Minimum Energy Consumption in Multicomponent Distillation:

I: The $V_{\text{min}}$-diagram for a single column.

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Abstract

The $V_{\text{min}}$-diagram is introduced to effectively visualize how the minimum energy consumption is related to the feed component distribution for all possible operating points in a two-product distillation column with a multicomponent feed. The classical Underwood equations are used to derive analytical expressions for the ideal case with constant relative volatility and constant molar flows. However, the diagram can also be used for non-ideal mixtures. The $V_{\text{min}}$-diagram is a simple tool for assessment of multicomponent separation, and becomes very useful when we later shall use it for assessment of Petlyuk arrangements.
1 Introduction

We assume constant molar flows, constant relative volatilities and infinite number of stages and use the classical Underwood equations to compute the distribution of all the components in the generalized multicomponent feed as a function of the degrees of freedom in a two-product distillation column (Figure 1).

A main result is a simple graphical visualization of minimum energy and feed component distribution for all possible operating points. We denote this the Minimum Energy Mountain Diagram or just the $V_{\text{min}}$-diagram.

The $V_{\text{min}}$-diagram can be used for quick determination of the minimum energy requirement in a single binary column with a multicomponent feed, for any feasible product specification.

The equations of Underwood (1945,1946ab,1948) have been applied successfully by many authors for analysis of multicomponent distillation, e.g. Shiras (1950), King (1980), Franklin and Forsyth (1953), Wachter et. al. (1988) and in a comprehensive review of minimum energy calculations by Koehler (1995). Minimum energy expressions for Petlyuk arrangements with three components have been presented by Fidkowski and Krolikowski (1986) and Carlberg and Westerberg (1989ab). However, minimum energy requirements for the general multicomponent case, the topic of this paper, has so far not been well understood.

Alternative methods for visualization of feed distribution regions for a single column have been presented by Wachter et. al. (1988) based on a continuum model and by Neri et.al. (1998), based on equilibrium theory.

Interestingly, the methods presented in this paper can also be used for Petlyuk arrangements and for arrangements with side strippers and side rectifiers. This is treated in detail in Halvorsen (2001) and in the succeeding papers (Halvorsen and Skogestad 200xa and 200xb).

We will also discuss briefly the behaviour of composition profiles and pinch zones, and how the required number of stages depends on the component distribution, but this is treated in more detail in Halvorsen (2001).
2 Problem Definition - Degrees of Freedom

With a given feed, a two-product distillation column normally has two steady-state degrees of freedom of operation. For a binary feed, this is sufficient to specify any product distribution. In the case of a multicomponent feed, however, we cannot freely specify the compositions in both products. In practice, one usually specifies the distribution of two key components, and the distribution of the non-key components is then completely determined for a given feed. In some cases, the column pressure could be considered as a third degree of freedom, but we will assume that the pressure is constant throughout this paper since the pressure has a limited impact on the product distribution.

For every possible operating point we want to find the normalized vapour flow rate \( \frac{V}{F} \) and the overall product split \( \frac{D}{F} \) or \( \frac{B}{F} \) and the distribution, here given by the set of recoveries \( R = [r_1, r_2, \ldots, r_{N_c}] \). This can be expressed for the top section as:

\[
\begin{bmatrix}
  V_T \\
  D \\
  R_T
\end{bmatrix}
= f(Spec_1, Spec_2, Feed \ properties)
\]

(1)

It is sufficient to consider only one of the top or bottom sections as the recoveries and flows in the other section can be found by a material balance at the feed stage. The feed properties are given by the composition vector \( z \), flow rate \( F \), liquid fraction \( q \) and relative volatilities \( \alpha \). The recovery \( r_i \) is the amount of component \( i \) transported in a stream or through a section divided by the amount in the feed. \( N_c \) is the number of components.

3 The Underwood Equations for Minimum Energy

Our original derivation of the \( V_{min} \)-diagram was based on computing pinch zone compositions for columns with infinite number of stages. However, the Underwood approach is simpler and may easily be extended to other kinds of column section interconnections and this approach is used here.

3.1 Some Basic Definitions

The starting point for Underwood’s methods for multicomponent mixtures (Underwood 1945, 1946ab, 1948) is the material balance equation at a cross-section in the column. The net material transport \( w_i \) of component \( i \) upwards through a stage \( n \) is the difference between the amount travelling upwards from a stage as vapour and the amount entering a stage from above as liquid:
At steady state, \( w_i \) is constant through each column section. In the following we assume constant molar flows (\( L = L_{n-1} \) and \( V = V_n = V_{n+1} \)) and constant relative volatility (\( \alpha_i \)).

The vapour liquid equilibrium (VLE) at an equilibrium stage is given by:

\[
y_i = \frac{\alpha_i x_i}{\sum_{i=1}^{N_c} \alpha_i x_i}
\]  

(3)

In the top section the net product flow is \( D = V_n - L_{n+1} \) and:

\[
w_{i,T} = x_{i,D} D = r_{i,D} z_{i} F
\]  

(4)

In the bottom section, \( B = L_{n+1} - V_n \), and the net material flow is:

\[
w_{i,B} = -x_{i,B} B = r_{i,B} z_{i} F
\]  

(5)

The positive direction of the net component flows is defined upwards, but in the bottom the components normally travel downwards from the feed stage and then we have \( w_{i,B} \leq 0 \). With a single feed stream the net component flow in the feed is given as:

\[
w_{i,F} = z_{i} F
\]  

(6)

A recovery can then be regarded as a normalized component flow:

\[
r_i = w_i / w_{i,F} = w_i / (z_i F)
\]  

(7)

At the feed stage, \( w_{i,F} \) is defined positive into the column. Note that with our definition in (7) the recovery is also a signed variable.

