous solution even for an ideal binary distillation column, is based on difference equations and is highly non-linear, and may be responsible for the apparently erratic behaviour of the optimum reflux ratios.

6.5 Conclusions

In Chapter 3, the sets of feasible products of a ternary system separated by two flash stages arranged in series and in parallel were compared. It was proposed that, for some product specifications, the serial arrangement of two flash stages costs less than the refluxed arrangement, and *vice versa*. It has been illustrated here that, likewise, some products which are feasible by both processes are associated with lower overall capacity variables for one process than for the other. The capacity variables have been shown, in this example, to allow the quantitative comparison of alternative separation processes.

This work has presented some examples showing how alternative separation processes may be compared, illustrating that the capacity variables are useful tools for process synthesis. For example, some products of the refluxed arrangement of two flash stages are associated with lower capacity variables than the serial arrangement, and some with higher capacity variables. It is not known what determines which process will be the most cost-effective. It has not been possible to generalize these observations and thereby develop rules for predicting which process will be associated with the lowest capacity variables for a given set of specifications.

It would be desirable to construct a region of feasible products in composition-capacity space for the distillation of a particular feed. The capacity-product composition curves of Fig. 6.32, for example, would lie on such a surface. Each of these curves is associated with a particular co-product; the difficulty is representing both the set of feasible products and the fixed co-product. Resolution of this problem would enable the process synthesis questions about what the total region of feasible products is, and where the local or global minima are in the cost surface, to be answered. However, even the composition space answers to these questions are not yet available; nor is it possible at this stage to generate a region in composition-capacity space of all possible distillation products of a given process feed.

The capacity variables of binary distillation processes have been considered in this study. Binary distillation processes are well understood, and the capacity variables have been shown to follow closely the trends in costs, both with respect to reflux ratio and product purity. Furthermore, costs and the capacity variables exhibit similar behaviour, in that a flat optimum may be observed for both.

Ternary distillation processes were also considered in this study. The costs and other operating trends (such as minimum reflux ratio as a function of product purity) of ternary distillation processes are not as well understood as those for binary distillation processes. It is argued that the capacity variables are effective cost indicators for ternary distillation systems, and that the "counter-intuitive" behaviour of κ_{ov} and λ_{ov} and the optimum reflux ratio is more a reflection of ternary distillation phenomena than an indictment of the capacity variables. The capacity variables are sensitive to the system thermodynamics and product specifications; this allows a process to be optimized specifically, rather than by using the very general heuristic optimization rules.

Process costs and the capacity variables are sensitive to product purity. Product purity is therefore an important optimization variable. The product specifications for a process should not be set too rigidly during flowsheet synthesis without considering their impact on process costs.

Results for both the boiling capacity and the condensing capacity are presented in this chapter. Both variables cannot be optimized simultaneously, since they are defined independently. Both variables are required, since both boiling and condensing processes have their costs. It is not yet completely clear what role each variable would play in the evaluation of a process. It is proposed that process synthesis decisions be made once information about both overall capacity variables have been calculated. These decisions would be based on the variable which dominates process costs. For example, if steam is the heating utility and cooling water the condensing utility, one would generally be more concerned with minimizing the boiling capacity; where refrigerants are used, the condensing capacity may be of greater interest. For distillation columns, both minimum capacity variables occur at similar reflux ratios and the capacity curves have flat minima with respect to reflux ratio in the region of the optimum reflux ratios: in this case, process synthesis decisions are not very sensitive to which optimization variable is selected.

Chapter 7

Conclusions

7.1 Introduction

In the synthesis of a separation process, the process design engineer is concerned with the range of product compositions that a particular choice of equipment may achieve, and with the cost-effectiveness of the processes being considered. The feasible products of separation processes and the assessment and comparison of flowsheet alternatives have been discussed in this work. This study has considered the vapour-liquid equilibrium (VLE) separation of ternary, homogeneous, non-reacting mixtures in constant pressure processes.

7.2 Composition of feasible products

Previous work on the feasible products of VLE separation processes has focused on column distillation, which is the most common of these processes. Some ambiguities and simplifications in past work have limited the general applicability of the solutions which were found. Boundaries of regions of feasible products were found to arise through processes which are only possible in the limit, such as very sharp splits, total reflux and reversible operation. The costs associated with these boundary points are therefore infinite. It is a limitation of composition space that process costs and product quantities are not explicitly represented.

Processes comprised of any number of simple distillation, simple condensation and mixing stages were examined for the region of feasible products. The product region of these processes was found to be the entire composition space. An important conclusion is that the products of VLE separation processes are not intrinsically restricted; limitations arise from the specific choice of separation equipment.

The product region of processes comprised of one or two flash stages and mixing were investigated. Three configurations of two flash stages were studied, namely two flash stages in parallel, in series, and in series with reflux (which is effectively a two-stage distillation column). It was found that the serial arrangement of two flash stages could achieve some product compositions which lie outside the region of feasible products of the refluxed configuration of two flash stages, and *vice versa*. Furthermore, the costs associated with achieving some particular product by the refluxed arrangement were estimated to be far greater than those of the serial arrangement. It was concluded that the two-stage distillation column is not inherently better than other two-stage VLE separation processes in terms of both composition and cost. It appears that a flexible approach to the choice of VLE separation equipment may be of benefit in the synthesis of processes.

7.3 Optimization of separation processes

An objective function for the assessment of the cost-effectiveness of alternative separation flowsheets was required. Previous research on the optimization of distillation columns showed that total annual cost, incorporating both capital and operating costs, is a suitable objective function.

The main optimization variable used previously for the optimization of distillation columns is the reflux ratio. The optimum reflux ratio is generally accepted as lying in the range of 1.03 to 1.3 times the minimum reflux ratio. This heuristic rule provides a simple alternative to full costing for the optimization of processes. The rule is well established for binary distillation columns, and it has been shown to hold for some examples of ternary separation which have been presented in the literature. However, it is not clear that it is generally applicable to multi-component separations.

The vast majority of the research done previously into the optimization of VLE separation processes has focused on column distillation. The heuristic rule for the optimization of distillation processes, which concerns reflux ratio, is not applicable to other separation processes. Short of costing processes fully, simple techniques for assessing cost which accommodate a range of VLE separation processes do not appear to exist.

7.4 The capacity variables

The capacity variables were defined for an equilibrium stage, and the definition was extended to overall capacity variables for processes comprised of one or more such stages. These overall capacity variables were investigated for their suitability as cost indicators. The criteria for cost indicators are that they should apply to a wide range of VLE separation processes, that both boiling and condensing costs should be accommodated, and that both capital and operating costs should be incorporated.

Two separate capacity variables were defined, one for boiling and one for condensing. For the range of steady-state VLE separation processes considered, consistent results are obtained for the overall capacity variables; that is, the equations for calculating the overall capacity variables are of the same form in each case. It was argued that the capital and operating costs of the process are incorporated by the overall capacity variables.

The overall capacity variables of a number of separation processes were calculated. The capacity variables of binary distillation columns were found to exhibit similar features to the total annual costs of these processes with respect to reflux ratio and to product purity. For the distillation columns studied, flat optima were observed in the capacity variables with respect to reflux ratio, as has also been previously shown to be the case for the process costs of distillation columns. The optimum reflux ratios, giving rise to minimum overall capacity values, were found to be close to the heuristic range. Product compositions close to the boundary of the region of feasible products were characterized by higher overall capacity variables, reflecting that points on the boundaries of product regions are attainable only under limiting conditions, and hence at high cost.

The overall capacity variables were thus found to fulfil the criteria for cost indicators of VLE separation processes. That they are simple to calculate and have a physical interpretation further advances the case that they may be used as tools for process synthesis and optimization.

In order to calculate the overall capacity variables of distillation processes, the difference equations describing the mass balance of the column and the equilibrium relationships must be solved simultaneously. Even for distillation columns separating ideal binary mixtures, some apparently erratic trends in the optimum reflux ratio with respect to product purity have been observed. The overall capacity variables are often minimized for an integral number of stages in one section of the column. The physical meaning, effects on cost, and mathematical consequences of using fractional stages are not completely clear. This work has observed how the overall capacity variables behave but has not completely analyzed the mathematics governing them.

Ternary distillation columns are well known to behave quite differently to binary columns. The forms of the equations giving the overall capacity variables as a function of reflux ratio and number of stages agree with our understanding of the costs of distillation. However, some strange, or counter-intuitive, trends have been noted in the relationships between the overall capacity variables and product purity. That costs of ternary distillation may decrease with increasing purity of one of the products is not known to have been reported previously. The unexpected results for ternary distillation columns may be an obstacle to the acceptance of the overall capacity variables as cost indicators, but follows logically from the column behaviour (minimum reflux ratio, optimum reflux ratio and optimum number of stages) with increasing product purity.

7.5 The overall capacity variables as tools for process synthesis

It is proposed that the overall capacity variables could prove useful tools for process synthesis and optimization. Since they may act as indicators of process cost, alternative column configurations and separation flowsheets may be evaluated and compared at the initial stages of process synthesis. Two separate variables have been defined. It is not completely clear how the pair of variables will be used to make process synthesis decisions. It is anticipated that one overall capacity variable will be more relevant to the particular process being considered (when, for example, boiling costs are far greater than condensing costs), or that one will be far greater than the other (when either boiling or condensing predominates), or that the overall capacity variables will be fairly evenly matched (as was often the case for the distillation columns studied), so that decisions may be based equally well on either variable.

It is clear from this work that the product composition may have a large effect on the minimum process costs of distillation, as indicated by the minimum overall capacity variables. It would be useful to construct a pair of minimum cost surfaces for a given feed in composition-capacity space. This would enable a more general examination to be made of the effects of product composition on process costs, since compositions would not be restricted to a single mass balance line. However, co-product composition must also have an impact on the overall capacity variables of distillation processes. There is thus no unique minimum cost or pair of minimum overall capacity variables associated with a product of a particular composition. Consequently, a unique pair of cost surfaces cannot be constructed.

It has been noted previously that composition space and composition-capacity space do not explicitly provide information about product quantities. In particular, it is not always apparent that some product is of zero quantity. This limitation would exist even if cost surfaces could be constructed. However, this information may be obtained by applying the lever arm rule.

Information about process costs may nevertheless be simply obtained for any specified pair of feasible products, and changes in cost may be observed with changes in reflux ratio, changes in product specifications or changes in feed composition. This allows the comparison of different flowsheet alternatives. For example, different column configurations, such as direct and indirect splits, may be compared. Different choices of entrainer may be compared, to an extent, since different entrainers will be associated with different optimum reflux ratios and associated number of stages and hence different costs. The quantity of entrainer to be added to a binary azeotrope may be varied, and the impact of the composition of the feed to the column on process costs may then be examined using the capacity variables.

7.6 Mean residence time: A capacity variable for processes involving reaction

The capacity variables of a separation process are analogous to the mean residence time of a process involving reaction. Mean residence time has become accepted as a cost indicator of such processes, because it is related to the size of the reactor required for a given feed flow rate, and because reactor volume dominates the costs of these processes. Different types and configurations of ideal reactors may be compared using mean residence time. For example, configurations of plug flow and continuous stirred-tank reactors arranged in series, in parallel and in complex series-parallel-recycle configurations may be compared. This facilitates the initial evaluation of process flowsheet alternatives during process synthesis.

Mean residence time is sensitive to the extreme operating conditions of equilibrium. Typically residence time (or the reactor volume required) increases sharply with conversion as the reaction approaches equilibrium. Thus, equilibrium gives a limit on the compositions which may be achieved by a process involving reaction, but mean residence time indicates what conversions may be practically achieved, and what the additional costs are of improving conversion by some amount.

Mean residence time is a useful tool, allowing alternative flowsheets to be evaluated and compared at the early stages of process synthesis. This variable has its shortcomings. For example, while the residence time might recommend the use of a stirred-tank reactor for the given system kinetics and process feed, this is not necessarily a practical solution for gas-phase reactions. Mean residence time cannot distinguish between vessels operating at high and ambient pressure; residence time does not accommodate different materials of construction; residence time does not incorporate costs of heating or cooling the feed or products of reaction. Mean residence time is not well-suited to indicating the costs of non-ideal reactors. In spite of these and other deficiencies, mean residence time has been accepted as a cost indicator and has proven useful in the synthesis of optimal flowsheets.

Mean residence time emerges naturally from the mass balance equations describing ideal reactors, obviating the need for complex costing calculations. This variable is a "capacity variable", in that it is a measure of the physical size or capacity of the reactor or sequence of reactors required. It is the ratio of the reactor volume to the volumetric flow rate of the feed, and thus has a physical interpretation, which aids the intuition of the design engineer.

7.7 Closing comments

A need for cost indicators for VLE separation processes has been shown to exist. In this work, a pair of new variables have been introduced, and some ideas concerning their use in process synthesis and optimization have been developed. The overall capacity variables have been proposed as useful tools for process synthesis in the light of the results for a number of binary and ternary distillation examples, as well as for a range of other separation processes. However, how these cost indicators behave is not yet understood at a fundamental level. Some of the issues which could be addressed in further work are noted below.

General rules about the behaviour of the minimum overall capacity variables with respect to product compositions are not known. It is not known what controls, for example, where the cost surfaces of two flash stages arranged in series and of two flash stages arranged in series with reflux intersect. Therefore, rules cannot be developed to describe the conditions under which it is more cost-effective to use the serial arrangement than the refluxed arrangement. It is not known what governs whether, for a sequence of two distillation columns, a direct or an indirect split is more cost-effective, nor is it known under what conditions the use of more complex columns and configurations of columns would be beneficial. The overall capacity variables of more complex columns (for example, with more than one feed, or with more than two products, or either without reflux or without reboil) have not been determined. Capacity variables for heterogeneous systems have not been defined.

A pair of new variables have been introduced in this work, arising out of a need to compare various separation processes without costing them fully. These new cost indicators have been explored theoretically and numerically. The capacity variables of a number of examples of simulated VLE separation processes have been presented and are shown to follow known trends in process costs. The foundations for a new tool for process synthesis and optimization have been laid.

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Appendix A

Transformation of Cost Functions to a Common Basis

The original form of the cost correlation may be expressed in terms of the number of stages, N, and the vapour flow rate, V, as presented in Table 4.2.

A.1 McCabe and Smith (1956)

Column cost is approximately proportional to the total plate area (which is the product of the number of plates and the cross-sectional area per tray). The tray cross-sectional area is approximately proportional to the vapour flow rate, *i.e.*, the diameter is proportional to $V^{½}$. Thus the column cost is approximately proportional to the product of the number of stages and the vapour flow rate:

$$C_{col} \propto NV \tag{A.1}$$

Utility costs increase with reflux ratio. The total cost is the sum of the column costs and the utility costs. Utility capital costs are not explicitly considered.

A.2 Nishimura and Hiraizumi (1971)

$$\begin{aligned} \text{TAC} &= a'(\text{column volume}) + b'(\text{heat duty}) \\ &= a''(N+2)\cdot(\text{cross sectional area}) + b'Q \\ &= a''(N+2)cV + b'V(\Delta \text{H}_{vap}) \\ &= [a(N+2) + b]V \end{aligned} \tag{A.2}$$

where the Q is the heat duty, ΔH_{vap} is the heat of vaporization of the mixture, which is taken as constant. The cross sectional area is proportional to the vapour flow rate (*i.e.*, the column diameter is proportional to $V^{½}$).

A.3 Malone *et al.* (1985)

Using the annualized capital cost correlation from Guthrie (1969):

$$\text{TAC} = C_o N^{0.82} V^{0.53} + C_1 V^{0.55} + C_2 V \tag{A.3}$$

since column height is proportional to the number of stages, N, and column diameter is proportional to $V^{½}$.

Linearizing the above equation, they obtained:

$$\text{TAC} = C_o + k_1 N + k_2 V \tag{A.4}$$

and found $k_1/k_2 = 0.1$ to 0.4, *i.e.*, that the TAC is more strongly dependent on the vapour flow rate in the column than on the number of stages in the column.

A.4 Fisher *et al.*, (1985a)

Using the correlations of Guthrie (1969), and assuming that the cost correlation for the column shell includes the cost of internals:

$$C(\text{column}) \propto N^{0.802} V^{0.533} \tag{A.5}$$

since the column diameter is assumed to be proportional to the square root of the vapour flow rate.

Therefore:

$$\begin{aligned} \text{TAC} &= C(\text{column}) + C(\text{heat exchangers}) + C(\text{utilities}) \\ &= aN^{0.802} V^{0.533} + bV^{0.65} + cV \end{aligned} \tag{A.6}$$

A.5 Cheng and Liu (1988)

Citing Rathore *et al.*, 1974:

$$dia \quad = \quad 1.7057\,(R + 1)D\,T/(vp) \tag{A.7}$$

where *dia* is the column diameter, T is the dew-point temperature of the vapour stream leaving at the top of the column in Kelvin, $(R+1)D$ is the vapour flow rate in the column and v is the vapour velocity in the column in m/hr, given by $v = 25.31/p$, where p is the operating pressure.

By rearranging the previous equation, it may be shown that the column diameter is proportional to the vapour flow rate in the column.

$$\text{Column height} \quad = \quad 0.61/\eta\, N + 4.27 = \alpha N + \beta \tag{A.8}$$

where η is the stage efficiency.

Citing Peters and Timmerhaus (1980), the installed column cost, C(column):

$$\begin{aligned} C(\text{column}) &= 4263.7\, dia^{1.1292}\, H \cdot (index) \\ &\propto V^{1.1292}(\alpha N + \beta) \end{aligned} \tag{A.9}$$

$$\begin{aligned} \text{TAC} &= C(\text{column}) + C(\text{heat exchangers}) + C(\text{utilities}) \\ &= aV^{1.1292}(\alpha N + \beta) + bV^{0.65} + cV \end{aligned} \tag{A.10}$$

where *index* is some cost index.

A.6 Knight and Doherty (1989)

Citing Peters and Timmerhaus (1980), for a column operating at 80% of the maximum vapour velocity, with 24-inch tray spacing:

$$dia = \left[\frac{4}{\pi 0.8 v_m}\right]^{\frac{1}{2}} v^{\frac{1}{2}} \tag{A.11}$$

where v is the vapour velocity in the column and v_m is the maximum vapour velocity, which may be considered fixed for a given system, since:

$$v_m = \sqrt{\frac{\rho_L - \rho_V}{\rho_V}} \tag{A.12}$$

where ρ_L is the density of the liquid phase and ρ_V the density of the vapour phase. The vapour velocity in the column may be given by the ratio of the volumetric flow rate of the vapour, Q, to the cross-sectional area of the column. For a vapour which obeys the ideal gas law, the following expression may be obtained:

$$\begin{aligned} dia &= \left[\frac{4}{\pi 0.8 v_m}\right]^{\frac{1}{2}} \left[\frac{4Q}{\pi dia^2}\right]^{\frac{1}{2}} \\ &= \left[\frac{4}{\pi 0.8 v_m}\right]^{\frac{1}{2}} \left[\frac{4VRT/p}{\pi dia^2}\right]^{\frac{1}{2}} \end{aligned} \tag{A.13}$$

Therefore:

$$dia \; \alpha \; \frac{V^{\frac{1}{2}}}{dia} \tag{A.14}$$

or, equivalently:

$$dia \propto V^{\frac{1}{4}}. \tag{A.15}$$

Using the cost correlations of Guthrie (1969), where column height is proportional to the number of stages, since tray spacing is fixed:

$$C(\text{shell}) \quad = \quad (\text{index}) \cdot 101.9\, dia^{1.066} H^{0.802}$$

$$
\begin{aligned}
&= aV^{0.267}N^{0.802} && \text{(A.16)}\\
C(\text{trays}) &= (\text{index})\cdot 4.7\,dia^{1.55}H\cdot N &&\\
&= bV^{0.388}N && \text{(A.17)}
\end{aligned}
$$

$$
\begin{aligned}
\text{TAC} &= C(\text{shell}) + C(\text{trays}) + C(\text{heat exchangers}) + C(\text{utilities}) &&\\
&= aV^{0.267}N^{0.302} + bV^{0.388}N + cV^{0.65} + dV && \text{(A.18)}
\end{aligned}
$$

A.7 Remer and Chai (1990)

Cost $\propto$ (Size)^R, where R is roughly constant for a given equipment type.

For towers, a number of values for R are presented. Two of these cited are:

1: C(tower, diameter fixed) $\propto$ (Size)$^{0.70}$;
C(tower, height fixed) $\propto$ (Size)$^{1.0}$ (Perry, 1963) (A.19)

2: C(tower, diameter fixed) $\propto$ (Size)$^{1.0}$;
C(tower, height fixed) $\propto$ (Size)$^{0.7}$ (IChE, 1977) (A.20)

If $dia \propto V^{\frac{1}{2}}$ and height $\propto N$, it follows:

$$1:\ C(\text{column}) \propto V^{\frac{1}{2}}N^{0.7} \qquad \text{(A.21)}$$

$$2:\ C(\text{column}) \propto V^{0.35}N \qquad \text{(A.22)}$$

The TAC would be calculated accordingly, adding utility capital costs and operating costs.

Appendix B

Derivation of Capacity Variables for VLE Separation Processes

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This appendix contains detailed derivations of the boiling and condensing capacity variables for a number of separation processes. The results are summarized and discussed in Chapter 5.

B.1 Non-steady state processes

B.1.1 Simple distillation

A liquid of quantity L_t is boiled at a rate $\dot{v}$ moles per unit time. An equilibrium stage is approximated by a differential time period. The "feed" to the equilibrium stage is $L|_t$, the "feed" capacity pair is $(\kappa|_t, \lambda|_t)$. The "product" capacity pair is $(\kappa|_{t+\Delta t}, \lambda|_{t+\Delta t})$. The amount of vapour produced, which is also the amount of vapour leaving the process is $\dot{v}\Delta t$ moles. The amount of liquid "produced" (*i.e.*, in the still at the end of the time period) is $L|_{t+\Delta t}$, while the amount of liquid leaving the stage is zero (for $t + \Delta t$ less than t_{final}) or $L|_{t,final}$ for t equal to t_{final}. Therefore definitions for κ given by eqs. (5.1a) and (5.1b) are identical in this case. However, the quantities of liquid "produced" in and leaving the stage are not identical. Therefore the condensing capacity of the process will be determined using both eqs. (5.2a) and (5.2b).

A mass balance over the stage gives:

$$L|_{t+\Delta t} = L|_t - \dot{v}\Delta t \tag{B.1}$$

Hence:

$$\frac{dL}{dt} = -\dot{v} \tag{B.2}$$

This equality is true for all finite values of $\dot{v}$.

Applying the definition of κ to the equilibrium stage, using either eq. (5.1b) or (5.1a):

$$\kappa\big|_{t+\Delta t} = \kappa\big|_t + \frac{\dot{v}\Delta t}{L\big|_t} \tag{B.3}$$

Therefore:

$$\frac{d\kappa}{dt} = \frac{\dot{v}}{L} \tag{B.4}$$

Substituting eq. (B.2) into eq. (B.4) and integrating with respect to L and κ from the initial conditions, namely $L = L_o$, $\kappa = \kappa_o$:

$$\kappa = \kappa_o - \ln\left[\frac{L}{L_o}\right] \tag{B.5}$$

The total amount of vapour produced, V^*, is:

$$V^* = \int_0^t \dot{v}\, dt = L_o - L \tag{B.6}$$

The capacity of the accumulated vapour is the weighted average of the capacity values of the incremental packets of vapour:

$$\begin{aligned} V^*\kappa^* &= \int_0^t \dot{v}\,\kappa\, dt \\ &= -\int_{L_o}^{L} \kappa\, dL \\ &= -\int_{L_o}^{L} (\kappa_o - \ln\left[\frac{L}{L_o}\right])\, dL \\ &= L_o\kappa_o - L\kappa + V^* \end{aligned} \tag{B.7}$$

Since V^* is given by eq. (B.6), κ^* may be found from eq. (B.7).

The overall capacity of the process, κ_{ov}, is the weighted average of the capacity variables of the product streams. The total feed to the process is L_o. The product streams are the residual liquid, of quantity L and capacity κ, and the accumulated vapour, of quantity V^* and capacity κ^*:

$$\begin{aligned} L_o\kappa_{ov} &= L\kappa + V^*\kappa^* \\ &= L\kappa + L_o\kappa_o - L\kappa + V^* \\ &= L_o\kappa_o + V^* \end{aligned} \tag{B.8}$$

Therefore:

$$\kappa_{ov} = \kappa_o + \frac{V^*}{L_o} \tag{B.9}$$

The change in the overall boiling capacity of the process is the ratio of the total amount of vapour formed in the process to the nett flow rate of the feed to the process.

The condensing capacity of the process is determined below in terms of the quantity of liquid leaving the equilibrium stage. It is supposed that only after completion of the process, at t_{final}, is the liquid removed from the still. Therefore, from eq. (5.2a):

$$\lambda|_{t+\Delta t} = \lambda|_t + 0 \tag{B.10}$$

for $t + \Delta t < t_{final}$. Therefore $\lambda = \lambda_o$. For $t + \Delta t = t_{final}$:

$$\lambda|_{t+\Delta t} = \lambda|_t + \frac{L|_{t+\Delta t}}{L|_t} \tag{B.11}$$

For small Δt, $L|_{t+\Delta t}$ and $L|_t$ are approximately equal. Therefore eq. (B.11) becomes:

$$d\lambda = 1 \tag{B.12}$$

Therefore $\lambda|_{t_{final}} = \lambda_o + 1$.

The condensing capacity of the process does not change during the process, except in step-wise fashion at $t = t_{final}$, as shown in Fig. B.1.

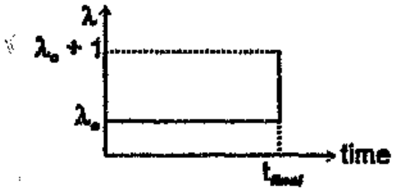

Fig. B.1 Condensing capacity of a simple distillation process.

The condensing capacity of the liquid in the still and the vapour leaving it are identical. The condensing capacity of the accumulated vapour, λ^*, is calculated from the following equation:

$$\begin{aligned} V^*\lambda^* &= \int_0^{t,final} \dot{v}\lambda \, dt \\ &= \int_0^{t,final-\Delta t} \dot{v}\lambda_o \, dt + \dot{v}\lambda|_{t,final}\Delta t \end{aligned} \tag{B.13}$$

The condensing capacity of all incremental amounts of vapour, except the last, is λ_o. The capacity of the last incremental amount of vapour is $\lambda_o + 1$. As Δt tends to zero, a negligible error is introduced by substituting $\dot{v}\Delta t\kappa_o$ for the term $\dot{v}\Delta t\lambda|_{t,final}$. Therefore the overall condensing capacity of the process may be calculated from the following:

$$\begin{aligned} L_o\lambda_{ov} &= L\lambda|_{t,final} + V^*\lambda^* \\ &= L\lambda|_{t,final} + \int_0^{t,final} \dot{v}\lambda_o \, dt \\ &= L(\lambda_o + 1) + V^*\lambda_o \\ &= L_o\lambda_o + L \end{aligned} \tag{B.14}$$

Therefore:

$$\lambda_{ov} = \lambda_o + \frac{L}{L_o} \tag{B.15}$$

That is, the change in the overall capacity of this process, in terms of quantities leaving the equilibrium stage, is the ratio of the total amount of liquid leaving the still to the nett feed to the process.

The condensing capacity of the process, in terms of the quantity of liquid "produced", is determined below. In each equilibrium stage, a quantity $L|_{t+\Delta t}$ of liquid is produced. Applying eq. (5.2b):

$$\begin{aligned} \lambda|_{t+\Delta t} &= \lambda|_t + \frac{L|_{t+\Delta t}}{L|_t} \\ &= \lambda|_t + \frac{L|_t - \dot{v}\Delta t}{L|_t} \\ &= \lambda|_t + 1 - \frac{\dot{v}\Delta t}{L|_t} \end{aligned} \tag{B.16}$$

In the limit, as Δt tends to zero:

$$d\lambda = 1 - \frac{\dot{v}dt}{L} \tag{B.17}$$

From eq. (B.17) it follows that λ increases infinitely with time, since in each of infinitely many differential time periods, a quantity $L|_{t+\Delta t}$ of liquid is "produced". It would appear that an analysis of condensing in a process comprised purely of boiling is not meaningful. Further mathematical examination of eq. (B.17) has not been attempted.

It is not clear whether eq. (5.2a) or eq. (5.2b) is a more suitable definition of λ for this process. Eq. (B.15), in terms of the quantities leaving the stage, gives a result which is consistent with eq. (B.9) and many results which will be presented later. The meaning of eq. (B.17), in terms of the quantities "produced" in the stage, is not clear.

The simple distillation process is equivalent to a series of flash stages in each of which a differential amount of vapour (of the bubble-point composition of the feed) is produced and the liquid product of which forms the feed to the next stage. In section B.2.1, it may be seen that the change in λ for each such flash stage is 1. Therefore λ increases infinitely with the production of vapour. Eq. (B.12), which applies eq. (5.2a), in terms of liquid leaving the stage, also reduces to this result if the series of flash stages is modelled assuming that each flash stage is a complete process, so that the remaining liquid is removed from the still after each incremental time step. It seems quite plausible that the condensing requirements of a pure boiling process are infinite.

The ambiguity arising from the alternative definitions of λ for this non-steady state process has not yet been resolved. The capacity variables are proposed as cost indicators for VLE separation processes. It is unlikely that the condensing costs of a pure boiling process would be of concern for the synthesis and optimization of such a process. It is concluded that this ambiguity is not a significant obstacle to the application of the capacity variables. For the rest of Section B.1, results of both definitions of κ and λ will be presented, for completeness, but contradictions obtained will not be discussed further.

B.1.2 Simple condensation

A vapour of quantity V associated with capacity pair (κ, λ), is condensed at a rate of $\dot{c}$ moles per unit time. An equilibrium stage may be approximated by a differential time interval. The "feed" to the process is $V|_t$, and the capacity pair of the feed is $(\kappa|_t, \lambda|_t)$. The quantity of liquid leaving the stage, which is equal to the quantity of liquid produced in the stage, is $\dot{c}\Delta t$. The quantity of vapour produced in the stage is $V|_{t+\Delta t}$, but no vapour leaves the stage, except when $t + \Delta t$ is equal to t_{final} and all the residual vapour is removed from the process.

The mass balance on the process is:

$$V|_{t+\Delta t} = V|_t - \dot{c}\Delta t \tag{B.18}$$

Hence:

$$\frac{dV}{dt} = -\dot{c} \tag{B.19}$$

Applying the definition of the condensation capacity to the equilibrium stage (eq. (5.2a) or (5.2b)):

$$\lambda|_{t+\Delta t} = \lambda|_t + \frac{\dot{c}\Delta t}{V|_t} \tag{B.20}$$

Therefore:

$$\frac{d\lambda}{dt} = \frac{\dot{c}}{V} \tag{B.21}$$

Substituting $dV = -\dot{c}dt$ from eq. (B.19) into eq. (B.21), and integrating, where the initial conditions are $\lambda = \lambda_o$ and $V = V_o$:

$$\begin{aligned} \int_{\lambda_o}^{\lambda} d\lambda &= \int_{V_o}^{V} -\frac{1}{V}\, dV \\ \lambda &= \lambda_o - \ln\left[\frac{V}{V_o}\right] \end{aligned} \tag{B.22}$$

The condensed liquid may be accumulated over the same time period, the quantity of which is L^*, and the condensing capacity of which is κ^*:

$$L^* = \int_0^t \dot{c}dt = V_o - V \tag{B.23}$$

The capacity of the condensed liquid is the weighted average of the capacity of the incremental packets of liquid:

$$\begin{aligned} L^*\lambda^* &= \int_0^t \dot{c}\,\lambda\, dt \\ &= -\int_{V_o}^{V} \lambda\, dV \\ &= -\int_{V_o}^{V} (\lambda_o - \ln\left[\frac{V}{V_o}\right])\, dV \\ &= V_o\lambda_o - V\lambda + L^* \end{aligned} \tag{B.24}$$

Since V^* is known, λ^* may be found from eq. (B.24).

The overall condensing capacity of the process, λ_{ov}, is the weighted average of the capacity of the two product streams. The total feed to the process is V_o. Hence:

$$\begin{aligned} V_o\lambda_{ov} &= V\lambda + L^*\lambda^* \\ &= V\lambda + V_o\lambda_o - V\lambda + L^* \\ &= V_o\lambda_o + L^* \end{aligned} \tag{B.25}$$

Therefore:

$$\lambda_{ov} = \lambda_o + \frac{L^*}{V_o} \tag{B.26}$$

The change in the overall condensing capacity of the process is the ratio of the total amount of liquid formed to the total feed to the process.

The boiling capacity of the process is determined below in terms of the quantity of vapour leaving the equilibrium stage. It is supposed that vapour is only removed from the process at t_{final}. Therefore, from eq. (5.1a):

$$\kappa\big|_{t+\Delta t} = \kappa\big|_t + 0 \qquad \text{(B.27}$$

for $t + \Delta t < t_{final}$.

Hence:

$$d\kappa = 0 \tag{B.28}$$

It follows that $\lambda = \kappa_o$ for $t + \Delta t < t_{final}$.

For $t = t_{final}$, vapour, of quantity $V\big|_{t,final}$, is removed from the process:

$$\kappa\big|_{t,final} = \kappa\big|_t + \frac{V\big|_{t+\Delta t}}{V\big|_t} \qquad \text{(B.29}$$

For small Δt, the right-hand term of eq. (B.29) is approximately equal to 1. Hence:

$$d\kappa = 1 \tag{B.30}$$

Therefore $\lambda\big|_{t,final} = \kappa_o + 1$. A step change in κ, analogous to the step change in κ illustrated in Fig. B.1, is thus obtained at t_{final}.

The boiling capacity of the accumulated liquid is given by:

$$\begin{aligned} L^*\kappa^* &= \int_0^{t,final} \hat{c}\kappa\, dt \\ &= \int_0^{t,final-\Delta t} \hat{c}\kappa\, dt + \hat{c}\Delta t\,\kappa\big|_{t,final} \end{aligned} \tag{B.31}$$

As Δt tends to zero, eq. (B.31) reduces to:

$$L^*\kappa^* = \int_0^t \dot{c}\kappa_o \, dt = L^*\kappa_o \tag{B.32}$$

The overall boiling capacity of the process is therefore:

$$\begin{aligned} L_o\kappa_{ov} &= V\kappa + L^*\kappa^* \\ &= V(\kappa_o + 1) + L^*\kappa_o \\ &= V_o\kappa_o + V \end{aligned} \tag{B.33}$$

Hence:

$$\kappa_{ov} = \kappa_o + \frac{V}{V_o} \tag{B.34}$$

The change in overall boiling capacity of this process, in terms of quantities leaving the process, is thus the ratio of the total amount of vapour leaving the process to the nett feed to the process.

The boiling capacity of the process may also be defined in terms of the quantities of vapour "produced" in the process. In each equilibrium stage, the quantity of vapour "produced" is $V|_{t+\Delta t}$. Applying eq. (5.1b):

$$\begin{aligned} \kappa|_{t+\Delta t} &= \kappa|_t + \frac{V|_{t+\Delta t}}{V|_t} \\ &= \kappa|_t + 1 - \frac{\dot{c}\Delta t}{V|_t} \end{aligned} \tag{B.35}$$

Hence:

$$d\kappa = 1 - \frac{\dot{c}dt}{V} \tag{B.36}$$

From eq. (B.36), it follows that κ increases infinitely with time, since in each of infinitely many differential time periods, a vapour of quantity $V|_{t+\Delta t}$ is produced.

The ambiguity arising from the alternative ways of extending the definitions of κ and λ to non-steady state processes was discussed in Section B.1.1; it is suggested that ambiguities arising out of an analysis of this pure condensing process in terms of its boiling requirements do not form a major obstacle to the application of the capacity variables.

B.1.3 Simple distillation with continuous addition of material

Consider a boiling process to which material is continuously added at a non-zero rate of $\dot{s}$ moles per unit time. The boiling and condensing capacity variables of the added material are κ' and λ', respectively. The equilibrium stage is approximated by a differential time period. The nett feed to the equilibrium stage is the sum of the residual liquid, of quantity L, and the material added, of quantity $\dot{s}\Delta t$. The vapour formed is in equilibrium with this mixture. The rate of vaporization is $\dot{v}$ moles per unit time.

From the mass balance:

$$L\big|_{t+\Delta t} = L\big|_t + \dot{s}\Delta t - \dot{v}\Delta t \tag{B.37}$$

Hence:

$$\frac{dL}{dt} = \dot{s} - \dot{v} \tag{B.38}$$

This equation is true for all values of $\dot{s}$ and $\dot{v}$.