### 3.2 Definition of Underwood Roots

The Underwood roots (\( \phi \)) in the top section are defined as the \( N_c \) solutions of:

\[
V_T = \sum_{i=1}^{N_c} \frac{\alpha_i w_{i,T}}{\alpha_i - \phi}
\]  

(8)
3 The Underwood Equations for Minimum Energy

In the bottom there is another set of Underwood roots $\psi$ given by the solutions of:

$$V_B = \sum_{i=1}^{N_c} \frac{\alpha_i w_{i,B}}{\alpha_i - \psi}$$  \hspace{1cm} (9)

Note that these equations are related via the material balance at the feed stage:

$$w_{i,T} - w_{i,B} = w_{i,F} = z_{i,F} F$$  \hspace{1cm} (10)

(which is equivalent to $r_{i,T} - r_{i,B} = 1$) and the change in vapour flow at the feed stage given by the liquid fraction ($q$) of the feed ($F$):

$$V_F = V_T - V_B = (1 - q) F$$  \hspace{1cm} (11)

Computation of the Underwood roots involves solving a straightforward polynomial root problem, but we should be careful and make sure that the vector of component flows $w_T$ or $w_B$ is feasible. This also implies that in the multicomponent case there is a “hidden” interaction between the unspecified elements in $w_T$ and the Underwood roots.

3.3 The Underwood Roots for Minimum Vapour Flow

Underwood showed a series of properties of the roots ($\phi$ and $\psi$) for a two-product column with a single reboiler and condenser. In this conventional column, all components flow upwards in the top section ($w_{i,T} \geq 0$), and downwards in the bottom section ($w_{i,B} \leq 0$). With $N_c$ components there are for each of $\phi$ and $\psi$, $N_c$ solutions obeying:

$$\alpha_1 > \phi_1 > \alpha_2 > \phi_2 > \alpha_3 > \ldots > \alpha_{N_c} > \phi_{N_c}$$  \hspace{1cm} (12)

$$\psi_1 > \alpha_1 > \psi_2 > \alpha_2 > \psi_3 > \alpha_3 > \ldots > \psi_{N_c} > \alpha_{N_c}$$  \hspace{1cm} (13)

When the vapour flow is reduced, the roots in the top section will decrease, while the roots in the bottom section will increase. Underwood (1946) showed that at minimum vapour flow for any given product distribution, one or more pairs of roots coincide to a common root (denoted $\theta_i$, i.e. $\phi_i = \psi_{i+1} = \theta_i$).

Recall that $V_T - V_B = (1 - q) F$. By subtracting the defining equations for the top and bottom sections (8)-(9), we obtain the following equation which is valid for the common roots only (denoted $\theta$):
We call this expression the *feed equation* since only the feed properties \( (q \text{ and } z) \) appear. It has also \( N_c \) roots, but one of these cannot be a common root due to (12) and (13), so there are \( N_c - 1 \) possible common roots that obey:

\[
\alpha_i > \theta_1 > \alpha_2 > \theta_2 > \ldots > \theta_{N_c - 1} > \alpha_{N_c} .
\]

We will denote a root \( \theta_k \) an *active* root for the case when \( \phi_k = \psi_k + l = \theta_k \).

Inserting the active root in the top and bottom defining equations gives the minimum flow for a given set of component distribution \( (w_T \text{ or } r_T) \).

\[
V_{Tmin} = \sum_{i} \frac{\alpha_i w_{i,T}}{\alpha_i - \theta_k} \quad \text{or} \quad V_{Tmin} = \sum_{i} \frac{\alpha_i f_{i,T} z_{i,F}}{\alpha_i - \theta_k}
\]

With \( N_a \) active roots, this represents a set of \( N_a \) independent linear equations, which may be used to find the exact set of the so-called distributing components that appear in both products.

Note that the subscript *min* indicates minimum vapour flow and then we use a common root \( \theta \) from equation (14) as opposed to an actual root \( \phi \) in equation (8).

### 3.4 Computation Procedure

Our task is to find the \( N_c \) product recoveries (or component flows) and the vapour flow, given any pair of feasible specifications. The procedure on how to apply Underwood’s equations for this purpose has been described by several authors, e.g. Shiras (1950) and Carlberg and Westerberg (1989).

The key to the general solution is to identify the *distributing* components. A component in the feed is distributing if it appears in both products, or is exactly at the limit of becoming distributing if the vapour flow is reduced with an infinitesimal amount.

The computation procedure is as follows:

Consider a set of \( N_d \) distributing components, denoted: \( \{d_1, d_2, \ldots, d_{N_d}\} \). The recoveries in the top are trivially \( r_{i,T} = 1 \) for all non-distributing light components \( (i < d_1) \), and \( r_{i,T} = 0 \) for the non-distributing heavy components \( (i > d_{N_d}) \). Then, with a given distribution set we know the \( N_c - N_d \) recoveries of the non-distributing components.
Then use another of Underwood’s results: For any minimum vapour flow solution, the active Underwood roots will only be those with values in the range between the volatilities of the distributing components \( \alpha_{d_j} > \theta_k > \alpha_{d_{Nd}} \). This implies that with \( N_d \) distributing components, the number of active roots is:

\[
N_a = N_d - 1
\]  

(17)

Thus, from Table 1, we see that by making two specifications we have enough information to determine the solution completely.