The mean capacity of the feed to the stage, $\bar{\kappa}$, is the weighted average of the capacity variables of the two streams making up the nett feed:

$$(L\big|_t + \dot{s}\Delta t)\bar{\kappa} = L\kappa\big|_t + \dot{s}\Delta t\kappa' \tag{B.39}$$

Applying the definition of κ (eq. (5.1a) or (5.1b)) to an equilibrium stage:

$$\begin{aligned} \kappa\big|_{t+\Delta t} &= \bar{\kappa} + \frac{\dot{v}\Delta t}{L\big|_t + \dot{s}\Delta t} \\ &= \frac{L\kappa\big|_t + \dot{s}\kappa'\Delta t + \dot{v}\Delta t}{L\big|_t + \dot{s}\Delta t} \end{aligned} \tag{B.40}$$

It is assumed that, for small Δt, the difference $\kappa' - \kappa$, evaluated at $t+\Delta t$, is approximately equal to that difference evaluated at t. Therefore:

$$L\frac{d\kappa}{dt} = \dot{s}(\kappa' - \kappa) + \dot{v} \tag{B.41}$$

It is further assumed that the rate of addition of feed, $\dot{s}$, and the boiling rate, $\dot{v}$, are constant, so eq. (B.38) may be integrated to obtain:

$$L = L_o + (\dot{s} - \dot{v})t \tag{B.42}$$

If κ' is constant, $\dot{s}\neq 0$, $\dot{v}\neq 0$ and $\dot{s}\neq\dot{v}$, eq. (B.41) may be integrated over a time period t as follows:

$$\begin{gathered}\int_{\kappa_o}^{\kappa} \frac{d\kappa}{\kappa' - \kappa + \frac{\dot{v}}{\dot{s}}} = \int_0^t \frac{\dot{s}}{L}\,dt = \int_0^t \frac{\dot{s}}{L_o + (\dot{s} - \dot{v})t}\,dt \\ -\ln\left[\frac{\kappa' - \kappa + \frac{\dot{v}}{\dot{s}}}{\kappa' - \kappa_o + \frac{\dot{v}}{\dot{s}}}\right] = \frac{\dot{s}}{\dot{s}-\dot{v}}\ln\left[\frac{L_o + (\dot{s}-\dot{v})t}{L_o}\right]\end{gathered} \tag{B.43}$$

Simplifying this equation:

$$\kappa = \kappa' + \frac{\dot{v}}{\dot{s}} - (\kappa' - \kappa_o + \frac{\dot{v}}{\dot{s}})\left[\frac{L}{L_o}\right]^{\frac{-\dot{s}}{\dot{s}-\dot{v}}} \tag{B.44}$$

The quantity of accumulated vapour, produced over a time period t, is V^*:

$$V^* = \int_0^t \dot{v}\,dt = L_o + \dot{s}t - L \tag{B.45}$$

The capacity of the accumulated vapour, κ^*, is given by:

$$\begin{aligned} V^*\kappa^* &= \int_0^t \dot{v}\kappa\,dt \\ &= \int_0^t \dot{v}\left(\kappa' + \frac{\dot{v}}{\dot{s}} - (\kappa' - \kappa_o + \frac{\dot{v}}{\dot{s}})\left[\frac{L_o + (\dot{s}-\dot{v})t}{L_o}\right]^{\frac{-\dot{s}}{\dot{s}-\dot{v}}}\right)dt \\ &= \dot{v}t(\kappa' + \frac{\dot{v}}{\dot{s}}) + (\kappa' - \kappa_o + \frac{\dot{v}}{\dot{s}})(L_o^{\frac{\dot{s}}{\dot{s}-\dot{v}}}L^{\frac{-\dot{s}}{\dot{s}-\dot{v}}} - L_o)\end{aligned} \tag{B.46}$$

Hence κ^* may be determined, since V^* is known from eq. (B.45).

The overall boiling capacity of the process, κ_{ov}, is the weighted average of the capacity variables of the product streams, where the nett feed to the process is $L_o + \dot{S}t$:

$$(L_o + \dot{S}t)\kappa_{ov} = L\kappa + \dot{V}^*\kappa^* \tag{B.47}$$

which, on substitution of eqs. (B.44) and (B.46), simplifies to:

$$(L_o + \dot{S}t)\kappa_{ov} = L_o\kappa_o + \dot{S}t\kappa' + \dot{v}t \tag{B.48}$$

The mean capacity of the nett feed, $\overline{\kappa}_o$, is:

$$\overline{\kappa}_o = \frac{\kappa_o L_o + \kappa' \dot{S}t}{L_o + \dot{S}t} \tag{B.49}$$

Therefore eq. (B.48) may be rewritten as follows:

$$\kappa_{ov} = \overline{\kappa}_o + \frac{\dot{v}t}{L_o + \dot{S}t} \tag{B.50}$$

That is, the change in the overall boiling capacity of the process is the ratio of the total amount of vapour produced to the total feed to the process.

The definition of condensing capacity of an equilibrium stage is applied to this process in terms of quantities leaving the process (eq. 5.2a). Since no liquid leaves an equilibrium stage, for $t + \Delta t < t_{final}$:

$$\lambda\big|_{t+\Delta t} = \overline{\lambda} \tag{B.51}$$

where $\overline{\lambda}$ is the mean capacity of the feed to an equilibrium stage, given by:

$$(L\big|_t + \dot{S}\Delta t)\overline{\lambda} = L\lambda\big|_t + \dot{S}\Delta t\lambda' \tag{B.52}$$

It is assumed that λ' is constant. If it is assumed that for small Δt, and $t + \Delta t < t_{final}$, the difference $\lambda' - \lambda$, evaluated at $t + \Delta t$, is approximately equal to the difference evaluated at t, then:

$$L\frac{d\lambda}{dt} = \dot{s}(\lambda' - \lambda) \tag{B.53}$$

which may be integrated for a time period t ($t < t_{final}$), where $\lambda = \lambda_o$ initially, and $\lambda' \neq \lambda$:

$$\int_{\lambda_o}^{\lambda} \frac{d\lambda}{\lambda' - \lambda} = \int_0^t \frac{\dot{s}}{L_o + (\dot{s} - \dot{v})t} dt \tag{B.54}$$

Hence, for $t + \Delta < t_{final}$:

$$\lambda = \lambda' - (\lambda' - \lambda_o)(\frac{L}{L_o})^{\frac{-\dot{s}}{\dot{s}-\dot{v}}} \tag{B.55}$$

The residual liquid is removed from the process at time t_{final}. Therefore:

$$\lambda|_{t,final} = \overline{\lambda} + 1 \tag{B.56}$$

Hence:

$$\lambda|_{t,final} = \lambda|_t + 1 + \frac{\dot{s}}{L_t}(\lambda' - \lambda|_t + 1)\Delta t \tag{B.57}$$

Therefore, as Δt tends to zero:

$$\lambda|_{t,final} = \lambda|_t + 1$$

The condensing capacity of the process for the accumulated vapour, λ^*, is given by the integral:

$$\begin{aligned} V^*\lambda^* &= \int_0^{t,final} \dot{v}\lambda \, dt \\ &= \int_0^{t\,final - \Delta t} \dot{v}\lambda \, dt + \dot{v}\lambda|_{t,final}\Delta t \end{aligned} \tag{B.58}$$

As Δt tends to zero, the right hand term of eq. (B.58) is approximately equal to $\dot{v}\Delta t\lambda$, where λ is given by eq. (B.55). Therefore:

$$\begin{aligned} V^{*}\lambda^{*} &= \int_{0}^{t} \dot{v}\lambda\,dt \\ &= \int_{0}^{t} \dot{v}\left[\lambda' - (\lambda' - \lambda_o)\left(\frac{L_o + (\dot{s}-\dot{v})t}{L_o}\right)^{\frac{-\dot{s}}{\dot{s}-\dot{v}}}\right]dt \qquad \text{(B.59)} \\ &= \dot{v}t\lambda' + (\lambda' - \lambda_o)\left(L_o^{\frac{\dot{s}}{\dot{s}-\dot{v}}} L^{\frac{-\dot{v}}{\dot{s}-\dot{v}}} - L_o\right) \end{aligned}$$

Since V^{*} is given by eq. (B.45), λ^{*} may be found.

The overall condensing capacity of the process, λ_{ov}, is given by: (B.60)

$$\begin{aligned} (L_o + \dot{s}t)\lambda_{ov} &= L\lambda\big|_{t,final} + V^{*}\lambda^{*} \\ &= L\left[\lambda' - (\lambda' - \lambda_o)\left(\frac{L}{L_o}\right)^{\frac{-\dot{s}}{\dot{s}-\dot{v}}} - 1\right] + \dot{v}t\lambda' + (\lambda' - \lambda_o)\left(L\left(\frac{L}{L_o}\right)^{\frac{-\dot{s}}{\dot{s}-\dot{v}}} - L_o\right) \\ &= L_o\bar{\lambda}_o + \dot{s}t\lambda' + L \\ &= (L_o + \dot{s}t)\bar{\lambda}_o + L \end{aligned}$$

where $\bar{\lambda}_o$ is the weighted average of the condensing capacity variables of the two feed streams, given by:

$$(L_o + \dot{s}t)\bar{\lambda}_o = L_o\lambda_o + \dot{s}t\lambda' \qquad \text{(B.61)}$$

Combining the above two equations:

$$\lambda_{ov} = \bar{\lambda}_o + \frac{L}{L_o + \dot{s}t} \qquad \text{(B.62)}$$

These results show that the change in the overall condensing capacity of the process, in terms of quantities of liquid leaving the process, is the ratio of the total amount of liquid removed from the process to the nett feed to the process.

These results assume that the rates of vaporization, $\dot{v}$, and feed addition, $\dot{s}$, are constant and non-zero, that the capacity values of the additional feed material, κ' and λ', are constant with time, that $\dot{v} \neq \dot{s}$, and that $\lambda' \neq \lambda$.

Eq. (5.2b) defines λ in terms of quantities "produced", *i.e.*, in the process at the end of the differential time period:

$$\lambda|_{t+\Delta t} + \bar{\lambda} + \frac{L|_t + (\dot{s}-\dot{v})\Delta t}{L|_t + \dot{s}\Delta t} \tag{B.63}$$

where $\bar{\kappa}$ is given by eq. (B.52). Substituting for $\bar{\kappa}$, and assuming that the difference $\lambda-\lambda'$ evaluated at $t + \Delta t$ is approximately equal to the difference evaluated at t:

$$d\lambda = 1 + \frac{\dot{s}(\lambda' - \lambda) + (\dot{s}-\dot{v})}{L}dt \tag{B.64}$$

Therefore λ increases infinitely with time.

B.1.4 Simple condensation with continuous addition of feed material

A vapour of quantity V is condensed at a rate of $\dot{c}$ moles per unit time. Material is continuously added to the process at a rate of $\dot{a}$ moles per unit time. In this discussion $\dot{a}$ and $\dot{c}$ are assumed constant. This capacity pair of the material added is (κ', λ'). An equilibrium stage is approximated by a differential time slice.

The mass balance gives:

$$V|_{t+\Delta t} = V|_t + \dot{a}\Delta t - \dot{c}\Delta t \tag{B.65}$$

Therefore:

$$\frac{dV}{dt} = \dot{a} - \dot{c} \tag{B.66}$$

Integrating over a time t, where $\dot{a}$ and $\dot{c}$ are constant and initially $V = V_o$:

$$V = V_o + (\dot{a} - \dot{c})t \tag{B.67}$$

The nett feed to the stage is associated with condensing capacity, $\bar{\lambda}$, which is the weighted average of the capacity variables of the two feed streams:

$$(V|_t + \dot{a}\Delta t)\bar{\lambda} = \lambda V|_t + \dot{a}\Delta t\lambda' \tag{B.68}$$

Applying the definition of λ to the equilibrium stage:

$$\lambda|_{t+\Delta t} = \bar{\lambda} + \frac{\dot{c}\Delta t}{V + \dot{a}\Delta t} \tag{B.69}$$

Therefore:

$$(V|_t + \dot{a}\Delta t)\lambda|_{t+\Delta t} = \lambda V|_t + \dot{a}\Delta t\lambda' + \dot{c}\Delta t \tag{B.70}$$

Assuming that the difference $\lambda' - \lambda$, evaluated at $t+\Delta t$, is approximately equal to the difference evaluated at t for small values of Δt, it may be shown that:

$$V\frac{d\lambda}{dt} = \dot{a}(\lambda' - \lambda) + \dot{c} \tag{B.71}$$

This expression may be integrated for a time period t, where initially $\lambda = \lambda_o$:

$$\begin{aligned} \int_{\lambda_o}^{\lambda} \frac{d\lambda}{\lambda' - \lambda + \frac{\dot{c}}{\dot{a}}} &= \int_0^t \frac{\dot{a}}{V_o + (\dot{a}-\dot{c})t}dt \\ -\ln\left[\frac{\lambda' - \lambda + \frac{\dot{c}}{\dot{a}}}{\lambda' - \lambda_o + \frac{\dot{c}}{\dot{a}}}\right] &= \frac{\dot{a}}{\dot{a}-\dot{c}}\ln\left[\frac{V_o + (\dot{a}-\dot{c})t}{V_o}\right] \end{aligned} \tag{B.72}$$

Therefore, for $t + \Delta t < t_{final}$:

$$\lambda = \lambda' + \frac{\dot{c}}{\dot{a}} - (\lambda' - \lambda_o + \frac{\dot{c}}{\dot{a}})\left[\frac{V}{V_o}\right]^{\frac{-\dot{a}}{\dot{a}-\dot{c}}} \tag{B.73}$$

The condensed liquid may be accumulated over time, t, to form a product of quantity L^* and condensing capacity λ^*:

$$L^* = \int_0^t \dot{c}dt = V_o + \dot{a}t - V \tag{B.74}$$

$$\begin{aligned} L^*\lambda^* &= \int_0^t \dot{c}\lambda\, dt \\ &= \int_0^t \dot{c}\left[\lambda' + \frac{\dot{c}}{\dot{a}} - (\lambda' - \lambda_o + \frac{\dot{c}}{\dot{a}})\left[\frac{V_o + (\dot{a}-\dot{c})t}{V_o})^{\frac{-\dot{a}}{\dot{a}-\dot{c}}}\right]\right]dt \\ &= \dot{c}t(\lambda' + \frac{\dot{c}}{\dot{a}}) + (\lambda' - \lambda_o + \frac{\dot{c}}{\dot{a}})(V_o^{\frac{\dot{a}}{\dot{a}-\dot{c}}}V^{\frac{-\dot{c}}{\dot{a}-\dot{c}}} - V_o) \end{aligned} \tag{B.75}$$

from which λ^* may be obtained.

The overall condensing capacity of the process, λ_{ov}, is the weighted average of the capacity variables of the two products:

$$\begin{aligned}(V_o + \dot{a}t)\lambda_{ov} &= V\lambda + L^*\lambda^* \\ &= V_o\lambda_o + \dot{a}t\lambda' + \dot{C}t\end{aligned} \tag{B.76}$$

The mean condensing capacity of the nett feed to the process, $\bar{\lambda}_o$, is given by:

$$(V_o + \dot{a}t)\bar{\lambda}_o = V_o\lambda_o + \dot{a}t\lambda' \tag{B.77}$$

Therefore:

$$\lambda_{ov} = \bar{\lambda}_o + \frac{L^*}{V_o + \dot{a}t} \tag{B.78}$$

That is, the change in overall condensing capacity for this process is the ratio of the total amount of liquid condensed in the process to the nett feed to the process.

The mean boiling capacity of the feed to an equilibrium stage is given by:

$$(V|_t + \dot{a}\Delta t)\bar{\kappa} = V\kappa|_t + \dot{a}\Delta t\kappa' \tag{B.79}$$

Since no vapour leaves the equilibrium stage, it follows from eq. (5.1a), which defines κ in terms of the quantities leaving the process:

$$\kappa|_{t+\Delta t} = \bar{\kappa} + 0 \tag{B.80}$$

for $t + \Delta t < t_{final}$.

Combining eqs. (B.79) and (B.80), for $t + \Delta t < t_{final}$:

$$(V|_t + \dot{a}\Delta t)\kappa|_{t+\Delta t} = V\kappa|_t + \dot{a}\Delta t\kappa' \tag{B.81}$$

It follows that:

$$V\frac{d\kappa}{dt} = \dot{a}(\kappa' - \kappa) \tag{B.82}$$

if it is assumed that the difference $\kappa' - \kappa$ evaluated at $t+\Delta t$ is equal to that at t for small Δt.

From the mass balance:

$$V = V_o + (\dot{a} - \dot{c})t \tag{B.67}$$

Integrating eq. (B.82) from the initial conditions, *i.e.*, $\kappa = \kappa_o$, where $\kappa' \neq \kappa$:

$$\begin{aligned} \int_{\kappa_o}^{\kappa} \frac{d\kappa}{\kappa' - \kappa} &= \int_0^t \frac{\dot{a}}{V_o + (\dot{a}-\dot{c})t} dt \\ -\ln\left[\frac{\kappa' - \kappa}{\kappa' - \kappa_o}\right] &= \frac{\dot{a}}{\dot{a}-\dot{c}} \ln\left[\frac{V_o + (\dot{a}-\dot{c})t}{V_o}\right] \end{aligned} \tag{B.83}$$

The following result is then obtained for $t + \Delta t < t_{final}$:

$$\kappa = \kappa' - (\kappa' - \kappa_o)\left(\frac{V}{V_o}\right)^{\frac{-\dot{a}}{\dot{a}-\dot{c}}} \tag{B.84}$$

When $t + \Delta t = t_{final}$, the amount of vapour removed from the equilibrium stage is approximately equal to the feed to the stage, therefore:

$$\kappa|_{t+\Delta t} = \bar{\kappa} + \frac{V|_{t+\Delta t}}{V|_t + \dot{a}\Delta t} = \bar{\kappa} + 1 \tag{B.85}$$

It follows from eq. (B.85) that:

$$\kappa|_{t,final} = \kappa|_t + 1 + \dot{a}(\kappa' - \kappa|_{t,final} + 1)\Delta t \tag{B.86}$$

As Δt tends to zero, $\kappa|_{t,final}$ is given by:

$$\kappa = \kappa' - (\kappa' - \kappa_o)\left(\frac{V}{V_o}\right)^{\frac{-\dot{a}}{\dot{a}-\dot{c}}} + 1 \tag{B.87}$$

The boiling capacity of the accumulated liquid, κ^*, is the weighted average of the capacity variables of the constituent liquid elements.

$$L^* \kappa_* = \int_0^{t,final} \dot{c}\kappa \, dt = \int_0^{t,final-\Delta t} \dot{c}\kappa \, dt + \dot{c}\Delta t \kappa|_{t,final} \tag{B.88}$$

For small Δt, a negligible error is introduced by using κ given by eq. (B.84) in the right hand term of eq. (B.88). Therefore:

$$
\begin{aligned}
L^{*}\kappa^{*} &= \int_0^t \dot{c}\,\kappa\,dt \\
&= \int_0^t \dot{c}\left[\kappa' - (\kappa' - \kappa_o)\left[\frac{V_o + (\dot{a}-\dot{c})t}{V_o}\right]^{\frac{-\dot{a}}{\dot{a}-\dot{c}}}\right]dt \\
&= \dot{c}\kappa' t + (\kappa' - \kappa_o)V_o^{\frac{\dot{a}}{\dot{a}-\dot{c}}}\left(V^{\frac{-\dot{c}}{\dot{a}-\dot{c}}} - V_o^{\frac{-\dot{c}}{\dot{a}-\dot{c}}}\right)
\end{aligned}
\tag{B.89}
$$

The overall boiling capacity of the process, κ_{ov}, may be obtained by combining eqs. (B.87) and (B.89):

$$
\begin{aligned}
(V_o + \dot{a}t)\kappa_{ov} &= V\kappa + L^{*}\kappa^{*} \\
&= V_o\kappa_o + \dot{a}t\kappa' + V
\end{aligned}
\tag{B.90}
$$

The weighted average of the boiling capacity variables of the feed streams to the process is given by:

$$
\bar{\kappa}_o = \frac{V_o\kappa_o + \dot{a}t\kappa'}{V_o + \dot{a}t}
\tag{B.91}
$$

Hence:

$$
\kappa_{ov} = \bar{\kappa}_o + \frac{V}{V_o + \dot{a}t}
\tag{B.92}
$$

The change in the overall boiling capacity of this process, in terms of quantities leaving the process, is the ratio of the total quantity of vapour to leave the process to the nett feed to the process.

These results assume that the rates of condensation, $\dot{c}$, and feed addition, $\dot{a}$, are constant and non-zero, that the capacity values of the additional feed material, κ' and λ', are constant with time, that $\dot{c} \neq \dot{a}$, and that $\kappa' \neq \kappa$.