Table 1: Number of unknown variables and equations

<table>
<thead>
<tr>
<th></th>
<th>( N_c + 1 )</th>
<th>( N_c - N_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of non-distributing components</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remaining unknown variables</td>
<td>( N_d + 1 )</td>
<td></td>
</tr>
<tr>
<td>Number of equations=number of active roots ( N_a )</td>
<td>( N_d - 1 )</td>
<td></td>
</tr>
<tr>
<td>Degrees of freedom</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Define the vector \( X \) containing the recoveries of the \( N_d \) distributing components and the normalized vapour flow in the top section:

\[
X = \begin{bmatrix} r_{d_1}, T, r_{d_2}, T, \ldots, r_{d_{Nd}}, T, V_T / F \end{bmatrix}^T
\]  

(18)

(superscript \( T \) denotes transposed). The equation set (16) can then be written as a linear equation set on matrix form:

\[
M \cdot X = Z
\]  

(19)

or

\[
\begin{bmatrix}
\frac{\alpha_{d_1} z_{d_1}}{\alpha_{d_1} - \theta_{d_1}}, & \frac{\alpha_{d_2} z_{d_2}}{\alpha_{d_2} - \theta_{d_1}}, & \ldots & \frac{\alpha_{d_{Nd}} z_{d_{Nd}}}{\alpha_{d_{Nd}} - \theta_{d_1}} \\
\frac{\alpha_{d_1} z_{d_1}}{\alpha_{d_1} - \theta_{d_2}}, & \frac{\alpha_{d_2} z_{d_2}}{\alpha_{d_2} - \theta_{d_2}}, & \ldots & \frac{\alpha_{d_{Nd}} z_{d_{Nd}}}{\alpha_{d_{Nd}} - \theta_{d_2}} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\alpha_{d_1} z_{d_1}}{\alpha_{d_1} - \theta_{d_{Nd-1}}}, & \frac{\alpha_{d_2} z_{d_2}}{\alpha_{d_2} - \theta_{d_{Nd-1}}}, & \ldots & \frac{\alpha_{d_{Nd}} z_{d_{Nd}}}{\alpha_{d_{Nd}} - \theta_{d_{Nd-1}}} \\
\end{bmatrix}
\begin{bmatrix} r_{d_1}, T, r_{d_2}, T, \ldots, r_{d_{Nd}}, T, V_T / F \end{bmatrix}
= \begin{bmatrix}
-\sum_{i=1}^{d_1} \alpha_i z_i \\
-\sum_{i=1}^{d_2} \alpha_i z_i \\
\vdots \\
-\sum_{i=1}^{d_{Nd}} \alpha_i z_i
\end{bmatrix}
\]
The elements in each column of M arise from the terms in (16) related to the distributing components, and we have one row for each active root. Z contains the part of (16) arising from the non-distributing light components with recovery one in the top. The recoveries for the heavy non-distributing components are zero in the top, so these terms disappear.

There are \( N_a = N_d - 1 \) equations (rows of M and Z) and \( N_d + 1 \) variables in X (columns in M). Thus by specifying any two of the variables in X as our degrees of freedom we are left with \( N_d - 1 \) unknowns which can be solved from the linear equation set in (19).

To specify the product split we introduce \( D/F \) as an extra variable in X and the following extra equation:

\[
D/F = \sum r_i z_i
\]  

(20)

Note that equation (19) is only valid in a certain region of the possible operating space, namely in the region where components numbered \( d_1 \) to \( d_{Nd} \) are distributing to both products.

For nonsharp key specifications, components lighter than the light key, and heavier than the heavy key, may or may not be distributing. Then we usually have to check several possible distribution sets. See Halvorsen (2001) for more details.

For \( V > V_{min} \) and an infinite number of stages there are no common Underwood roots. Thus, at most one component may be distributing and its recovery is independent of the actual value of \( V \), but it is uniquely related to \( D/F \) through (20):

\[
D/F = z_1 + z_2 + \ldots + r_{d_1} z_{d_1}
\]  

(21)

4 The \( V_{min} \)-diagram (Minimum Energy Mountain)

A nice feature, since there are only two degrees of freedom, is that we can visualize the entire operating range in two dimensions, even with an arbitrary number of feed components. We choose to use

- top vapour flow \( (V_T/F) \) and,
- product split, expressed by the distillate \( (D/F) \),

as degrees of freedom. The choice of vapour flow rate on the ordinate provides a direct visualization of the energy consumption and column load.
An important boundary is the transition from \( V > V_{\text{min}} \) to \( V = V_{\text{min}} \). It looks like mountain peaks in the D-V-plane, as illustrated in Figure 7, the \( V_{\text{min}} \)-diagram.

There is a unique minimum energy solution for each feasible pair of product recovery specifications, and the solution is always found below or at the \( V_{\text{min}} \)-boundary.

Above the \( V_{\text{min}} \)-boundary, the operation is not unique since we can always reduce the vapour rate down to the \( V_{\text{min}} \)-boundary without changing the product specifications. Below the \( V_{\text{min}} \)-boundary we can identify a set of polygon regions for each set of distributing components. For the ternary case in Figure 7, the regions where AB, BC or all of ABC are distributing are indicated. The boundaries between regions of distributing components are straight line segments in the D-V plane due to the linear properties of equation (19-20).

Feasible operation requires positive vapour and liquid flows in all sections:

\[
V_T > 0, \ V_B > 0, \ L_T > 0, \ L_B > 0
\] (22)

In an ordinary two product column we must also require \( D = V_T - L_T \geq 0 \) and \( B = L_B - V_B \geq 0 \) (note that this is not a feasibility requirement for directly coupled sections) which with a single feed translates to (see Figure 3):

\[
V_T \geq \max((1 - q)F, \ D) \quad \text{and} \quad 0 \leq D/F \leq 1
\] (23)

The procedure for computing points to draw the \( V_{\text{min}} \)-mountain-diagram for a general multicomponent case (\( N_c \) components) is given in Table 2.
Since we assume constant relative volatility only adjacent groups of components can be distributing.

In the $V_{min}$-diagram, each peak represents minimum energy operation for sharp splits between adjacent components ($\theta_j$, $\theta_{j+1}$, $\theta_{N_c-1}$). Then there is only a single active Underwood root, and the minimum vapour flow and the corresponding distillate flow solved from equation (16) is simplified to:

$$\frac{V_{Tmin}^{j+1}}{F} = \sum_{i=1}^{j} \frac{\alpha_i z_i}{\alpha_i - \theta_j} \quad \text{and} \quad \frac{D}{F} = \sum_{i=1}^{j} z_i \quad \quad (24)$$

### 4.1 Binary Case

Before we explore the multicomponent cases, let us look closer at a binary case. Consider a feed with light component A and heavy component B with relative volatilities $[\alpha_A, \alpha_B]$, feed composition $z = [z_A, z_B]$, feed flow rate $F=I$ and liquid fraction $q$. In this case we obtain from the feed equation (14) a single common root $\theta_A$ obeying $\alpha_A > \theta_A > \alpha_B$. The minimum vapour flow is found by applying this root in the defining equation (16):
We also have from (20):

\[
\frac{D}{F} = r_A, T^A_T + r_B, T^B_B
\]

(26)

The procedure in Table 2 becomes very simple in the binary case since there is only one possible pair of key components (A,B). We obtain the following results as illustrated in Figure 3. There is one sharp split (between A and B):

\[
P_{AB}: [r_A, T^*], r_B, T = [1, 0] \Rightarrow [D, V_{T_{min}}] = \left[ z_A A \frac{\alpha_A z_A}{\alpha_A - \theta_A} \right] F
\]

The two asymptotic points are:

\[
P_0: [r_A, T^*], r_B, T = [0, 0] \Rightarrow [D, V_{T_{min}}] = [0, 0]
\]

\[
P_1: [r_A, T^*], r_B, T = [1, 1] \Rightarrow [D, V_{T_{min}}] = [I, (1-q)]F
\]

Figure 3: The $V_{min}$-diagram, or minimum energy mountain.
Visualization of the regions of distributing components for a binary feed case.
These three points make up a triangle as shown in Figure 3. Along the straight line \( P_0 - P_{AB} \) we have \( V = V_{min} \) for a pure top product \((r_{B,T} = 0)\), and from (25) the line can be expressed by the recovery \( r_{A,T} \) or \( D/F \):

\[
\frac{V_T}{F} = \frac{\alpha_A r_{A,T} z_A}{\alpha_A - \theta_A} = \frac{\alpha_A}{\alpha_A - \theta_A} D \quad \text{since} \quad \frac{D}{F} = r_{A,T} z_A
\]

Similarly, along the straight line \( P_{AB} - P_1 \), we have \( V = V_{min} \) for a pure bottom product \((r_{A,T} = 1)\), and the line can be expressed by the recovery \( r_{B,T} \) or \( D/F \):

\[
\frac{V_T}{F} = \frac{\alpha_A z_A}{\alpha_A - \theta_A} + \frac{\alpha_B r_{B,T} z_B}{\alpha_B - \theta_A} \quad \text{where} \quad \frac{D}{F} = z_A + r_{B,T} z_B
\]

Inside the triangle, we may specify any pair of variables among \((V_T, D, r_A, r_B)\) and use the equation set (25-26) to solve for the others. This is exactly the same equation set as given in (19-20) for the general multicomponent case when both components are distributing.

Above the triangle (\( V_{min} \) mountain), where \( V > V_{min} \), we have no active Underwood roots, so (25) no longer applies. However, since only one component is distributing, we have either \( r_{A,T} = 1 \) or \( r_{B,T} = 0 \). This implies that the recoveries are directly related to \( D \), and we have:

\[
\frac{D}{F} = r_{A,T} z_A \quad \text{for} \quad \frac{D}{F} \leq z_A \quad \text{or} \quad \frac{D}{F} = z_A + r_{B,T} z_B \quad \text{for} \quad \frac{D}{F} \geq z_A
\]

which is equivalent to (21) in the general multicomponent case. Anywhere above the triangle we obviously waste energy since the same separation can be obtained by reducing the vapour flow until we hit the boundary to region AB.