Using eq. (5.1b) to define κ in terms of the quantities in the process at the end of the time interval:

$$
\kappa\big|_{t+\Delta t} = \bar{\kappa} + \frac{V\big|_t + \dot{a}\Delta t - \dot{c}\Delta t}{V\big|_t + \dot{a}\Delta t}
\tag{B.93}
$$

where $\bar{\lambda}$ is defined by eq. (B.79). Assuming that the difference $\kappa' - \kappa$ evaluated at $t + \Delta t$ is approximately equal to that difference at t:

$$d\kappa = 1 + \frac{\dot{a}(\kappa' - \kappa) + (\dot{a} - \dot{c})}{V} dt \tag{B.94}$$

Therefore κ increases infinitely with time.

B.2 Equilibrium flash processes

B.2.1 Single flash stage

A single flash stage, with a feed of molar flow rate F and capacity variables κ_F and λ_F is partially vaporized in a single flash stage into a liquid product of flow rate L and a vapour product of flow rate V. The flash stage is an equilibrium separation stage. The definitions of κ and λ may be applied as follows:

$$\kappa = \kappa_F + \frac{V}{F} \tag{B.95}$$

$$\lambda = \lambda_F + \frac{L}{F} \tag{B.96}$$

The capacity values of the vapour and liquid streams are identical, as they are the equilibrium products from a single stage.

The overall capacity of the process is the weighted average of the capacity variables of the two product streams, therefore $\kappa_{av} = \kappa$ and $\lambda_{av} = \lambda$.

B.2.2 Single flash stage with recycle

Consider a flash process where a fraction α (where $0 \leq \alpha \leq 1$) of the vapour product is recycled and mixed with the feed to the process of flow rate F_P, as shown in Fig. B.2. The nett feed to the flash stage, of flow rate F_1, is a mixture of the feed to the process and the recycled vapour product, of quantity αV, where the v[illegible] product flow rate from the flash stage is V. The capacity variables of the ne[illegible] feed to the equilibrium flash stag[illegible] κ_1 and λ_1.

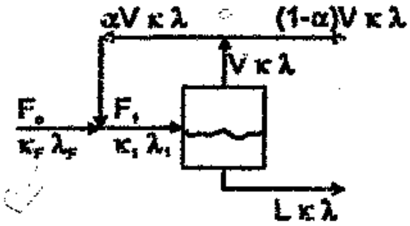

Fig. B.2 A single flash stage with a portion of the vapour recycled.

Applying the definitions of κ and λ to the equilibrium flash stage:

$$\kappa = \kappa_1 + \frac{V}{F_1} \tag{B.97}$$

$$\lambda = \lambda_1 + \frac{L}{F_1} \tag{B.98}$$

But κ_1 and λ_1 are given by the weighted averages of the capacity variables of the two streams making up the nett feed to the equilibrium stage:

$$F_1\kappa_1 = F_o\kappa_F + \alpha V\kappa \tag{B.99}$$

$$F_1\lambda_1 = F_o\lambda_F + \alpha V\lambda \tag{B.100}$$

Therefore it can be shown that:

$$\begin{aligned}\kappa &= \frac{F_o}{F_1}\kappa_F + \frac{\alpha V}{F_1}\kappa + \frac{V}{F_1}\\ &= \kappa_F + \frac{V}{F_o}\end{aligned} \tag{B.101}$$

$$\begin{aligned}\lambda &= \frac{F_o}{F_1}\lambda_F + \frac{\alpha V}{F_1}\lambda + \frac{L}{F_1}\\ &= \lambda_F + \frac{L}{F_o}\end{aligned} \tag{B.102}$$

Since the two product streams, of quantities $(1-\alpha)V$ and L, both are associated with the capacity variables κ and λ, the overall process capacity $\kappa_{ov} = \kappa$ and $\lambda_{ov} = \lambda$, as given by eqs. (B.101) and (B.102) above: that is, the change in the overall boiling (or condensing) capacity of the process is the ratio of the total rate of vapour (or liquid, respectively) production within the process to the total flow rate of the feed to the process. (While the total vapour product obtained from this process is of flow rate $(1-\alpha)V$, the total vapour production rate within the process is V.) This result arises from the definitions of κ and λ for an equilibrium stage, which are based on the feed and product flow rates to that equilibrium stage, as opposed to the process as a whole.

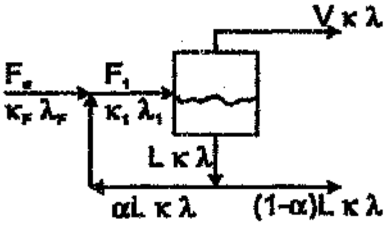

Fig. B.3 A single flash stage with a portion of the liquid recycled.

Consider also the process shown in Fig. B.3, in which a portion α (where $0 \leq \alpha \leq 1$) of the liquid product from the flash stage is recycled and mixed with the feed, of flow rate F_F and capacity variables κ_F and λ_F as in the previous case. The mixing rule is applied to find the capacity variables of the feed to the equilibrium stage, κ_1 and λ_1:

$$\kappa_1 = \frac{F_o}{F_1}\kappa_F + \frac{\alpha L}{F_1}\kappa \tag{B.103}$$

$$\lambda_1 = \frac{F_o}{F_1}\kappa_F + \frac{\alpha L}{F_1}\kappa \tag{B.104}$$

The definitions of κ and λ for an equilibrium stage are applied to show that:

$$\kappa = \kappa_1 + \frac{V}{F_1} \tag{B.105}$$

$$\lambda = \lambda_1 + \frac{L}{F_1} \tag{B.106}$$

By combining eqs. (B.101), (B.103), (B.102) and (B.104), it may be shown that:

$$\kappa = \kappa_F + \frac{V}{F_o} \tag{B.107}$$

$$\lambda = \lambda_F + \frac{L}{F_o} \tag{B.108}$$

Since, as before, both product streams have the same capacity variables, κ and λ, the overall capacity variables of the process are $\kappa_{ov} = \kappa$ and $\lambda_{ov} = \lambda$: that is, the change in the overall boiling (or condensing) capacity of the process is the ratio of the total rate of production of vapour (or liquid, respectively) within the process to the total flow rate of the feed to the process.

B.2.3 Two flash stages arranged in series

The product of the first flash stage may form the feed to a second flash stage, as shown in Fig. B.4. The feed to the second stage, of flow rate F', is the mixture of some portion of the two products of the first flash stage:

$$F' = \alpha V_1 + \beta L_1 \tag{B.109}$$

where $0 \leq \alpha \leq 1$ and $0 \leq \beta \leq 1$, and V_1 and L_1 are the vapour and liquid product flow rates, respectively, of the first flash stage.

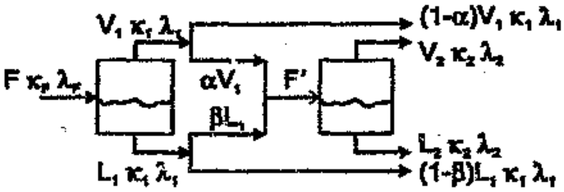

Fig. B.4 Two flash stages arranged in series.

The capacity pair of the feed to the second-stage is (κ_1, λ_1):

$$\kappa_1 = \kappa_F + \frac{V_1}{F} \tag{B.95}$$

$$\lambda_1 = \lambda_F + \frac{L_1}{F} \tag{B.96}$$

In the second flash stage, the flow rates of the vapour and liquid products formed are V_2 and L_2 respectively. Applying the capacity definitions to the second flash stage:

$$\begin{aligned} \kappa_2 &= \kappa_1 + \frac{V_2}{F'} \\ \lambda_2 &= \lambda_1 + \frac{L_2}{F'} \end{aligned} \tag{B.110}$$

Eqs. (B.95) and (B.96) may be substituted into the above equations to show that:

$$\begin{aligned} \kappa_1 &= \kappa_F + \frac{V_1}{F} \\ \lambda_1 &= \lambda_F + \frac{L_1}{F} \end{aligned} \tag{B.111}$$

Combining eqs. (B.110) and (B.111):

$$\begin{aligned} \kappa_2 &= \kappa_F + \frac{V_1}{F} + \frac{V_2}{F'} \\ \lambda_2 &= \lambda_F + \frac{L_1}{F} + \frac{L_2}{F'} \end{aligned} \tag{B.112}$$

The process then has a number of product streams, with quantities and capacity variables as follows:

Product quantity	*Boiling capacity*	*Condensing capacity*
$(1-\alpha)V_1$	κ_1	λ_1

$(1-\beta)L_1$	κ_1	λ_1
V_2	κ_2	λ_2
L_2	κ_2	λ_2

The overall process capacity is the weighted average of the capacity variables of the product streams:

$$\begin{aligned} F\kappa_{ov} &= (1-\alpha)V_1\kappa_1 + (1-\beta)L_1\kappa_1 + V_2\kappa_2 + L_2\kappa_2 \\ &= (F - F')\kappa_1 + F'\kappa_2 \\ &= (F - F')\left[\kappa_F + \frac{V_1}{F}\right] + F'\left[\kappa_F + \frac{V_1}{F} + \frac{V_2}{F'}\right] \\ &= F\kappa_F + V_1 + V_2 \end{aligned} \tag{B.113}$$

$$\begin{aligned} F\lambda_{ov} &= (1-\alpha)V_1\lambda_1 + (1-\beta)L_1\lambda_1 + V_2\lambda_2 + L_2\lambda_2 \\ &= (F - F')\lambda_1 + F'\lambda_2 \\ &= (F - F')\left[\lambda_F + \frac{L_1}{F}\right] + F'\left[\lambda_F + \frac{L_1}{F} + \frac{L_2}{F'}\right] \\ &= F\lambda_F + L_1 + L_2 \end{aligned} \tag{B.114}$$

Therefore:

$$\kappa_{ov} = \kappa_F + \frac{V_1 + V_2}{F} \tag{B.115}$$

$$\lambda_{ov} = \lambda_F + \frac{L_1 + L_2}{F} \tag{B.116}$$

The change in the overall boiling (or condensing) capacity of the process is the ratio of the total rate of formation of vapour (or liquid, respectively) *within* the process to the nett flow rate of the feed to the process.

B.2.4 Two flash stages arranged in parallel

A feed may be split into two portions, of flow rates αF and $(1-\alpha)F$, where $0 \leq \alpha \leq 1$. These two streams are fed into two flash stages arranged in parallel, as shown in Fig. B.5.

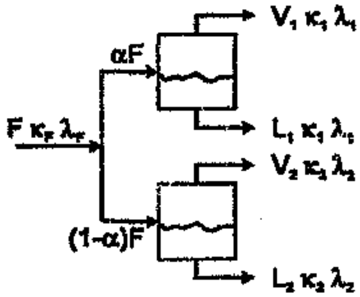

Fig. B.5 Two flash stages arranged in parallel.

The definition of the capacity variables may be applied to each of equilibrium stages.

Stream flow rate	*Boiling capacity*	*Condensing capacity*
V_1, L_1	κ_1	λ_1
V_2, L_2	κ_2	λ_2

where:

$$\begin{aligned}\kappa_1 &= \kappa_F + \frac{V_1}{\alpha F}\\ \kappa_2 &= \kappa_F + \frac{V_2}{(1-\alpha)F}\end{aligned} \tag{B.117}$$

$$\begin{aligned}\lambda_1 &= \lambda_F + \frac{L_1}{\alpha F}\\ \lambda_2 &= \lambda_F + \frac{L_2}{(1-\alpha)F}\end{aligned} \tag{B.118}$$

The overall capacity of the process is the weighted average of the capacity variables of the product streams:

$$\begin{aligned} F\kappa_{ov} &= V_1\kappa_1 + L_1\kappa_1 + V_2\kappa_2 + L_2\kappa_2 \\ &= \alpha F(\kappa_F + \frac{V_1}{\alpha F}) + (1-\alpha)F(\kappa_F + \frac{V_2}{(1-\alpha)F}) \\ &= F\kappa_F + V_1 + V_2 \end{aligned} \tag{B.119}$$

Similarly:

$$\begin{aligned} F\lambda_{ov} &= V_1\lambda_1 + L_1\lambda_1 + V_2\lambda_2 + L_2\lambda_2 \\ &= \alpha F(\lambda_F + \frac{L_1}{\alpha F}) + (1-\alpha)F(\lambda_F + \frac{L_2}{(1-\alpha)F}) \\ &= F\lambda_F + L_1 + L_2 \end{aligned} \tag{B.120}$$

Therefore:

$$\kappa_{ov} = \kappa_F + \frac{V_1 + V_2}{F} \tag{B.121}$$

$$\lambda_{ov} = \lambda_F + \frac{L_1 + L_2}{F} \tag{B.122}$$

i.e., the change in the overall boiling (or condensing) capacity of the process is the ratio of the rate of vapour (or liquid, respectively) production within the process to the flow rate of the feed to the process.

B.2.5 Two flash stages arranged in series with reflux

Consider the process illustrated in Fig. B.6, in which the feed, of flow rate F, is added to the first flash stage of two flash stages arranged in series with reflux. The vapour and liquid products of the first stage are of flow rates V_1 and L_1, respectively, with capacity pair (κ_1, λ_1). The flow rates of the products of the second stage are V_2 and L_2, with capacity pair (κ_2, λ_2). The flow rate of the nett feed to the first stage is F^*, where $F^* = F + L_2$.

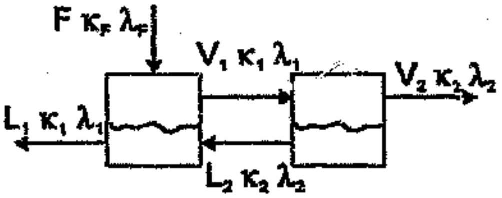

Fig. B.6 Two flash stages arranged in series with reflux, with feed added to the first flash stage.

The mean boiling capacity of the feed to the first stage, κ^*, is given by:

$$F^*\kappa^* = F\kappa_F + L_2\kappa_2 \tag{B.123}$$

The definition of the capacity variables may be applied to the two equilibrium flash stages:

$$\kappa_2 = \kappa_1 + \frac{V_2}{V_1} \tag{B.124}$$

$$\kappa_1 = \kappa^* + \frac{V_1}{F^*} \tag{B.125}$$

Therefore eq. (B.125) becomes:

$$\kappa_1 = \frac{F}{F^*}\kappa_F + \frac{L_2}{F^*}\kappa_2 + \frac{V_1}{F^*} \tag{B.126}$$

Combining eqs. (B.124) and (B.126), it may be shown that:

$$\begin{aligned} \kappa_1 &= \kappa_F + \frac{L_2}{F}\frac{V_2}{V_1} + \frac{V_1}{F} \\ \kappa_2 &= \kappa_F + \frac{F + L_2}{F}\frac{V_2}{V_1} + \frac{V_1}{F} \end{aligned} \tag{B.127}$$

The overall process capacity, κ_{ov}, is the weighted average of the capacity variables of the two products:

$$\begin{aligned} F\kappa_{ov} &= L_1\kappa_1 + V_2\kappa_2 \\ &= L_1\left[\kappa_F + \frac{L_2}{F}\frac{V_2}{V_1} + \frac{V_1}{F}\right] + V_2\left[\kappa_F + \frac{F+L_2}{F}\frac{V_2}{V_1} + \frac{V_1}{F}\right] \\ &= F\kappa_f + (L_1 + V_2)\frac{V_1}{F} + (L_2 + V_2)\frac{V_2}{V_1} \\ &= F\kappa_F + V_1 + V_2 \end{aligned} \tag{B.128}$$

Therefore:

$$\kappa_{ov} = \lambda_F + \frac{V_1 + V_2}{F} \tag{B.129}$$

that is, the change in the overall boiling capacity of the process is the ratio of the total amount of liquid produced within the process to the feed to the process.

The condensing capacity may be similarly treated. Applying the definition of λ to the first stage:

$$\lambda_1 = \lambda^* + \frac{L_1}{F^*} \tag{B.130}$$

where $F^* = F + L_2$ and $F^*\lambda^* = F\lambda_F + L_2\lambda_2$.

Applying the definition of λ to the second stage:

$$\lambda_2 = \lambda_1 + \frac{L_2}{V_1} \tag{B.131}$$

λ_1 and λ_2 may thus be determined:

$$\begin{aligned} \lambda_1 &= \lambda_F + \frac{L_2}{F}\frac{L_2}{V_1} + \frac{L_1}{F} \\ \lambda_2 &= \lambda_F + \frac{L_2}{F}\frac{L_2}{V_1} + \frac{L_1}{F} + \frac{L_2}{V_1} \end{aligned} \tag{B.132}$$

The overall process capacity, λ_{ov}, may therefore be determined:

$$\begin{aligned} F\lambda_{ov} &= L_1\lambda_1 + V_2\lambda_2 \\ &= L_1\lambda_1 + V_2(\lambda_1 + \frac{L_2}{V_1}) \\ &= F(\lambda_F + \frac{L_2}{F}\frac{L_2}{V_1} + \frac{L_1}{F}) + V_2\frac{L_2}{V_1} \\ &= F\lambda_F + L_1 + L_2 \end{aligned} \tag{B.133}$$

Therefore:

$$\lambda_{ov} = \lambda_F + \frac{L_1 + L_2}{F} \tag{B.134}$$

that is, the change in the overall condensing capacity of the process is the ratio of the total amount of liquid produced within the process to the feed to the process.

For the case where the feed is added to the second stage of the process, as shown in Fig. B.7, the definition of the capacity variables may be applied to each stage as before:

$$\begin{aligned} \kappa_1 &= \kappa_2 + \frac{V_1}{L_2} \\ \kappa_2 &= \kappa^* + \frac{V_2}{F^*} \end{aligned} \qquad \text{(B.135)}$$

where $F^* = F + V_1$ and $F^*\kappa^* = F\kappa_F + V_1\kappa_1$.

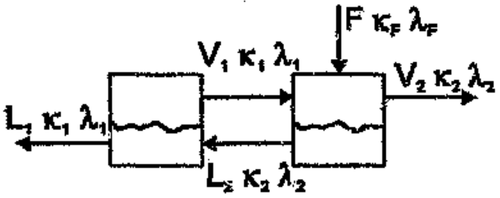

Fig. B.7 Two flash stages with reflux; feed added to the second flash stage.

It may be shown that:

$$\begin{aligned} \kappa_1 &= \kappa_F + \frac{V_1}{F}\frac{V_1}{L_2} + \frac{V_2}{F} + \frac{V_1}{L_2} \\ \kappa_2 &= \kappa_F + \frac{V_1}{F}\frac{V_1}{L_2} + \frac{V_2}{F} \end{aligned} \qquad \text{(B.136)}$$

As before, the overall boiling capacity of the process may then be shown to be:

$$\kappa_{ov} = \kappa_F + \frac{V_1 + V_2}{F} \qquad \text{(B.137)}$$

Similarly, for the condensing capacity:

$$\begin{aligned} \lambda_1 &= \lambda_2 + \frac{L_1}{L_2} \\ \lambda_2 &= \lambda^* + \frac{L_2}{F^*} \end{aligned} \qquad \text{(B.138)}$$

where $F^*\lambda^* = F\lambda_F + V_1\lambda_1$.