\( V_T > D \) and \( V_T > (1-q)F \) are required for feasible operation of a conventional two-product distillation column. The shaded area represents an infeasible region where a flow rate somewhere in the column would be negative. Note that the asymptotic points \((P_0 \text{ and } P_1)\) are infeasible in this case.

We may also visualise the non-sharp split solutions with specified component recoveries. This is illustrated in Figure 4 for the example \( V_{T|r_A} = 0.85(D) \) and \( V_{T|r_B} = 0.25(D) \) (dashed lines). Note that for \( V > V_{min} \) these become vertical lines. The unique solution with both specifications fulfilled is at the intersection inside region AB denoted “Solution” in Figure 4.
4 The Vmin-diagram (Minimum Energy Mountain)

4.2 Ternary Case

Figure 5 shows an example of the Vmin-diagram, or “Minimum Energy Mountain” for a ternary feed (ABC). To plot this diagram we apply the procedure in Table 2 and identify the following five points:

The peaks, which give \( V_{\text{min}} \) for sharp splits A/B and B/C (no distributing components):

\[
P_{\text{AB}}: \ [r_{A,T}, r_{B,T}] = [1, 0] \Rightarrow [D, V_{T_{\text{min}}}] = \left[ z_A + \frac{\alpha_A z_A}{\alpha_A - \theta_A} \right] F
\]

\[
P_{\text{BC}}: \ [r_{B,T}, r_{C,T}] = [1, 0] \Rightarrow [D, V_{T_{\text{min}}}] = \left[ z_A + z_B + \frac{\alpha_A z_A}{\alpha_A - \theta_A} + \frac{\alpha_B z_B}{\alpha_B - \theta_B} \right] F
\]

The preferred split, which gives \( V_{\text{min}} \) for sharp A/C-split (B is distributing):

\[
P_{\text{AC}}: \ [r_{A,T}, r_{C,T}] = [1, 0] \Rightarrow [D, V_{T_{\text{min}}}] = \left[ z_A + \beta z_B + \frac{\alpha_A z_A}{\alpha_A - \theta_A} + \frac{\alpha_B \beta z_B}{\alpha_B - \theta_B} \right] F
\]

where \( \beta \) is the recovery of B: \( \beta = r_{A/C}^{A/B} = \frac{\alpha_A z_A (\alpha_B - \theta_A)(\alpha_B - \theta_B)}{\alpha_B \beta z_B (\alpha_A - \theta_A)(\alpha_A - \theta_B)} \)

and the trivial asymptotic points:
The two peaks ($P_{AB}$ and $P_{BC}$) give us the minimum vapour flow for a sharp split between A/B and B/C, respectively. The valley, $P_{AC}$, gives us the minimum vapour flow for a sharp A/C split and this occurs for a specific distribution of the intermediate component B, known as the “preferred split” (Stichlmair 1988).

One part of the $V_{min}$-boundary, namely the V-shaped $P_{AB}$-$P_{AC}$-$P_{BC}$ curve, has been presented by several authors, e.g. Fidkowski (1986), Christiansen and Skogestad (1997). It gives the minimum vapour flow for a sharp A/C split and this occurs for a specific distribution of the intermediate component B, known as the “preferred split” (Stichlmair 1988).

Figure 5: $V_{min}$-diagram for a ternary feed mixture (ABC). $V > V_{min}$ above the $V_{min}$-boundary (the “Mountain” $P_0$-$P_{AB}$-$P_{AC}$-$P_{BC}$-$P_1$). All minimum energy solutions, ($V=V_{min}$ (spec 1, spec 2)) are found in the distribution regions AB, BC and ABC. The active Underwood roots are also indicated in each region (when $\phi_i = \theta_i$).

$$P_0 : [r_{A,T}, r_{B,T}] = [0, 0] \Rightarrow [D, V_{Tmin}] = [0, 0]$$

$$P_1 : [r_{A,T}, r_{B,T}] = [1, 1] \Rightarrow [D, V_{Tmin}] = [1, (1 - q)]F$$

The two peaks ($P_{AB}$ and $P_{BC}$) give us the minimum vapour flow for a sharp split between A/B and B/C, respectively. The valley, $P_{AC}$, gives us the minimum vapour flow for a sharp A/C split and this occurs for a specific distribution of the intermediate component B, known as the “preferred split” (Stichlmair 1988).
4 The $V_{\text{min}}$-diagram (Minimum Energy Mountain)

At boundaries B/AB and ABC/BC: $r_{A,T}=1$ ($r_{A,B}=0$)
At boundary A/AB: $r_{B,T}=0$ ($r_{B,B}=1$)
At boundary C/CB: $r_{B,T}=1$ ($r_{B,B}=0$)
At boundaries B/BC and AB/ABC: $r_{C,T}=0$ (or $r_{C,B}=1$)

4.3 Five Component Example

A 5-component example is shown in Figure 6. Here we also plot the contour lines for constant values of the recoveries in the top for each component in the range 0.1 to 0.9.

![Diagram](image)

Figure 6: The $V_{\text{min}}$-diagram for a 5-component feed ($F=1$). Contour lines for constant top product recoveries are included.

Note that the boundary lines (solid bold) are contour lines for top recoveries equal to zero or one and that any contour line is vertical for $V > V_{\text{min}}$. This diagram clearly shows how each component recovery depends on the operating point $(D,V)$.

To draw the $V_{\text{min}}$-diagram for $N_c$ components, we must identify the $N_c(N_c-1)/2$ points $(P_{ij})$ given in the procedure in Table 2, corresponding to the following distribution regions: AB, BC, CD, DE, ABC, BCD, CDE, ABCD, BCDE, ABCDE.

Figure 6 also illustrates that some combinations of recovery specifications can be infeasible, e.g. $r_{A,T}=0.9$ and $r_{C,T}=0.6$. Observe that combined specification of $D$ and an intermediate recovery may have multiple solutions, e.g. $D=0.2$ and $r_{B,T}=0.3$. The specification of $V$ and a recovery will be unique, as will the specification of $D$ and $V$. The specification of two (feasible) recoveries will also be unique, and the solution will always be a minimum energy solution $(V=V_{\text{min}})$. 

Note: The image contains a graph with labels and data points, which are not transcribed here.
5 The $V_{\text{min}}$-diagram by Rigorous Simulation

So far, we have used analytic expressions to compute the $V_{\text{min}}$-diagram for ideal mixtures with constant molar flows and constant relative volatility. However, for real mixtures, we may replace the analytic Underwood equations with numerical property calculations and draw the $V_{\text{min}}$-diagram. To approximate the vapour flow with infinite number of stages, we should use at least $4 \times N_{\text{min}}$ stages in the simulations, where $N_{\text{min}}$ is the minimum number of stages for the separation (with infinite flows).

In the example described below, we applied the Hysys process simulator, using the Peng-Robinson equation of state, for an equimolar feed mixture of n-Pentane (A), n-Hexane (B) and n-Heptane (C) at 745 kPa with 80% liquid fraction. The results are visualized in Figure 7 and the numerical values are listed in Table 3. The main diagram can be constructed by three simulations at the three characteristic points of the diagram ($P_{\text{AC}}, P_{\text{AB}}, P_{\text{BC}}$). In addition, we have also simulated some additional operating points to verify the internals of the diagram.

Figure 7: $V_{\text{min}}$-diagram based on numerical simulations (solid) and constant relative volatility (dashed). Each numerical simulation from Table 3 are indicated (circles). The contour lines for the selected constant (nonsharp) recoveries (dotted) are computed with constant relative volatility. (Constant $\alpha$-values are from the simulation at $P_{\text{AC}}$)
The $V_{\text{min}}$ diagram for the real mixture (solid), drawn through the results of the rigorous simulations (circles), is very close to the ideal $V_{\text{min}}$ diagram (dashed) computed with the assumption of constant relative volatility ($\alpha=[1.683, 0.9266, 0.5234]$, which are the K-values at the feed stage from simulation no. 3 in Table 3). The contour lines for constant recovery $r_{A,T}=0.8$ and $r_{C,T}=0.222$ for the constant relative volatility case are also shown (dotted). The match in region ABC is very good, as expected, since the pinch zone composition and thereby the relative volatilities will be constant for the real mixture too. Further away from region ABC we observe a certain deviation between the real and ideal diagrams. The explanation is that the pinch-zone composition at the feed stage will change a little outside region ABC and so will also the relative volatility.

However, we conclude that the $V_{\text{min}}$ diagram can be applied for assessment of real mixtures too. Obviously there can be some non-linearities of the distribution boundaries and some deviations in the height of the peaks for the real mixture due to that the relative volatility and molar flows are not constants, but the main picture is very similar.

Note that the vapour flow is the amount leaving the feed stage. In order to get an exact prediction of the reboiler and condenser flows, we have to take into account the difference in heat of vaporization for the mixture at the feed stage and in the respective column ends. We also expect that the pinch zone compositions in each of the column ends will be slightly different from the ideal case since the relative volatilities and molar flows will not be completely constant along the column.

Table 3: Rigorous simulation results for the given set of specifications

<table>
<thead>
<tr>
<th>Specification of 2 DOFs ($\varepsilon=0.001$)</th>
<th>Simulation $D$</th>
<th>$V_T$</th>
<th>Constant $\alpha$ $V_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:$P_{AB}$</td>
<td>$x_{B,T}=\varepsilon$</td>
<td>$x_{A,B}=\varepsilon$</td>
<td>0.333</td>
</tr>
<tr>
<td>2</td>
<td>$r_{B,T}=0.2$</td>
<td>$x_{A,B}=\varepsilon$</td>
<td>0.399</td>
</tr>
<tr>
<td>3:$P_{AC}$</td>
<td>$x_{C,T}=\varepsilon$</td>
<td>$x_{A,B}=\varepsilon$</td>
<td>0.467</td>
</tr>
<tr>
<td>4</td>
<td>$x_{C,T}=\varepsilon$</td>
<td>$r_{B,T}=0.6$</td>
<td>0.534</td>
</tr>
<tr>
<td>5</td>
<td>$x_{C,T}=\varepsilon$</td>
<td>$r_{B,T}=0.8$</td>
<td>0.601</td>
</tr>
<tr>
<td>6:$P_{BC}$</td>
<td>$x_{C,T}=\varepsilon$</td>
<td>$x_{B,B}=\varepsilon$</td>
<td>0.667</td>
</tr>
<tr>
<td>7</td>
<td>$r_{A,T}=0.8$</td>
<td>$x_{B,T}=\varepsilon$</td>
<td>0.267</td>
</tr>
<tr>
<td>8</td>
<td>$r_{A,T}=0.8$</td>
<td>$x_{C,T}=\varepsilon$</td>
<td>0.374</td>
</tr>
<tr>
<td>9</td>
<td>$r_{A,T}=0.8$</td>
<td>$r_{C,T}=0.222$</td>
<td>0.492</td>
</tr>
<tr>
<td>10</td>
<td>$x_{A,B}=\varepsilon$</td>
<td>$r_{C,T}=0.222$</td>
<td>0.585</td>
</tr>
<tr>
<td>11</td>
<td>$r_{B,T}=0.8$</td>
<td>$r_{C,T}=0.222$</td>
<td>0.674</td>
</tr>
</tbody>
</table>
Table 3: Rigorous simulation results for the given set of specifications