Combining the above equations, it may be shown that:

$$\lambda_{av} = \lambda_F + \frac{L_1 + L_2}{F} \tag{B.139}$$

Again, the change in the overall process capacity is the ratio of the total amount of liquid produced to the feed to the process.

B.3 Distillation column

The capacity variables for a simple distillation column are determined below. The following simplifying assumptions are used to describe the behaviour of the column:

- the feed is saturated liquid
- the products are saturated liquids
- there is constant molar overflow
- each stage is ideal, *i.e.*, an equilibrium stage.

It follows from these assumptions that:

- the liquid flow rate, L, is constant in the rectifying section, and equal to rD, where r is the reflux ratio and D is the distillate flow rate.
- the vapour flow rate, V, is constant throughout the column, and equal to $(r+1)D$ or equivalently sB, where s is the reboil ratio and B the flow rate of the bottoms product.
- the liquid flow rate in the stripping section, L', is constant, and equal to $F+L$ (where F is the feed flow rate) or equivalently, $(s+1)B$.

The capacity variables for the column will be determined by applying the capacity definition to equilibrium separation stages in the rectifying and stripping sections of the column, and by applying the mixing rules to the stage at which the feed is introduced. Results will be proved by induction.

B.3.1 Boiling capacity

It will be shown that the overall boiling capacity of the process is the ratio of the total rate of vapour production within the process to the feed flow rate to the process. This will be proved by applying the definition of κ to the condenser and the first tray in the rectification section of the column, and proving results for the boiling capacity of an arbitrary stage in this section of the column by induction. The definition of κ will then be applied to the reboiler and the first stage of the stripping section of the column. The boiling capacity for an arbitrary stage in this section of the column will be found by induction. Lastly, these results will be applied to the stage at which the feed is introduced, and general results will be obtained by proving a number of smaller results by induction, and combining these results using the definition of overall process capacity.

B.3.1.1 Rectification section

Condenser

The definition of κ is applied to the condenser shown in Fig. B.8; no vapour is formed in the condenser:

$$\kappa_D = \kappa_o = \kappa_1 \tag{B.140}$$

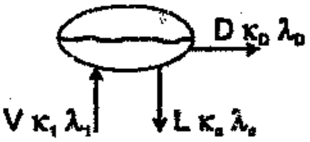

Fig. B.8 Condenser: distillation column. Flow rates and capacity of process streams.

First stage

As shown in Fig. B.9, the first stage of the rectification section is fed by the vapour from the second stage and the liquid from the condenser (zeroth stage).

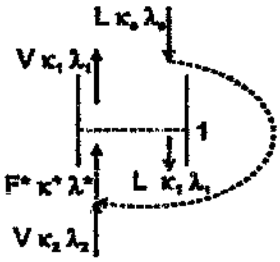

Fig. B.9 First stage of rectification section. Flow rates and capacity of process streams.

The nett feed has quantity $F^* = L+V = 2(r+1)D$ and capacity, κ^*, given by $(L+V)\kappa^* = L\kappa_p + V\kappa_2$. Applying the definition of κ to the first stage:

$$\begin{aligned}\kappa_1 &= \kappa^* + \frac{V}{F^*} \\ &= \frac{r}{2r+1}\kappa_o + \frac{r+1}{2r+1}\kappa_2 + \frac{r+1}{2r+1}\end{aligned} \tag{B.141}$$

By substituting eq. (B.140) it may be shown that:

$$\kappa_1 = \kappa_2 + 1 \tag{B.142}$$

N stages

The following shall be proved by induction:

$$\kappa_n = \kappa_{n+1} + \sum_{k=0}^{n-1} \left(\frac{r}{r+1}\right)^k \tag{B.143}$$

For case $n = 1$, it has been shown in eq. (B.142) that $\kappa_1 = \kappa_2 + 1$. Thus eq. (B.143) holds for $n = 1$.

Eq. (B.143) is assumed to be true for j and shown to be true for $j+1$.

The $(j+1^{th})$ stage in the rectification section is fed by the liquid leaving the j^{th} stage and the vapour leaving the $(j+2^{th})$ stage. Therefore $F^*\kappa^* = V\kappa_{j+2} + L\kappa_j$. Applying the definition of κ to the $(j+1^{th})$ stage:

$$\begin{aligned}\kappa_{j+1} &= \kappa_{j+2}\frac{r+1}{2r+1} + \kappa_j\frac{r}{2r+1} + \frac{r+1}{2r+1} \\ &= \kappa_{j+2}\frac{r+1}{2r+1} + \frac{r}{2r+1}[\kappa_{j+1} + \sum_{k=0}^{j-1}(\frac{r}{r+1})^k] + \frac{r+1}{2r+1}\end{aligned} \tag{B.144}$$

Therefore, it can be shown that:

$$\kappa_{j+1} = \kappa_{j+2} + \sum_{k=0}^{j}(\frac{r}{r+1})^k \tag{B.145}$$

Thus eq. (B.143) is shown true for all $n \geq 1$.

The symbol s_n is introduced to denote the sum:

$$s_n = \sum_{k=0}^{n-1}(\frac{r}{r+1})^k \tag{B.146}$$

The following equations may then be written:

$$\begin{aligned}\kappa_D &= \kappa_o \\ &= \kappa_1 \\ &= \kappa_2 + s_1 \\ &= \kappa_3 + s_1 + s_2 \\ &= \ldots \\ &= \kappa_N + \sum_{i=1}^{N-1} s_i\end{aligned} \tag{B.147}$$

where N is the total number of stages in the rectification section of the column.

B.3.1.2 Stripping section

The stripping section is numbered from the bottom of the column: the reboiler is thus the zeroth stage of the column section.

Reboiler

The reboiler is illustrated in Fig. B.10. Applying the definition of κ to the reboiler, it is found that:

$$\kappa_B' = \kappa_0' = \kappa_1' + \frac{V}{L'} = \kappa_1 + \frac{s}{s+1} \tag{B.148}$$

Fig. B.10 Reboiler of distillation column. Flow rates and capacity of process streams.

First stage

As shown in Fig. B.11, the first stage of the stripping section is fed by the vapour leaving the reboiler (the zeroth stage) and the liquid leaving the second stage. Therefore $F^* = (2s+1)B$ and $F^*\kappa^* = sB\kappa_0' + (s+1)B\kappa_2'$.

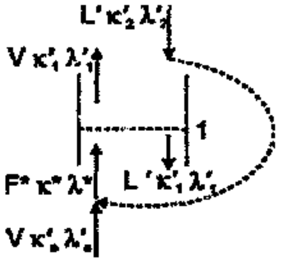

Fig. B.11 First stage of stripping section. Flow rates and capacity of process streams.

Applying the definition of κ to the first stage, and substituting eq. (B.148), it may be shown that:

$$\kappa_1' = \kappa_2' + \left(\frac{s}{s+1}\right)^2 + \frac{s}{\lambda+1} \tag{B.149}$$

M stages

The following will be proved by induction:

$$\kappa_m' = \kappa_{m+1}' + \sum_{k=0}^{m}\left(\frac{s}{s+1}\right)^{k+1} \tag{B.150}$$

For case $m = 0$, it has been shown in eq. (B.148) that eq. (B.150) is true.

Eq. (B.150) is assumed to be true for j and shown to be it true for $j+1$.

The ($j+1^{th}$) stage in the stripping section is fed by the liquid from the ($j+2^{th}$) tray above and by the vapour from the j^{th} tray below. Applying the definition of κ:

$$\begin{aligned}
\kappa^{l}_{j+1} &= \kappa^{*} + \frac{V}{F^{*}} \\
&= \frac{s}{2s+1}\kappa^{l}_{j} + \frac{s+1}{2s+1}\kappa^{l}_{j+2} + \frac{s}{2s+1} \\
&= \frac{s}{2s+1}\left[\kappa^{l}_{j+1} + \sum_{k=0}^{j}\left(\frac{s}{s+1}\right)^{k+1}\right] + \frac{s+1}{2s+1}\kappa^{l}_{j+2} + \frac{s}{2s+1}
\end{aligned} \qquad \text{(B.151)}$$

The above equation may be rearranged to give:

$$\kappa^{l}_{j+1} = \kappa^{l}_{j+2} + \sum_{k=0}^{j+1}\left(\frac{s}{s+1}\right)^{k+1} \qquad \text{(B.152)}$$

Thus eq. (B.150) is shown to be true for all $m \geq 0$.

The symbol σ_m is introduced to denote the sum:

$$\sigma_m = \sum_{k=0}^{m}\left(\frac{s}{s+1}\right)^{k+1} \qquad \text{(B.153)}$$

The following equations may then be written:

$$\begin{aligned}
\kappa^{l}_{B} &= \kappa^{l}_{o} \\
&= \kappa^{l}_{1} + \sigma_{o} \\
&= \kappa^{l}_{2} + \sigma_{1} + \sigma_{0} \\
&= \ldots \\
&= \kappa^{l}_{M+1} + \sum_{k=0}^{M}\sigma_{k}
\end{aligned} \qquad \text{(B.154)}$$

where M is the total number of stages in the stripping section of the column.

B.3.1.3 Feed tray mixing

For a column with N stages in the rectification section and M stages in the stripping section, the feed is introduced as a saturated liquid above the M^{th} tray of the stripping section, as shown in Fig. B.12.

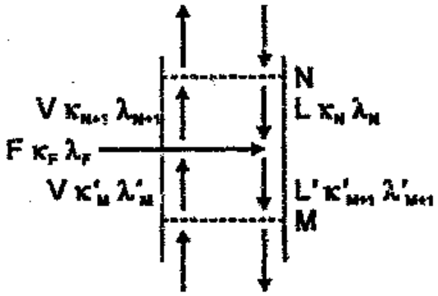

Fig. B.12 Mixing of streams at the feed tray. Flow rates and capacity of process streams.

The feed is of flow rate F and capacity κ_F. The vapour leaving the M^{th} stage and that entering the N^{th} stage are identical in flow rate, composition and capacity. The liquid entering the M^{th} stage is a mixture of the liquid leaving the N^{th} stage and the feed. Therefore this mixture has a mean capacity, $\bar{\kappa}$, which is the weighted average of the capacity of the two constituent streams. For consistency, the liquid stream entering the M^{th} stage of the stripping section will be denoted by the subscript $M+1$, and the vapour stream entering the N^{th} stage of the rectification section will be denoted by the subscript $N+1$. It may therefore be written:

$$\kappa_{N+1} = \kappa'_M \tag{B.155}$$

$$\kappa'_{M+1} = \frac{F}{F+L}\kappa_F + \frac{L}{F+L}\kappa_N \tag{B.156}$$

Combining eqs. (B.147), (B.154), (B.155) and (B.156):

$$\kappa_D = \kappa_F + (1 + \frac{L}{F})(\sigma_M + s_N) + \sum_{k=0}^{N-1} s_k \tag{B.157}$$

and:

$$\kappa'_B = \kappa_F + \frac{L}{F}(\sigma_M + s_N) + \sum_{k=0}^{M} \sigma_k \qquad \text{(B.158)}$$

From eqs. (B.157) and (B.158), the overall capacity of the process may be determined:

$$\begin{aligned} F\kappa_{ov} &= D\kappa_D + B \\ &= F\kappa_F + D(rs_N + \sum_{k=1}^{N} s_k) + B(s\sigma_M + \sum_{k=0}^{M} \sigma_k) \end{aligned} \qquad \text{(B.159)}$$

The following will be proved by induction:

$$F\kappa_{ov} = F\kappa_F + V(N + M + 1) \qquad \text{(B.160)}$$

It is noted that $V = D(r+1)$ and that $V = sB$.

First it is shown that the following is true for all n:

$$r(\frac{r}{r+1})^n + s_{n+1} = r(\frac{r}{r+1})^n + \sum_{i=0}^{n} (\frac{r}{r+1})^i = r + 1 \qquad \text{(B.161)}$$

Eq. (B.161) is true for case $n = 0$ since:

$$r(\frac{r}{r+1})^0 + (\frac{r}{r+1})^0 = r + 1 \qquad \text{(B.162)}$$

It is assumed that eq. (B.161) is true for j and shown to be true for $j+1$:

$$\begin{aligned} r(\frac{r}{r+1})^{j+1} + \sum_{i=0}^{j+1} (\frac{r}{r+1})^i &= r(\frac{r}{r+1})^{j+1} + (\frac{r}{r+1})^{j+1} + \sum_{i=0}^{j} (\frac{r}{r+1})^i \\ &= r(\frac{r}{r+1})^j + \sum_{i=0}^{j} (\frac{r}{r+1})^i \\ &= r + 1 \end{aligned} \qquad \text{(B.163)}$$

Thus eq. (B.161) is true for all $n \geq 0$.

Using this result, the following will be proved by induction:

$$rs_N + \sum_{i=1}^{N} s_i = (r + 1)n \qquad \text{(B.164)}$$

It is first shown that eq. (B.164) is true for case $N = 1$:

$$rs_1 + \sum_{i=1}^{1} s_i = (r + 1)s_1 = (r+1)\sum_{k=0}^{0}(\frac{r}{r+1})^k = r + 1 \tag{B.165}$$

It is then assumed that eq. (B.164) is true for case j, and shown to be true for case $j+1$:

$$\begin{aligned} rs_{j+1} + \sum_{i=1}^{j+1} s_i &= r\sum_{k=0}^{j}(\frac{r}{r+1})^k + s_{j+1} + \sum_{i=1}^{j} s_i \\ &= r(\frac{r}{r+1})^j + rs_j + s_{j+1} + \sum_{i=1}^{j} s_i \\ &= r(\frac{r}{r+1})^j + s_{j+1} + (r + 1)j \\ &= (r + 1) + (r + 1)j \\ &= (r + 1)(j + 1) \end{aligned} \tag{B.166}$$

Thus eq. (B.164) is true for $N \geq 1$.

The following is assumed to be true for all m:

$$\sigma_m + s(\frac{s}{s+1})^{m+1} = \sum_{k=0}^{m}(\frac{s}{s+1})^{k+1} + s(\frac{s}{s+1})^{m+1} = s \tag{B.167}$$

First, eq. (B.167) is shown to be true for $m = 0$:

$$\sum_{k=0}^{0}(\frac{s}{s+1})^{k+1} + s(\frac{s}{s+1})^1 = \frac{s}{s+1} + s\frac{s}{s+1} = s \tag{B.168}$$

Then it is assumed that eq. (B.167) is true for j and shown to be true for $j+1$:

$$\begin{aligned} \sum_{k=0}^{j+1}(\frac{s}{s+1})^{k+1} + s(\frac{s}{s+1})^{j+2} &= \sum_{k=0}^{j}(\frac{s}{s+1})^{k+1} + (s + 1)(\frac{s}{s+1})^{j+2} \\ &= \sum_{k=0}^{j}(\frac{s}{s+1})^{k+1} + s(\frac{s}{s+1})^{j+1} \\ &= s \end{aligned} \tag{B.169}$$

Thus eq. (B.167) is true for all $m \geq 0$.

It must be shown that the following is true for all m:

$$s\sigma_m + \sum_{i=0}^{m}\sigma_i = s(m + 1) \tag{B.170}$$

First it is shown that eq. (B.170) is true for $m = 0$:

$$s\sigma_0 + \sum_{i=0}^{0}\sigma_i = (s+1)\sigma_0 = (s+1)\sum_{i=0}^{0}\left(\frac{s}{s+1}\right)^{k+1} = s \tag{B.171}$$

It is then assumed that eq. (B.170) is true for j and shown to be true for $j+1$:

$$\begin{aligned} s\sigma_{j+1} + \sum_{i=0}^{j+1}\sigma_i &= (s+1)\sigma_{j+1} + \sum_{i=0}^{j}\sigma_i \\ &= (s+1)\sum_{k=0}^{j+1}\left(\frac{s}{s+1}\right)^{k+1} + \sum_{i=0}^{j}\sigma_i \\ &= \sigma_j + s\left(\frac{s}{s+1}\right)^{j+1} + s\sigma_j + \sum_{i=0}^{j}\sigma_i \\ &= s + s(j+1) \\ &= s(j+2) \end{aligned} \tag{B.172}$$

It follows that eq. (B.170) is true for all $M \geq 0$.

It has been shown that:

$$F\kappa_{ov} = F\kappa_F + D(rs_N + \sum_{k=1}^{N}s_k) + B(s\sigma_M + \sum_{k=0}^{M}\sigma_k) \tag{B.159}$$

and that:

$$rs_N + \sum_{i=1}^{N}s_i = (r+1)N \tag{B.164}$$

and that:

$$s\sigma_M + \sum_{i=0}^{M}\sigma_i = s(M+1) \tag{B.170}$$

Since $V = (r+1)D$ and $V = sB$, it follows that:

$$F\kappa_{ov} = F\kappa_F + V(N+M+1) \tag{B.160}$$

i.e.:

$$\kappa_{ov} = \kappa_F + \frac{V(N+M+1)}{F} \tag{B.173}$$

In other words, the change in overall capacity of the column distillation process is the ratio of the total amount of vapour produced (a flow rate V in each of N

stages, plus a flow rate V produced in the reboiler) to the total flow rate of the feed to the process. This result has been proved for $N \geq 1$ and $M \geq 0$ and will be proved for $N = 0$ in the following section, so that eq. (B.173) holds for all $N \geq 0$.

B.3.1.4 Completion of proof

Eq. (B.173) is valid for $N \geq 1$ and $M \geq 0$. To further generalize this result, it is necessary to show that eq. (B.173) is true for all values of N. In particular, this equation must be shown true for N equal to zero, which is the case where the feed is added immediately below the condenser, as shown in Fig. B.13.

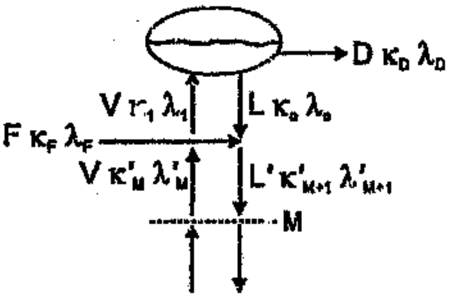

Fig. B.13 Flow rates and capacity variables of process streams for the case N equal to zero.

In this case, the results for the stripping section, namely, eqs. (B.150) and (B.154), hold. The rectification section consists only of a total condenser, which is the zeroth stage. Therefore:

$$\kappa_D = \kappa_0 = \kappa_1 \tag{B.140}$$

The liquid leaving the zeroth stage is mixed with the feed to form the liquid feed to the M^{th} stage of the stripping section, and the vapour leaving the M^{th} stage is the vapour feed to the condenser, as shown in Fig. B.13. Therefore:

$$\kappa'_M = \kappa_1 = \kappa_D \tag{B.174}$$

and:

$$\kappa'_{M+1} = \frac{F}{L+F}\kappa_F + \frac{L}{L+F}\kappa_D = \frac{F}{L+F}\kappa_F + \frac{L}{L+F}\kappa'_M \tag{B.175}$$

But eq. (B.154) holds for the stripping section, hence:

$$\kappa'_B = \kappa'_{M+1} + \sum_{k=0}^{M} \sigma_k \tag{B.176}$$

Similarly, eq. (B.150) holds, hence:

$$\kappa'_M = \kappa'_{M+1} + \sigma_M \tag{B.177}$$

Eqs. (B.175) and (B.177) may be combined to show that:

$$\begin{aligned} \kappa'_{M+1} &= \frac{F}{L+F}\kappa_F + \frac{L}{L+F}(\kappa'_{M+1} + \sigma_M) \\ &= \kappa_F + \frac{L}{F}\sigma_M \end{aligned} \tag{B.178}$$

Eqs. (B.174), (B.176) and (B.178) may be combined to determine the overall boiling capacity of this distillation column:

$$\begin{aligned} \kappa_{ov} &= D\kappa_D + B\kappa'_B \\ &= D\kappa'_M + B(\kappa'_{M+1} + \sum_{k=0}^{M}\sigma_k) \\ &= F\kappa_F + B(s\sigma_M + \sum_{k=0}^{M}\sigma_k) \end{aligned} \tag{B.179}$$

From eq. (B.170) it follows that:

$$\kappa_{ov} = \kappa_F + \frac{V}{F}(M+1) \tag{B.180}$$

which is identical to eq. (B.173) for the case N equal to zero. Hence eq. (B.173) is true for all $N \geq 0$ and all $M \geq 0$.