<table>
<thead>
<tr>
<th>Specification of 2 DOFs (ε=0.001)</th>
<th>Simulation D</th>
<th>V_T</th>
<th>Constant α/V_T</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 x_{B,B}=ε x_{C,T}=0.222</td>
<td>0.740</td>
<td>1.35</td>
<td>1.32</td>
</tr>
<tr>
<td>13 r_{A,T}=0.5 x_{B,T}=ε</td>
<td>0.167</td>
<td>0.647</td>
<td>0.672</td>
</tr>
<tr>
<td>14 x_{C,T}=0.2 x_{B,B}=ε</td>
<td>0.833</td>
<td>0.937</td>
<td>0.917</td>
</tr>
</tbody>
</table>

In the example Fenske’s minimum reflux formula gives $4N_{min} = 4\log \varepsilon^{-2}/\log \min(\alpha_{jj}) = 100$, which is the stage number used in the simulations. Note that with a finite number of stages we reach an approximate distribution boundary by specifying a small composition (here $\varepsilon=0.001$) of the component to be removed in the appropriate product instead of zero recovery. In practice, $N=4xN_{min}$ can be regarded as close to infinite number of stages in a simulation.

6 Discussion

In this section we provide some insight into the properties of the Underwood solutions.

6.1 Simple Expression for the Regions Under the Peaks

A single Underwood root is active at the peaks, and also in the region just under each peak. Thus, operation here is very similar to the binary case presented in Section 4.1 since only two components ($j$ and $j+1$) are distributing, and from (16) we find:

$$V_{T_{min}}(r_j, r_{j+1}, T, r_j, r_{j+1}, T, r_j, r_{j+1}, T, r_j, r_{j+1}, T, r_j, r_{j+1}, T, r_j, r_{j+1}, T, r_j, r_{j+1}, T) = \sum_{i=1}^{j-l} \frac{\alpha_{j,i}z_i}{\alpha_{j,i} - \theta_j} + \frac{\alpha_{j,j}z_j}{\alpha_{j,j} - \theta_j} + \frac{\alpha_{j+1,j+1}z_{j+1}}{\alpha_{j+1,j+1} - \theta_{j+1}} + \frac{\alpha_{j+1,j+1}z_{j+1}}{\alpha_{j+1,j+1} - \theta_{j+1}}$$

$$D = \left( \sum_{i=1}^{j-l} z_i \right) + z_j + z_j + z_{j+1} + z_{j+1} + z_{j+1} + z_{j+1}$$

Recall $\alpha_j > \theta_j > \alpha_{j+1}$ and observe that the slopes under the peaks are given by:
The contour lines under the peaks $P_{AB}$, $P_{BC}$, $P_{CD}$ and $P_{DE}$ in Figure 6 are examples of lines where the slopes are given by equation (32). Equation (24) gives us the peaks and (30) describes the behaviour in the region under the peaks. Thus we can use these simple linear equations to describe the local behaviour for a 2-product column where we specify a reasonable sharp split between two groups of components. Note that the slopes of all contour lines under each top peak are constant and equal to the slope of the $V_{min}$-boundary lines (see Figure 6).

6.2 Behaviour of the Underwood Roots

The $V_{min}$-diagram is also very well suited to illustrate the behaviour of the Underwood roots in each section $\left(\phi, \psi\right)$ as we change the vapour flow. Recall that Underwood showed that as the vapour flow ($V$) is reduced, a certain pair of roots will coincide, and we get $V=V_{min}$. But how do we find which pair, and what happen to the other roots?

We illustrate the behaviour with a ternary example in Figure 8. We have two common roots $\left(\theta_A, \theta_B\right)$. In each of the three cases $i$-$iii$, $D$ is kept constant and $V$ is reduced from a large value in the region where $V>V_{min}$ until we are in region $ABC$ where all feed components distribute. The behaviour of the roots is computed from the defining equations (8) and (9). Observe how the pair $\phi_A, \psi_B$ approaches the common root $\theta_A$ and how $\phi_B, \psi_C$ approaches the other common root $\theta_B$ as we cross a distribution boundary to the region where each common root becomes active.

Note also that in case $ii$, where we pass through the preferred split, both common roots become active at the same time. Observe that one root $\left(\phi_C\right)$ in the top and one $\left(\psi_A\right)$ in the bottom, never coincide with any other root.
Figure 8: Observe how a pair of Underwood roots coincide as vapour flow ($V$) is reduced and the operation cross a distribution boundary in the $V_{\text{min}}$-diagram.

Figure 9a shows how the important root $\phi_A$ in the top, behaves outside the regions AB or ABC where it is constant $\phi_A = \theta_A$. A similar result is shown in Figure 9b) for the root $\psi_C$ in the bottom, outside the regions ABC or BC where $\psi_C = \theta_B$. Note that these contours are linear in each distribution region.

Figure 9: Contour plot of the most important roots a) in the top- and b) in the bottom sections outside the region when these roots are active. Same feed as in Figure 8
6.3 Composition Profiles and Pinch Zones

At minimum energy operation with infinite number of stages, the composition profile will have certain pinch-zones where there are no changes from stage to stage. Shiras (1950) denoted these as points of infinitude. The pinch zone is a central issue in the deduction of Underwood’s equations for minimum energy calculations. In Underwood (1945) the following expression is used to find a pinch zone composition in the top section for component $i$, related to Underwood root $k$:

$$x_i, PT = \frac{x_i^D D}{L_T} \frac{\phi_k}{(\alpha_i - \phi_k)} = \frac{w_i, T}{L_T} \frac{\phi_k}{(\alpha_i - \phi_k)}$$

(33)

It can be shown for the ternary case that the pinch zone composition when one component is removed completely somewhere in one of the column ends, depends only on the actual Underwood root between the volatilities of the remaining components. In the top we obtain (Halvorsen 2001):

$$x_A, PT = \frac{\alpha_B (\alpha_A - \phi_A)}{\phi_A (\alpha_A - \alpha_B)}$$

(34)

Note that within regions AB and ABC the actual Underwood root $\phi_A = \theta_A$ is constant. Surprisingly, from (34), we observe that the pinch-zone composition in the top section will also be constant and independent of the operating point $(V,D)$ within this region. This issue was not pointed out by Underwood, and it is not at all obvious from (33) since all variables in (33), except $\alpha_A$ are varying in region AB. A similar expression can be found for the pinch zone in the bottom section, and similarly, there will be a constant pinch zone composition within region ABC and BC.

An important implication of equation (34) is that the pinch zone composition $(x_A, PT)$ will be constant when the actual Underwood root $(\phi_A)$ is constant. Thus, in Figure 9, the contour plot of a constant Underwood roots will also be contour plot of the corresponding pinch zone compositions.

**Example.** We illustrate the composition profiles and pinch zones for the ternary case where $F=1$, $z=[0.33~0.33~0.33]$, $\alpha=[4~2~1]$, $q=1$. The composition profile has been computed using a stage-by-stage model with 50 stages in each section, which in practice is an infinite number of stages for this example. The composition profiles along the column are shown as molar fractions against stage number in Figure 10 for four different operating points, as indicated in the small $V_{min}$ diagrams.
In the general case we will find that in every region where one or more components are completely removed from one of the products, we will have an invariant pinch zone composition.

This behaviour of the pinch zones plays an important role in directly (or so-called fully thermally) coupled columns. In the ternary case, the top pinch represents the maximum composition of the light (A) component which can be obtained in the first column when the reflux into the column is in equilibrium with the vapour leaving the column. When the columns are connected, the minimum vapour flow in the succeeding column will have its minimum when there is a pinch zone across the feed region. And this minimum will be as low as possible when the amount of light component is as high as possible.

Furthermore, in the Petlyuk column, we know that the energy requirement in the succeeding column is constant in a certain operation region. This is easy to explain from the fact that when the feed pinch composition in a binary column is constant, the energy requirement will also be constant.

Figure 10: Composition profiles by stage number for four operating points at the boundary of and inside region AB. Note the constant pinch composition in the top.
6.4 Finite Number of Stages

The calculations in this paper is for an infinite number of stages, but the results hold well for most real columns, because the economic optimum is typically at $V = 1.1 V_{min}$, corresponding to $N = 2 N_{min}$ from the Fenske formula:

$$N_{min} = \frac{\log(S_{LH, TF})}{\log(\alpha_L/\alpha_H)}$$

where

$$S_{LH, TF} = \frac{x_{L,T}/x_{H,T}}{x_{L,F}/x_{H,F}}$$

(35)

A more detailed study (Halvorsen 2001) shows that the largest number of stages in order to carry out a sharp split between the two most extreme components is required close to the preferred split. When we move away from the preferred split, the number of required stages in one of the sections is reduced. The lesson learned from this is that if the column is designed for operation on one side of the preferred split, this can be taken advantage of by reducing number of stages in the appropriate section. However, if the column is to be operated at, or on both sides of the preferred split, both sections have to be designed with its maximum number of stages.

7 Summary

The distribution of feed components and corresponding minimum energy requirement is easily found by just a glance at the $V_{min}$-diagram. The characteristic peaks and knots are easily computed from Underwood’s equations for infinite number of stages.

Although the theory has been deduced for a single conventional column, the simple $V_{min}$-diagram for a two-product column contains all the information needed for optimal operation of a complex directly (fully thermally) coupled arrangement, such as the Petlyuk column. This is described in more detail in Part II and III (Halvorsen and Skogestad 2001a, 2001b),(Halvorsen 2001).

The $V_{min}$-diagrams can be computed for non-ideal systems using a commercial simulator with a large number of stages.

8 References