B.3.2 Condensing capacity

In this section the condensing capacity of a simple distillation column will be determined. The same assumptions are made as for the determination of the boiling capacity of the column, as discussed in Section B.3.1 of this appendix. The results are proved by induction.

B.3.2.1 Rectification section

Condenser

Applying the definition of λ to the condenser of Fig. B.8:

$$\lambda_D = \lambda_o = \lambda_1 + 1 \tag{B.181}$$

First stage

The first stage is fed by the vapour from the second stage and the liquid from the first stage, as shown in Fig. B.9. This mixture has capacity λ^*. Applying the capacity definition to the first stage:

$$\begin{aligned} \lambda_1 &= \lambda^* + \frac{L}{F^*} \\ &= \frac{r}{2r+1}\lambda_o + \frac{r+1}{2r+1}\lambda_2 + \frac{r}{2r+1} \end{aligned} \tag{B.182}$$

Substituting eq. (B.181) into the above, it may be shown that:

$$\lambda_1 = \lambda_2 + 2\frac{r}{r+1} \tag{B.183}$$

N stages

The following will be proved by induction:

$$\lambda_n = \lambda_{n+1} + (\frac{r}{r+1})^n + \sum_{k=1}^{n}(\frac{r}{r+1})^k \tag{B.184}$$

For the case $n = 1$, it has been shown in eq. (B.188) that eq. (B.189) holds.

Eq. (B.184) is assumed to be true for j, and shown to be true for $j+1$. The ($j+1^{th}$) stage is fed by the vapour leaving the ($j+2^{th}$) stage and the liquid leaving the j^{th} stage. Applying the definition of λ:

$$\begin{aligned}\lambda_{j+1} &= \lambda^{*} + \frac{L}{F^{*}} \\ &= \frac{r+1}{2r+1}\lambda_{j+2} + \frac{r}{2r+1}\lambda_{j} + \frac{r}{2r+1} \\ &= \frac{r+1}{2r+1}\lambda_{j+2} + \frac{r}{2r+1}\left[\lambda_{j+1} + (\frac{r}{r+1})^{j} + \sum_{k=1}^{j}(\frac{r}{r+1})^{k}\right] + \frac{r}{2r+1}\end{aligned} \tag{B.185}$$

from which it may be shown:

$$\lambda_{j+1} = \lambda_{j+2} + (\frac{r}{r+1})^{j+1} + \sum_{k=1}^{j+1}(\frac{r}{r+1})^{k} \tag{B.186}$$

Thus eq. (B.184) is shown true for all $n \geq 1$.

The following shall be proved true by induction:

$$\lambda_{D} = \lambda_{n+1} + \sum_{k=1}^{n}(n + 2 - k)(\frac{r}{r+1})^{k} + 1 \tag{B.187}$$

This statement is true for case $n = 1$, since eqs. (B.181) and (B.183) may be combined as follows:

$$\lambda_{D} = \lambda_{2} + 2\frac{r}{r+1} + 1 \tag{B.188}$$

Eq. (B.187) is assumed to be true for j and shown to be true for $j+1$ by substituting eq. (B.186) into eq. (B.187):

$$\begin{aligned}\lambda_{D} &= \lambda_{j+1} + \sum_{k=1}^{j}(j+2 - k)(\frac{r}{r+1})^{k} + 1 \\ &= [\lambda_{j+2} + (\frac{r}{r+1})^{j+1} + \sum_{k=1}^{j+1}(\frac{r}{r+1})^{k}] + \sum_{k=1}^{j}(j+2 - k)(\frac{r}{r+1})^{k} + 1 \\ &= \lambda_{j+2} + \sum_{k=1}^{j+1}(j+1 + 2 - k)(\frac{r}{r+1})^{k} + 1\end{aligned} \tag{B.189}$$

Thus eq. (B.187) is true for all $n \geq 1$.

B.3.2.2 Stripping section

Reboiler

Applying the definition of λ to the reboiler illustrated in Fig. B.10:

$$\lambda'_B = \lambda'_o = \lambda'_1 + \frac{B}{L'} = \lambda'_1 + \frac{1}{s+1} \tag{B.190}$$

First stage

The first stage is fed by the vapour from the reboiler (zeroth) stage and the liquid from the second stage, as shown in Fig. B.11. The capacity of the nett feed to the first stage is therefore given by: $(V+L')\lambda^* = V\lambda'_o + L'\lambda'_2$. Applying the definition of λ to the first stage:

$$\begin{aligned}\lambda'_1 &= \lambda^* + \frac{L'}{F^*} \\ &= \frac{s}{2s+1}\lambda'_o + \frac{s+1}{2s+1}\lambda'_2 + \frac{s+1}{2s+1} \\ &= \frac{s}{2s+1}(\lambda'_1 + \frac{1}{s+1}) + \frac{s+1}{2s+1}\lambda'_2 + \frac{s+1}{2s+1} \\ &= \lambda'_2 + \frac{1}{s+1}\frac{s}{s+1} + 1\end{aligned} \tag{B.191}$$

M stages

It is proposed that the following statement is true:

$$\lambda'_m = \lambda'_{m+1} + \frac{1}{s+1}(\frac{s}{s+1})^m + \sum_{k=0}^{m-1}(\frac{s}{s+1})^k \tag{B.192}$$

This will be proved true by induction.

For case $m = 1$, it has been shown in eq. (B.191) that eq. (B.192) is true.

Eq. (B.192) is assumed true for j and shown to be true for $j+1$. The $(j+1^{th})$ stage is fed by the vapour leaving the j^{th} stage and the liquid leaving the $(j+2^{th})$ stage. Therefore the capacity of the nett feed to the $(j+1^{th})$ stage is the weighted average of the capacity of these stages:

$$\begin{aligned}\lambda'_{j+1} &= \lambda^{*} + \frac{L'}{F^{*}} \\ &= \frac{s}{2s+1}\lambda'_{j} + \frac{s+1}{2s+1}\lambda'_{j+2} + \frac{s+1}{2s+1} \\ &= \frac{s}{2s+1}\left[\lambda'_{j+1} + \frac{1}{s+1}\left(\frac{s}{s+1}\right)^{j} + \sum_{k=0}^{j-1}\left(\frac{s}{s+1}\right)^{k}\right] + \frac{s+1}{2s+1}\lambda'_{j+2} + \frac{s+1}{2s+1} \\ &= \lambda'_{j+2} + \frac{1}{s+1}\left(\frac{s}{s+1}\right)^{j+1} + \sum_{k=0}^{j}\left(\frac{s}{s+1}\right)^{k}\end{aligned} \tag{B.193}$$

Thus eq. (B.192) is shown true for all $m \geq 1$.

The following will be shown to be true by induction:

$$\lambda'_{B} = \lambda'_{m+1} + \frac{1}{s+1}\sum_{k=0}^{m}\left(\frac{s}{s+1}\right)^{k} + \sum_{k=0}^{m}(m-k)\left(\frac{s}{s+1}\right)^{k} \tag{B.194}$$

For case $m = 1$, eqs. (B.190) and (B.191) may be combined to show that eq. (B.194) is true:

$$\begin{aligned}\lambda'_{B} = \lambda'_{o} &= \lambda'_{1} + \frac{1}{s+1} \\ &= \lambda'_{2} + \frac{1}{s+1}\frac{s}{s+1} + \frac{1}{s+1} + 1\end{aligned} \tag{B.195}$$

Eq. (B.194) is assumed to be true for case j, and shown to be true for case $j+1$:

$$\begin{aligned}\lambda'_{B} &= \lambda'_{j+1} + \frac{1}{s+1}\sum_{k=0}^{j}\left(\frac{s}{s+1}\right)^{k} + \sum_{k=0}^{j}(j-k)\left(\frac{s}{s+1}\right)^{k} \\ &= \left[\lambda'_{j+2} + \frac{1}{s+1}\left(\frac{s}{s+1}\right)^{j+1} + \sum_{k=0}^{j}\left(\frac{s}{s+1}\right)^{k}\right] + \frac{1}{s+1}\sum_{k=0}^{j}\left(\frac{s}{s+1}\right)^{k} + \sum_{k=0}^{j}(j-k)\left(\frac{s}{s+1}\right)^{k} \\ &= \lambda'_{j+2} + \frac{1}{s+1}\sum_{k=0}^{j+1}\left(\frac{s}{s+1}\right)^{k} + \sum_{k=0}^{j+1}(j+1-k)\left(\frac{s}{s+1}\right)^{k}\end{aligned} \tag{B.196}$$

Thus eq. (B.194) is shown true for all $m \geq 1$.

B.3.2.3 Feed stage

Consider a column which has N stages in the rectification section and M stages in the stripping section. The saturated liquid feed is introduced above the M^{th} stage of the stripping section, as shown in Fig. B.12. Since the feed is saturated liquid, the capacity of the vapour stream leaving the M^{th} stage of the stripping section is equal to the capacity of the vapour stream entering the N^{th} stage of the rectifying section, that is:

$$\lambda_{N+1} = \lambda'_M \tag{B.197}$$

The mixture of the feed and the liquid leaving the N^{th} stage of the rectification section has capacity λ^* given by:

$$(F + L)\lambda^* = (F + L)\lambda'_{M+1} = F\lambda_F + L\lambda_N \tag{B.198}$$

The sums f_n and g_m are defined in the following way:

$$f_n = \left(\frac{r}{r+1}\right)^n + \sum_{k=1}^{n}\left(\frac{r}{r+1}\right)^k \tag{B.199}$$

and:

$$g_m = \frac{1}{s+1}\left(\frac{s}{s+1}\right)^m + \sum_{k=0}^{m-1}\left(\frac{s}{s+1}\right)^k \tag{B.200}$$

Therefore eqs. (B.184) and (B.192) may be rewritten as follows:

$$\lambda_n = \lambda_{n+1} + f_n \tag{B.201}$$

and:

$$\lambda'_m = \lambda'_{m+1} + g_m \tag{B.202}$$

Substituting in the relationships given above for λ_{N+1} and λ'_{M+1}, it may be shown that:

$$\lambda_N = \lambda_F + \frac{F+L}{F}(f_N + g_M) \tag{B.203}$$

and:

$$\lambda'_{M+1} = \lambda_F + \frac{L}{F}(f_N + g_M) \tag{B.204}$$

It follows from eqs. (B.201) and (B.203) that:

$$\lambda_{N+1} = \lambda_F + \frac{L}{F} f_N + \frac{F+L}{F} g_M \tag{B.205}$$

The overall condensing capacity of the process is the weighted average of the capacity of the process streams. By combining eqs. (B.187) and (B.194), it may be shown that:

$$\begin{aligned} F\lambda_{ov} = F\lambda_F + D[rf_N + \sum_{k=1}^{N}(N+2 - k)(\frac{r}{r+1})^k + 1] + \\ B[sg_M + \frac{1}{s+1}\sum_{k=0}^{M}(\frac{s}{s+1})^k + \sum_{k=0}^{M}(M - k)(\frac{s}{s+1})^k] \end{aligned} \tag{B.206}$$

It will be proved by induction that the change in overall condensing capacity of this distillation column is the ratio of the total rate of liquid production in the column to the feed flow rate to the column. The total rate of liquid production is a rate $L = rD$ in each of the N stages of the rectification section, and a rate $L+D$ in the condenser, a rate $L' = (s+1)B$ in each of the M stages of the stripping section, and a rate B in the reboiler. Therefore, it will be shown that eq. (B.206) is equivalent to:

$$F\lambda_{ov} = F\lambda_F + D(r(N+1) + 1) + B((s+1)M + 1) \tag{B.207}$$

This equivalence will be proved inductively, by showing that the coefficients of D in eqs. (B.206) and (B.207) are equal, as are the coefficients of B.

First, it is shown that the following is true for all n:

$$r(\frac{r}{r+1})^n + \sum_{k=1}^{n}(\frac{r}{r+1})^k = r \tag{B.208}$$

Eq. (B.208) is true for case $n = 1$ since:

$$r(\frac{r}{r+1})^1 + (\frac{r}{r+1})^1 = r \tag{B.209}$$

Eq. (B.208) is assumed true for j and shown true for $j+1$:

$$\begin{aligned} r\left(\frac{r}{r+1}\right)^{j+1} + \sum_{k=1}^{j+1}\left(\frac{r}{r+1}\right)^{k} &= r\left(\frac{r}{r+1}\right)^{j+1} + \left(\frac{r}{r+1}\right)^{j+1} + \sum_{k=1}^{j}\left(\frac{r}{r+1}\right)^{k} \\ &= (r+1)\left(\frac{r}{r+1}\right)^{j+1} + \sum_{k=1}^{j}\left(\frac{r}{r+1}\right)^{k} \\ &= r\left(\frac{r}{r+1}\right)^{j} + \sum_{k=1}^{j}\left(\frac{r}{r+1}\right)^{k} = r \end{aligned} \tag{B.210}$$

It will further be shown that the following is true, where f_n is given by eq. (B.199):

$$rf_n + \sum_{k=1}^{n}(n+2-k)\left(\frac{r}{r+1}\right)^{k} + 1 = r(n+1) + 1 \tag{B.211}$$

Eq. (B.211) is true for case $n = 1$ since:

$$\begin{aligned} & rf_1 + \sum_{k=1}^{1}(1+2-k)\left(\frac{r}{r+1}\right)^{k} + 1 \\ &\quad = r\left[\left(\frac{r}{r+1}\right)^{1} + \sum_{k=1}^{1}\left(\frac{r}{r+1}\right)^{k}\right] + 2\frac{r}{r+1} + 1 \\ &\quad = 2r\frac{r}{r+1} + 2\frac{r}{r+1} + 1 \\ &\quad = 2r + 1 \end{aligned} \tag{B.212}$$

Eq. (B.211) is assumed to be true for j and shown to be true for $j+1$, using eq. (B.208):

$$\begin{aligned} & rf_{j+1} + \sum_{k=1}^{j+1}(j+1+2-k)\left(\frac{r}{r+1}\right)^{k} + 1 \\ &\quad = r\left(\frac{r}{r+1}\right)^{j+1} + \sum_{k=1}^{j+1}\left(\frac{r}{r+1}\right)^{k} + \sum_{k=0}^{j+1}(j+1+2-k)\left(\frac{r}{r+1}\right)^{k} + 1 \\ &\quad = (2r+2)\left(\frac{r}{r+1}\right)^{j+1} + r\sum_{k=0}^{j}\left(\frac{r}{r+1}\right)^{k} + \sum_{k=1}^{j}(j+2-k)\left(\frac{r}{r+1}\right)^{k} + \sum_{k=1}^{j}\left(\frac{r}{r+1}\right)^{k} + 1 \\ &\quad = r\left[\left(\frac{r}{r+1}\right)^{j} + \sum_{k=1}^{j}\left(\frac{r}{r+1}\right)^{k}\right] + \sum_{k=1}^{j}(j+2-k)\left(\frac{r}{r+1}\right)^{k} + 1 + r\left(\frac{r}{r+1}\right)^{j} + \sum_{k=1}^{j}\left(\frac{r}{r+1}\right)^{k} \\ &\quad = rf_j + \sum_{k=1}^{j}(j+2-k)\left(\frac{r}{r+1}\right)^{k} + 1 + r \\ &\quad = r(j+2) + 1 \end{aligned} \tag{B.213}$$

Thus eq. (B.211) has been shown to be true for all $n \geq 1$. It follows that the coefficients of D in eqs. (B.206) and (B.207) are equal.

It will be proved by induction that the following is true:

$$s(\frac{s}{s+1})^m + \sum_{k=0}^{m}(\frac{s}{s+1})^k = s + 1 \tag{B.214}$$

Eq. (B.214) is true for case $m = 1$ since:

$$s(\frac{s}{s+1})^1 + (\frac{s}{s+1})^1 + (\frac{s}{s+1})^0 = (s + 1)(\frac{s}{s+1}) + 1 = s + 1 \tag{B.215}$$

Eq. (B.214) is assumed to be true for j and shown to be true for $j+1$:

$$\begin{aligned} s(\frac{s}{s+1})^{j+1} + \sum_{k=0}^{j+1}(\frac{s}{s+1})^k &= s(\frac{s}{s+1})^{j+1} + (\frac{s}{s+1})^{j+1} + \sum_{k=0}^{j}(\frac{s}{s+1})^k \\ &= s(\frac{s}{s+1})^j + \sum_{k=0}^{j}(\frac{s}{s+1})^k \\ &= s + 1 \end{aligned} \tag{B.216}$$

Thus eq. (B.214) is true for all $m \geq 1$.

The following will be shown to be true, where g_m is given by eq. (B.200):

$$sg_m + \frac{1}{s+1}\sum_{k=0}^{m}(\frac{s}{s+1})^k + \sum_{k=0}^{m}(m - k)(\frac{s}{s+1})^k = (s + 1)m + 1 \tag{B.217}$$

Eq. (B.217) is shown to be true for $m = 1$:

$$\begin{aligned} &sg_1 + \frac{1}{s+1}\sum_{k=0}^{1}(\frac{s}{s+1})^k + \sum_{k=0}^{1}(1 - k)(\frac{s}{s+1})^k \\ &= s\frac{1}{s+1}\frac{s}{s+1} + s + \frac{1}{s+1}\frac{s}{s+1} + \frac{1}{s+1} + 1 \\ &= (s + 1) + 1 \end{aligned} \tag{B.218}$$

It is assumed that eq. (B.217) is true for j and shown to be true for $j+1$:

$$\begin{aligned} &sg_{j+1} + \frac{1}{s+1}\sum_{k=0}^{j+1}(\frac{s}{s+1})^k + \sum_{k=0}^{j+1}(j+1 - k)(\frac{s}{s+1})^k \\ &= s[\frac{1}{s+1}(\frac{s}{s+1})^{j+1} + \sum_{k=0}^{j+1}(\frac{s}{s+1})^k] + \frac{1}{s+1}\sum_{k=0}^{j+1}(\frac{s}{s+1})^k + \sum_{k=0}^{j+1}(j+1 - k)(\frac{s}{s+1})^k \\ &= s\frac{1}{s+1}(\frac{s}{s+1})^j + s\sum_{0}^{j-1}(\frac{s}{s+1})^k + s(\frac{s}{s+1})^j + \sum_{0}^{j}(\frac{s}{s+1})^k + \frac{1}{s+1}\sum_{0}^{j}(\frac{s}{s+1})^k + \sum_{0}^{j}(j-k)(\frac{s}{s+1})^k \\ &\quad sg_j + \frac{1}{s+1}\sum_{0}^{j}(\frac{s}{s+1})^k + \sum_{0}^{j}(j-k)(\frac{s}{s+1})^k + s+1 \\ &= (s+1)(j+1) + 1 \end{aligned} \tag{B.219}$$

Therefore eq. (B.217) is true for all $m \geq 1$, and the coefficients of F in eqs. (B.206) and (B.207) are shown to be equal.

Thus, by proving eqs. (B.211) and (B.217), it has been proved that eqs. (B.206) and (B.207) are equivalent. In other words, the change in overall condensing capacity is the ratio of the total rate of liquid production in the column to the flow rate of the feed to the column. This result is valid for $N \geq 1$ and $M \geq 1$. In the following section eq. (B.207) will be proved for $N = 0$ and $M = 0$, so that the result holds for $N \geq 0$ and $M \geq 0$.

B.3.2.4 Completion of proof

Eq. (B.207) has been proved true for all $N \geq 1$ and all $M \geq 1$. It is required to generalize this result by proving it true for N equal to zero and for M equal to zero. These two cases will be presented separately.

N equal to zero

Consider a column in which the feed is added immediately below the condenser, as shown in Fig. B.13. Therefore N is equal to zero. Eqs. (B.194), (B.202) and (B.217) hold for the stripping section.

The condensing capacity of the products of the condenser is:

$$\lambda_D = \lambda_0 = \lambda_1 + 1 \tag{B.181}$$

The vapour leaving the M^{th} stage of the stripping section is the vapour feed to the condenser, therefore:

$$\lambda'_M = \lambda_1 \tag{B.220}$$

Eq. (B.202) holds for the stripping section, and therefore eqs. (B.181) and (B.220) may be combined as follows:

$$\lambda_D = \lambda'_{M+1} + g_M + 1 \tag{B.221}$$

The feed is mixed with the liquid product of the condenser to form the liquid feed to the M^{th} stage of the stripping section. Therefore:

$$\begin{aligned}\lambda'_{M+1} &= \frac{F}{L+F}\lambda_F + \frac{L}{L+F}\lambda_0 \\ &= \frac{F}{L+F}\lambda_F + \frac{L}{L+F}(\lambda'_{M+1} + g_M + 1) \\ &= \frac{L}{F}(g_M + 1) + \lambda_F\end{aligned} \qquad \text{(B.222)}$$

Since eqs. (B.194) and (B.217) hold, the overall condensing capacity may be determined as follows:

$$\begin{aligned}F\kappa_{ov} &= D\lambda_D + B\lambda'_B \\ &= D(\lambda'_{M+1} + g_M + 1) + B\left[\sum_{k=0}^{M}(M-k+\frac{1}{s+1})(\frac{s}{s+1})^k\right] \\ &= F\lambda_F + L(g_M + 1) + Dg_M + D + B\left[\sum_0^M(M-k+\frac{1}{s+1})(\frac{s}{s+1})^k\right] \\ &= F\lambda_F + V + B\left[sg_M + \frac{1}{s+1}\sum_0^M(\frac{s}{s+1})^k + \sum_0^M(M-k)(\frac{s}{s+1})^k\right]\end{aligned} \qquad \text{(B.223)}$$

Eq. (B.217) may be substituted into the above equation, giving the following result:

$$F\lambda_{ov} = F\lambda_F + V + B[M(s+1) + 1] \qquad \text{(B.224)}$$

This is identical to eq. (B.173) for the case N equal to zero.

Case M equal to zero

Consider the case in which the feed to the column is added directly above the reboiler, as shown in Fig. B.14. It is necessary to prove that eq. (B.207) is valid for this case, in which M is equal to zero. The rectification section has N stages, and eqs. (B.187), (B.197) and (B.201) hold.

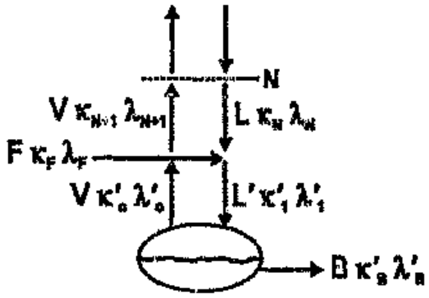

Fig. B.14 Flow rates and capacity variables of process streams for the case M equal to zero.

The condensing capacity of the products of the reboiler is given by:

$$\lambda'_B = \lambda'_0 = \lambda'_1 + \frac{1}{s+1} \tag{B.190}$$

The vapour produced by the reboiler forms the vapour feed to the N^{th} stage of the rectification section. Hence:

$$\lambda_{N+1} = \lambda'_0 = \lambda'_B \tag{B.225}$$

The liquid product of the N^{th} stage is mixed with the feed to form the feed to the reboiler. Therefore:

$$\lambda'_1 = \frac{F}{L+F}\lambda_F + \frac{L}{L+F}\lambda_N \tag{B.226}$$

By combining eqs. (B.190), (B.201) and the two previous equations, it may be shown that:

$$\begin{aligned}\lambda'_B &= \frac{F}{L+F}\lambda_F + \frac{L}{L+F}\lambda_N + \frac{1}{S+1} \\ &= \frac{F}{L+F}\lambda_F + \frac{L}{L+F}(\lambda'_B + f_N) + \frac{1}{s+1}\end{aligned} \tag{B.227}$$

Rearranging this equation:

$$\lambda'_B = \lambda_F + \frac{L}{F}f_N + \frac{L+F}{F}\frac{1}{s+1} \tag{B.228}$$

From eqs. (B.187) and (B.225), it follows that:

$$\lambda_D = \lambda_B' + \sum_{k=1}^{N} (N+2-k)\left(\frac{r}{r+1}\right)^k + 1 \qquad \text{(B.229)}$$

where, for convenience, the right hand term of eq. (B.229) will be denoted by A, *i.e.*, $\lambda_D = \lambda_B' + A$.

From eqs. (B.187) and (B.229), it follows:

$$\begin{aligned} F\lambda_{av} &= D\lambda_D + B\lambda_B' \\ &= D(\lambda_B' + A) + B(\lambda_B') \\ &= F\lambda_B' + DA \\ &= F\lambda_F + Lf_N + \frac{F+L}{s+1} + DA \end{aligned} \qquad \text{(B.230)}$$

Since $F + L = L' = (s+1)B$, and since, from eq. (B.211), $rf_N + A = r(N+1)+1$, it follows:

$$\begin{aligned} F\lambda_{av} &= F\lambda_F + B + D(rf_N + A) \\ &= F\lambda_F + D[r(N+1)+1] + B \end{aligned} \qquad \text{(B.231)}$$

Therefore eq. (B.207) holds for the case where M is equal to zero. This concludes the proof of eq. (B.207) for a distillation column.

Appendix C

Case Studies – Data

This appendix details the results of the distillation simulations presented in Section 6.4. The thermodynamic data used is presented in Chapter 6, and the feed and product compositions are noted. The minimum capacity variables (κ_{ov} and λ_{ov}), the optimum reflux ratios associated with them (R_{opt}), the minimum reflux ratio (R_{min}), the optimum number of stages (N) and the ratio R_{opt}/R_{min} are presented for both κ_{ov} and λ_{ov} for a range of product specifications. For each product specification, it is noted in the last two columns whether an integral number of stages was required in either the rectification (R) or stripping (S) section: for example, an entry S5 in the Int(κ) means that exactly five stages were required in the stripping section in order to minimize κ_{ov} for the given product composition.

Table C.1 Ideal binary distillation. x_F: 0.38, x_B: 0.10

$x_{D,1}$	κ_{ov}	$R_{opt}(\kappa_{ov})$	λ_{ov}	$R_{opt}(\lambda_{ov})$	R_{min}	$N(\kappa_{ov})$	$N(\lambda_{ov})$	R_{opt}/R_{min} (κ_{ov})	R_{opt}/R_{min} (λ_{ov})	Int(κ)	Int(λ)
0.65	5.551	0.625	7.548	0.662	0.215	5.709	5.564	2.906	3.076		S4
0.70	6.360	0.863	8.589	0.969	0.440	6.317	5.934	1.960	2.202		S4
0.75	7.340	1.269	9.666	1.277	0.665	6.510	6.483	1.908	1.920		S4
0.80	8.229	1.549	10.685	1.585	0.890	7.099	6.968	1.730	1.780	R3	S4
0.85	9.363	1.815	11.835	1.892	1.115	7.911	7.675	1.627	1.697		S4
0.90	10.674	2.148	13.110	2.200	1.340	8.688	8.532	1.603	1.642		S4
0.93	11.666	2.385	14.024	2.385	1.475	9.217	9.217	1.617	1.617	S4	S4
0.95	12.504	2.390	14.788	2.508	1.565	10.199	9.848	1.527	1.602	R6	S4
0.96	13.100	2.569	15.266	2.569	1.610	10.273	10.273	1.596	1.596	S4	S4
0.965	13.416	2.431	15.544	2.600	1.633	11.080	10.527	[illegible]	1.593		S4
0.97	13.732	2.487	15.825	2.563	1.655	11.235	10.994	1.503	1.548	R7	
0.975	14.176	2.662	16.156	2.662	1.678	11.098	11.098	1.586	1.586	S4	S4
0.98	14.676	2.431	16.584	2.630	1.700	12.443	11.726	1.430	1.547	R8	
0.985	15.285	2.711	17.043	2.711	1.723	12.018	12.018	1.574	1.574	R8	R8
0.99	16.127	2.598	17.710	2.598	1.745	13.248	13.248	1.488	1.488	R9	R9
0.995	17.570	2.720	18.795	2.720	1.768	14.099	14.099	1.538	1.538	R10	R10

Table C.2 Non-ideal binary distillation. x_F: 0.38, x_B: 0.05.

$x_{D,1}$	κ_{ov}	$R_{opt}(\kappa_{ov})$	λ_{ov}	$R_{opt}(\lambda_{ov})$	R_{min}	$N(\kappa_{ov})$	$N(\lambda_{ov})$	R_{opt}/R_{min} (κ_{ov})	R_{opt}/R_{min} (λ_{ov})	Int(κ)	Int(λ)
0.6	7.321	0.495	8.845	0.631	0.188	7.163	6.513	2.63	3.35		S5
0.630	8.189	0.657	9.795	0.853	0.350	7.683	6.816	1.88	2.44		S5
0.650	8.800	0.965	10.406	1.002	0.458	7.142	6.998	2.11	2.19		S5
0.680	9.818	1.117	11.412	1.224	0.620	7.854	7.440	1.80	1.97		S5
0.700	10.439	1.208	12.058	1.372	0.729	8.314	7.695	1.66	1.88		S5
0.720	11.059	1.441	12.691	1.521	0.837	8.200	7.934	1.72	1.82	R3	S5
0.750	12.166	1.658	13.735	1.743	0.999	8.708	8.414	1.66	1.75		S5
0.770	12.861	1.729	14.431	1.891	1.107	9.283	8.725	1.56	1.71		S5
0.800	14.041	2.095	15.532	2.114	1.269	9.311	9.249	1.65	1.67		S5
0.830	15.272	2.213	16.713	2.336	1.431	10.234	9.839	1.55	1.63	R5	S5
0.850	16.245	2.473	17.583	2.484	1.539	10.339	10.303	1.61	1.61		S5
0.880	17.795	2.707	18.994	2.707	1.701	11.074	11.074	1.59	1.59	S5	S5
0.900	19.028	2.731	20.102	2.855	1.809	12.136	11.723	1.51	1.58		S5
0.930	21.267	3.031	22.060	3.065	1.971	13.071	12.958	1.54	1.56	R8	
0.950	23.277	3.226	23.768	3.226	2.079	14.023	14.023	1.55	1.55	S5	S5
0.960	24.564	3.193	24.859	3.240	2.133	15.156	14.978	1.50	1.52	R10	
0.970	26.168	3.263	26.188	3.287	2.187	16.113	16.016	1.49	1.50		
0.980	28.317	3.426	27.950	3.426	2.241	17.030	17.030	1.53	1.53	R12	R12
0.990	31.891	3.522	30.839	3.522	2.295	19.087	19.087	1.53	1.53	S5	S5

Table C.3 Ideal ternary distillation. $\bar{x}_F$: (0.3, 0.3, 0.4), $x_{D,1}$: 0.999, $x_{B,1}$: 0.01

$x_{D,3}$	κ_{opt}	$R_{opt}(\kappa_{opt})$	λ_{opt}	$R_{opt}(\lambda_{opt})$	R_{min}	$N(\kappa_{opt})$	$N(\lambda_{opt})$	R_{opt}/R_{min} (κ_{opt})	R_{opt}/R_{min} (λ_{opt})	Int(κ)	Int(λ)
1E-12	24.499	2.335	29.583	2.538	2.016	23.521	22.437	1.16	1.26	S11	S10
2E-12	24.623	2.401	29.776	2.601	2.099	23.163	22.097	1.14	1.24	S11	S10
3E-12	24.676	2.350	30.192	2.693	2.124	23.589	21.784	1.11	1.27	R12	S10
4E-12	25.052	2.534	30.610	2.779	2.163	22.659	21.555	1.17	1.28	S11	S10
5E-12	25.248	2.586	30.835	2.827	2.226	22.503	21.418	1.16	1.27	S11	S10
6E-12	25 364	2.618	30.971	2.858	2.266	22.398	21.322	1.16	1.26	S11	S10
7E-12	25.438	2.641	31.059	2.880	2.294	22.318	21.247	1.15	1.26	S11	S10
8E-12	25.485	2.658	31.118	2.896	2.314	22.254	21.186	1.15	1.25	S11	S10
9E-12	25.516	2.671	31.159	2.909	2.33	22.200	21.134	1.15	1.25	S11	S10
1E-11	25.535	2.681	31.186	2.918	2.342	22.153	21.087	1.14	1.25	S11	S10
2E-11	26.265	2.696	32.418	2.884	2.442	22.719	21.634	1.10	1.18	S12	S11
3E-11	26.871	2.828	33.073	3.009	2.592	22.431	21.375	1.09	1.16	S12	S11
4E-11	27.105	3.069	33.363	3.069	2.661	21.236	21.236	1.15	1.15	S11	S11
5E-11	27.218	3.104	33.515	3.104	2.701	21.139	21.139	1.15	1.15	S11	S11
6E-11	27.274	3.126	33.603	3.412	2.728	21.062	20.056	1.15	1.25	S11	R10
7E-11	27.311	3.124	33.703	3.152	2.746	21.105	20.985	1.14	1.15	R10	S11
8E-11	27.584	3.014	34.362	3.272	2.76	21.938	20.813	1.09	1.19	S12	S11
9E-11	28.054	3.108	34.853	3.361	2.787	21.794	20.693	1.12	1.21	S12	S11
1E-10	28.418	3.181	35.234	3.451	2.869	21.689	20.602	1.11	1.20	S12	S11
2E-10	29.916	3.486	36.797	3.726	3.206	21.260	20.214	1.09	1.16	S12	S11
3E-10	30.321	3.581	37.228	3.819	3.309	21.092	20.051	1.08	1.15	S12	S11
4E-10	30.892	3.706	38.439	3.706	3.359	20.910	20.910	1.10	1.10	S12	S12
5E-10	32.352	3.988	40.060	3.988	3.573	20.650	20.650	1.12	1.12	S12	S12
6E-10	33.289	4.167	41.095	4.167	3.769	20.502	20.502	1.11	1.11	S12	S12
7E-10	33.939	4.293	41.801	4.660	3.902	20.404	19.345	1.10	1.19	S12	S11
8E-10	34.415	4.385	42.289	4.751	4.00	20.332	19.280	1.10	1.19	S12	S12
9E-10	34.776	4.456	42.660	4.821	4.075	20.276	19.229	1.09	1.18	S12	S11
1E-09	35.059	4.512	42.951	4.876	4.135	20.231	19.186	1.09	1.18	S12	S11
2E-09	36.975	4.618	45.429	4.949	4.394	20.969	19.873	1.05	1.13	S13	S12
3E-09	41.802	5.822	50.418	5.822	5.206	19.453	19.453	1.12	1.12	S12	S12
4E-09	44.022	6.242	52.814	6.242	5.639	19.289	19.289	1.11	1.11	S12	S12
5E-09	45.320	6.490	54.214	6.490	5.893	19.196	19.196	1.10	1.10	S12	S12
6E-09	46.163	6.654	55.125	6.654	6.061	19.131	19.131	1.10	1.10	S12	S12
7E-09	46.749	6.771	55.761	6.771	6.178	19.081	19.081	1.10	1.10	S12	S12
8E-09	47.175	6.857	56.226	6.857	6.268	19.040	19.040	1.09	1.09	S12	S12
8.5E-9	47.346	6.893	56.413	6.893	6.303	19.021	19.021	1.09	1.09	S12	S12
9E-09	47.495	6.925	56.577	6.925	6.335	19.004	19.004	1.09	1.09	S12	S12
9.5E-9	47.961	6.729	57.485	6.729	6.364	19.713	19.713	1.06	1.05	R7	R7
1E-08	49.213	6.849	58.995	6.849	6.389	19.928	19.928	1.07	1.07	S13	S13
1.05E-8	50.701	7.121	60.591	7.121	6.569	19.839	19.839	1.08	1.08	S13	S13
1.1E-08	52.051	7.367	62.037	7.367	6.819	19.765	19.765	1.08	1.08	S13	S13
1.2E-08	54.406	7.795	64.555	7.795	7.254	19.648	19.648	1.07	1.07	S13	S13
1.5E-08	59.551	8.725	70.041	8.725	8.189	19.438	19.438	1.07	1.07	S13	S13
2E-08	64.642	9.645	75.459	9.645	9.104	19.270	19.270	1.06	1.06	S13	S13
3E-08	69.655	10.555	80.784	11.256	10.013	19.120	18.100	1.05	1.12	S13	S12
4E-08	72.102	11.008	83.307	11.719	10.463	19.042	18.025	1.05	1.12	S13	S12
5E-08	76.810	11.239	88.694	11.940	10.736	19.947	18.880	1.05	1.11	S14	S13

Table C.4A Non-ideal ternary distillation. $\bar{x}_F$: (0.2, 0.5, 0.3), $\bar{x}_D$: (0.3, 0.15, 0.55)

$x_{B,1}$	$x_{B,3}$	κ_{av}	$R_{opt}(\kappa_{av})$	λ_{av}	$R_{opt}(\lambda_{av})$	R_{min}	$N(\kappa_{av})$	$N(\lambda_{av})$ (κ_{av})	R_{opt}/R_{min} (λ_{av})	R_{opt}/R_{min}	Int(κ)	Int(λ)
0.0025	0.081	15.146	0.645	20.234	0.641	0.526	15.944	16.011	1.226	1.218	R3	
0.005	0.082	13.194	0.648	17.330	0.648	0.527	13.794	13.794	1.229	1.229	R3	R3
0.01	0.084	11.209	0.672	14.400	0.656	0.530	11.482	11.607	1.268	1.238		R3
0.0125	0.085	10.558	0.683	13.444	0.661	0.532	10.726	10.889	1.284	1.242		R3
0.015	0.086	10.034	0.704	12.679	0.668	0.534	10.051	10.304	1.319	1.250		R3
0.02	0.088	9.210	0.725	11.468	0.684	0.540	9.109	9.363	1.342	1.266		R3
0.025	0.09	8.584	0.737	10.539	0.705	0.547	8.438	8.519	1.346	1.288		R3
0.03	0.092	8.067	0.740	9.782	0.724	0.557	7.927	8.016	1.329	1.300		R
0.035	0.094	7.679	0.765	9.185	0.761	0.565	7.456	7.477	1.354	1.346		R3
0.04	0.096	7.316	0.786	8.655	0.786	0.579	7.034	7.035	1.358	1.358		R3
0.045	0.098	7.062	0.843	8.225	0.759	0.589	6.587	7.149	1.432	1.288	R3	
0.05	0.1	6.821	0.888	7.843	0.770	0.605	6.225	6.970	1.468	1.272	R3	
0.0525	0.101	6.700	0.906	7.663	0.775	0.613	6.068	6.868	1.477	1.265	R3	
0.055	0.102	6.629	0.949	7.488	0.782	0.620	5.873	6.758	1.530	1.260	R3	
0.0575	0.103	6.595	1.008	7.318	0.763	0.626	5.669	6.836	1.611	1.218	R3	S3
0.06	0.104	6.552	1.031	7.178	0.763	0.632	5.588	6.864	1.631	1.208		R4
0.0625	0.105	6.501	1.049	7.048	0.790	0.636	5.512	6.701	1.649	1.242		R4
0.0675	0.107	6.377	1.080	6.802	0.832	0.661	5.343	6.424	1.633	1.259		R4
0.07	0.108	6.307	1.093	6.684	0.849	0.672	5.289	6.305	1.626	1.264		R4
0.0725	0.109	6.235	1.071	6.568	0.864	0.681	5.321	6.194	1.572	1.269	S2	R4
0.075	0.11	6.204	0.971	6.452	0.877	0.689	5.645	6.092	1.409	1.273	S2	R4
0.0775	0.111	6.216	0.944	6.341	0.891	0.697	5.791	5.990	1.354	1.278		R4
0.08	0.112	6.219	0.972	6.290	0.928	0.703	5.737	5.930	1.383	1.320		
0.0825	0.113	6.209	1.001	6.235	0.940	0.708	5.671	5.974	1.413	1.328	R4	
0.085	0.114	6.190	1.045	6.177	0.952	0.713	5.547	6.005	1.466	1.335	R4	
0.0875	0.115	6.164	1.084	6.116	0.962	0.726	5.438	6.023	1.493	1.325	R4	
0.0925	0.117	6.093	1.147	5.985	0.980	0.760	5.257	6.028	1.509	1.289	R4	
0.0975	0.119	5.999	1.195	5.846	0.995	0.787	5.107	6.00	1.518	1.264	R4	
0.0988	0.1195	5.973	1.205	5.810	0.999	0.792	5.074	5.988	1.521	1.261	R4	
0.1	0.12	5.945	1.214	5.773	1.002	0.798	5.041	5.975	1.522	1.256	R4	
0.1013	0.1205	5.917	1.223	5.736	1.006	0.803	5.010	5.961	1.523	1.253	R4	
0.1025	0.121	5.907	1.202	5.699	1.009	0.807	5.077	5.945	1.490	1.251	S1	
0.1038	0.1215	5.911	1.169	5.661	1.013	0.812	5.198	5.928	1.439	1.247	S1	
0.105	0.122	5.919	1.136	5.623	1.016	0.816	5.324	5.909	1.392	1.245	S1	
0.1063	0.1225	5.933	1.105	5.584	1.019	0.820	5.455	5.889	1.347	1.243	S1	
0.1075	0.123	5.951	1.075	5.545	1.023	0.823	5.593	5.868	1.306	1.243	S1	
0.1088	0.1235	5.974	1.046	5.506	1.026	0.827	5.738	5.846	1.264	1.241	S1	
0.11	0.124	6.001	1.040	5.467	1.018	0.830	5.811	5.890	1.253	1.226		S1
0.1113	0.1245	6.025	1.063	5.442	1.009	0.833	5.788	5.979	1.276	1.211		R5
0.1125	0.125	6.044	1.084	5.443	1.041	0.835	5.768	5.912	1.298	1.247		R5
0.1138	0.1255	6.058	1.103	5.444	1.072	0.838	5.748	5.852	1.316	1.279		R5
0.115	0.126	6.068	1.120	5.443	1.099	0.840	5.730	5.801	1.333	1.308		
0.1175	0.127	6.071	1.151	5.435	1.122	0.844	5.697	5.836	1.364	1.329		
0.1225	0.129	6.069	1.236	5.398	1.161	0.873	5.538	5.877	1.415	1.330	R5	
0.125	0.13	6.051	1.271	5.371	1.179	0.896	5.471	5.884	1.418	1.315	..	
0.1275	0.131	6.026	1.302	5.339	1.195	0.916	5.412	5.884	1.421	1.304	R	
0.13	0.132	5.994	1.329	5.301	1.210	0.935	5.358	5.877	1.422	1.294	R	
0.1375	0.135	5.865	1.394	5.165	1.252	0.980	5.220	5.816	1.422	1.277	R5	
0.14	0.136	5.813	1.410	5.112	1.265	0.992	5.181	5.753	1.421	1.275	R5	
0.1425	0.137	5.756	1.424	5.056	1.278	1.003	5.144	5.745	1.419	1.274	R5	
0.15	0.14	5.533	1.454	4.871	1.316	1.029	5.046	5.600	1.413	1.279	R5	
0.1525	0.141	5.492	1.460	4.804	1.329	1.036	5.016	5.542	1.410	1.283	R5	
0.155	0.142	5.447	1.439	4.734	1.342	1.041	5.084	5.479	1.382	1.289	S0	
0.1575	0.143	5.439	1.387	4.663	1.355	1.046	5.277	5.411	1.326	1.296	S0	

$x_{B,1}$	$x_{B,S}$	κ_{av}	$R_{opt}(\kappa_{av})$	λ_{av}	$R_{opt}(\lambda_{av})$	R_{min}	$N(\kappa_{av})$	$N(\lambda_{av})$	R_{opt}/R_{min} (κ_{av})	R_{opt}/R_{min} (λ_{av})	Int(κ)	Int(λ)
0.1625	0.145	5.440	1.289	4.520	1.289	1.054	5.699	5.691	1.222	1.222	S0	S0
0.1675	0.147	5.570	1.200	4.453	1.200	1.059	6.311	6.311	1.133	1.133	S0	S0
0.17	0.148	5.738	1.159	4.477	1.159	1.061	6.768	6.768	1.093	1.093	S0	S0
0.1725	0.149	6.067	1.121	4.585	1.121	1.062	7.470	7.470	1.055	1.055	S0	S0
0.1738	0.1495	6.307	1.102	4.677	1.102	1.062	7.941	7.941	1.038	1.038	S0	S0
0.175	0.15	6.813	1.084	4.906	1.084	1.062	8.806	8.806	1.021	1.021	S0	S0
0.1755	0.1502	7.147	1.077	5.065	1.077	1.062	9.349	9.349	1.014	1.014	S0	S0
0.176	0.1504	7.654	1.070	5.312	1.070	1.062	10.151	10.151	1.008	1.008	S0	S0
0.1763	0.1505	8.118	1.067	5.544	1.067	1.062	10.862	10.862	1.005	1.005	S0	S0

Table C.4B Non-ideal ternary distillation. $\tilde{x}_F$: (0.2, 0.5, 0.3), $\tilde{x}_D$: (0.2, 0.05, 0.75)

x_B	κ_{av}	$R_{opt}(\kappa_{av})$	λ_{av}	$R_{opt}(\lambda_{av})$	R_{min}	$N(\kappa_{av})$	$N(\lambda_{av})$	R_{opt}/R_{min} (κ_{av})	R_{opt}/R_{min} (λ_{av})	Int(κ)	Int(λ)
0.01	33.143	3.162	44.404	3.305	2.318	19.322	18.772	1.364	1.426	S17	
0.02	28.753	3.081	38.553	3.362	2.342	17.371	16.266	1.315	1.435	S15	S14
0.03	25.961	3.240	34.591	3.512	2.368	15.327	14.498	1.366	1.483	S13	
0.04	23.834	3.242	32.256	3.636	2.395	14.345	13.214	1.353	1.518	S12	S11
0.05	22.092	3.314	30.081	3.611	2.425	13.338	12.554	1.367	1.489	S11	
0.06	20.619	3.453	28.190	3.474	2.457	12.311	12.263	1.406	1.414	[illegible]	
0.07	19.299	3.258	26.499	3.678	2.491	12.400	11.263	1.308	1.477	S10	S9
0.08	18.072	3.455	25.098	3.716	2.527	11.354	10.780	1.367	1.470	S9	
0.09	17.021	3.408	23.682	3.755	2.567	11.137	10.287	1.328	1.463		S8
0.10	15.959	3.562	22.516	3.803	2.609	10.368	9.895	1.365	1.458	S8	
0.11	15.037	3.429	21.291	3.969	2.657	10.436	9.281	1.291	1.494	S8	S7
0.12	14.127	3.772	20.244	3.802	2.708	9.361	9.113	1.393	1.404	S7	
0.13	13.255	3.635	19.234	4.149	2.763	9.483	8.540	1.316	1.502	S7	
0.14	12.484	3.699	18.183	4.127	2.825	9.129	8.332	1.309	1.461		S6
0.15	11.666	3.962	17.299	4.071	2.892	8.404	8.248	1.370	1.408	S6	
0.16	10.896	3.851	16.404	4.421	2.967	8.466	7.633	1.298	1.490	S6	
0.17	10.202	3.871	15.449	4.505	3.054	8.346	7.357	1.267	1.475		S5
0.18	9.479	4.286	14.620	4.343	3.151	7.549	7.429	1.360	1.378		S5
0.19	8.743	4.242	13.826	4.715	3.263	7.491	6.944	1.300	1.445	S5	
0.20	8.072	4.195	12.952	5.153	3.392	7.545	6.430	1.237	1.519	S5	
0.21	7.428	4.471	12.084	5.034	3.545	7.147	6.443	1.261	1.420		S4
0.22	6.726	4.934	11.326	5.166	3.728	6.512	6.318	1.323	1.386	S4	
0.23	6.035	4.922	10.522	5.755	3.949	6.570	5.880	1.246	1.457	S4	
0.24	5.383	5.006	9.620	6.406	4.231	6.619	5.457	1.183	1.514	S4	S3
0.25	4.733	5.616	8.752	6.303	4.606	6.155	5.538	1.221	1.370		S3
0.26	4.006	6.427	7.931	7.198	5.109	5.607	5.231	1.258	1.409	S3	
0.27	3.276	6.866	6.971	8.811	5.874	5.663	4.783	1.169	1.500	S3	
0.28	2.541	7.921	5.844	10.115	7.196	5.693	5.044	1.101	1.406		S2
0.29	1.655	12.361	4.669	15.309	10.339	4.697	4.238	1.196	1.481	S2	

Table C.4C Non-ideal ternary distillation. $\bar{x}_F$: (0.2, 0.5, 0.3), $\bar{x}_B$: (0.2, 0.75, 0.05)

$x_{D,2}$	$x_{D,3}$	κ_{sw}	$R_{opt}(\kappa_{sw})$	λ_{sw}	$R_{opt}(\lambda_{sw})$	R_{min}	$N(\kappa_{sw})$	$N(\lambda_{sw})$ (κ_{sw})	R_{opt}/R_{min} (λ_{sw})	R_{opt}/R_{min}	Int(κ)	Int(λ)
0.334	0.466	25.656	0.486	37.409	0.486	27.722	27.723	0.485	1.00	1.00	R0	R0
0.333	0.467	22.616	0.503	32.972	0.503	24.106	24.107	0.496	1.01	1.01	R0	R0
0.332	0.468	21.263	0.519	30.981	0.519	22.407	22.408	0.507	1.02	1.02	R0	R0
0.331	0.469	20.391	0.535	29.689	0.535	21.260	21.260	0.518	1.03	1.03	R0	R0
0.33	0.47	19.782	0.552	28.779	0.552	20.416	20.416	0.529	1.04	1.04	R0	R0
0.325	0.475	18.171	0.637	26.317	0.637	17.874	17.874	0.583	1.09	1.09	R0	R0
0.32	0.48	17.531	0.725	25.271	0.725	16.482	16.482	0.638	1.14	1.14	R0	R0
0.31	0.49	17.128	0.912	24.449	0.912	14.760	14.760	0.747	1.22	1.22	R0	R0
0.3	0.5	17.256	1.116	24.400	1.116	13.681	13.681	0.858	1.30	1.30	R0	R0
0.29	0.51	17.639	1.336	24.695	1.336	12.885	12.885	0.969	1.38	1.38	R0	R0
0.28	0.52	18.217	1.576	25.278	1.576	12.293	12.293	1.08	1.46	1.46	R0	R0
0.27	0.53	18.871	1.784	26.013	1.838	12.015	11.802	1.191	1.50	1.54	S12	
0.265	0.535	19.218	1.861	26.458	1.911	12.030	11.842	1.246	1.49	1.53	S12	
0.26	0.54	19.560	1.939	26.892	1.952	12.046	11.998	[illegible]	1.49	1.50	S12	
0.25	0.55	20.225	2.093	27.731	2.093	12.080	12.080	1.409	1.49	1.49	S12	S12
0.24	0.56	20.862	2.245	28.533	2.245	12.116	12.116	1.514	[illegible]	1.48	S12	S12
0.23	0.57	21.467	2.394	29.294	2.394	12.155	12.155	1.617	[illegible]	1.48	S12	S12
0.22	0.58	22.027	2.430	30.007	2.540	12.613	12.196	1.715	1.42	1.48		S12
0.21	0.59	22.523	2.441	30.665	2.679	13.139	12.242	1.808	1.35	1.48		S12
0.20	0.600	22.951	2.516	31.257	2.810	13.361	12.292	1.894	1.33	1.48	S13	S12
0.195	0.605	23.141	2.570	31.526	2.872	13.390	12.319	1.934	1.33	1.49	S13	S12
0.19	0.610	23.314	2.621	31.774	2.931	13.421	12.348	1.972	1.33	1.49	S13	S12
0.185	0.615	23.467	2.670	31.999	2.986	13.453	12.378	2.007	1.33	1.49	S13	S12
0.18	0.620	23.598	2.714	32.200	3.038	13.487	12.411	2.038	1.33	1.49	S13	S12
0.175	0.625	23.707	2.754	32.373	3.085	13.524	12.445	2.067	1.33	1.49	S13	S12
0.17	0.630	23.790	2.790	32.517	3.127	13.563	12.482	2.092	1.33	1.49	S13	S12
0.165	0.635	23.845	2.820	32.627	3.163	13.605	12.522	2.112	1.34	1.50	S13	S12
0.16	0.640	23.868	2.845	32.701	3.192	13.650	12.565	2.128	1.34	1.50	S13	S12
0.155	0.645	23.856	2.863	32.733	3.214	13.700	12.611	2.14	1.34	1.50	S13	S12
0.15	0.650	23.806	2.873	32.721	3.228	13.753	12.662	2.144	1.34	1.51	S13	S12
0.145	0.655	23.711	2.874	32.656	3.232	13.812	12.718	2.174	1.32	1.49	S13	S12
0.14	0.660	23.567	2.865	32.534	3.223	13.877	12.785	2.218	1.29	1.45	S13	
0.135	0.665	23.366	2.845	32.345	3.184	13.949	12.906	2.26	1.26	1.41	S13	
0.13	0.670	23.175	2.908	32.080	3.135	13.707	13.204	2.298	1.27	1.36	R1	
0.125	0.675	23.149	3.132	31.780	3.156	13.006	12.930	2.335	1.34	1.35	S12	R1
0.12	0.680	23.310	3.179	31.865	3.426	13.056	12.352	2.367	1.34	1.45	S12	R1
0.115	0.685	23.448	3.221	32.027	3.629	13.109	12.018	2.396	1.34	1.51	S12	S11
0.11	0.690	23.558	3.258	32.185	3.641	13.165	12.145	2.42	1.35	1.50	S12	
0.105	0.695	23.635	3.287	32.302	3.635	13.225	12.300	2.438	1.35	1.49	S12	
0.10	0.700	23.674	3.307	32.372	3.623	13.291	12.449	2.45	1.35	1.48	S12	
0.095	0.705	23.668	3.317	32.387	3.605	13.363	12.595	2.454	1.35	1.47	S12	
0.09	0.710	23.608	3.315	32.338	3.579	13.444	12.735	2.448	1.35	1.46	S12	
0.085	0.715	23.484	3.298	32.212	3.543	13.534	12.870	2.432	1.36	1.46	S12	
0.08	0.720	23.281	3.263	31.992	3.495	13.638	13.000	2.401	1.36	1.46	S12	
0.075	0.725	22.982	3.204	31.659	3.431	13.759	13.136	2.415	1.33	1.42	S12	
0.070	0.730	22.561	3.117	31.182	3.346	13.904	13.249	2.437	1.28	1.37	S12	
0.065	0.735	22.170	3.202	30.519	3.232	13.457	13.373	2.452	1.31	1.32	R2	
0.060	0.740	22.151	3.345	30.174	3.585	13.070	12.431	2.457	1.36	1.46	S11	R2
0.055	0.745	22.165	3.341	30.176	3.665	13.194	12.352	2.45	1.36	1.50	S11	
0.050	0.750	22.092	3.314	30.081	3.611	13.338	12.554	2.425	1.37	1.49	S11	
0.045	0.755	21.898	3.255	29.838	3.536	13.513	12.751	2.376	1.37	1.49	S11	
0.040	0.760	21.533	3.150	29.381	3.431	13.735	12.944	2.38	1.32	1.44	S11	

$x_{4,2}$	$x_{4,3}$	κ_{ov}	$R_{opt}(\kappa_{ov})$	λ_{ov}	$R_{opt}(\lambda_{ov})$	R_{min}	$N(\kappa_{ov})$	$N(\lambda_{ov})$	R_{opt}/R_{min} (κ_{ov})	R_{opt}/R_{min} (λ_{ov})	Int(κ)	Int(λ)
0.035	0.765	20.965	3.054	28.603	3.279	13.790	13.136	2.379	1.28	1.38	R3	
0.030	0.770	20.888	3.256	28.012	3.594	13.134	12.242	2.356	1.38	1.53	S10	
0.025	0.775	20.802	3.181	27.840	3.483	13.428	12.598	2.303	1.38	1.51	S10	
0.020	0.780	20.402	3.008	27.249	3.311	13.862	12.968	2.298	1.31	1.44	S10	
0.015	0.785	20.242	3.194	26.452	3.426	13.190	12.559	2.249	1.42	1.52	S9	
0.010	0.790	20.027	2.966	25.933	3.176	13.945	13.304	2.223	1.33	1.43	S9	
0.005	0.795	20.222	2.964	25.239	3.037	14.204	13.936	2.166	1.37	1.40	R6	S8

Author: Jobson Megan Ruth.

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