Analytic Expressions for Minimum Energy Consumption in Multicomponent Distillation:
A Revisit of the Underwood Equations

by

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Motivation

1. Multicomponent separation can be difficult to understand

2. Extend Underwood's minimum reflux calculations to the entire operating range of product splits D/F and feasible component distribution

3. This is needed for integrated column sequences, e.g. Petlyuk columns

Main results:

1. Simple graphical visualization of minimum energy for all possible product splits, just based on feed data.

2. Obtain minimum energy for the Petlyuk column directly from the same diagram.

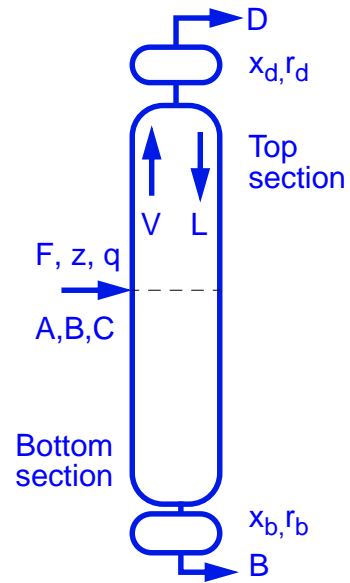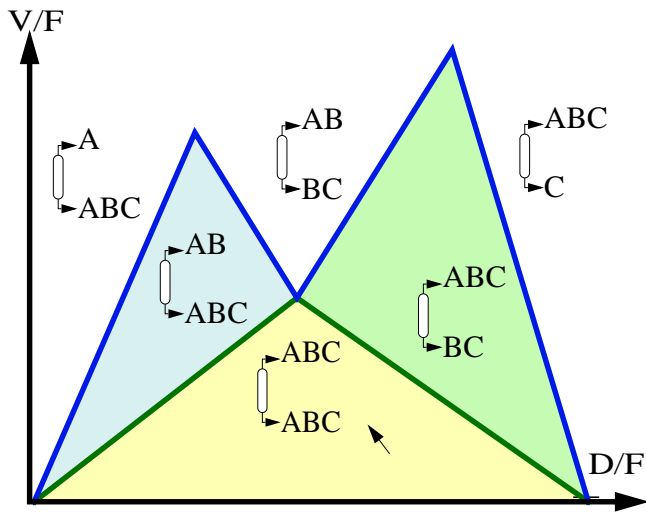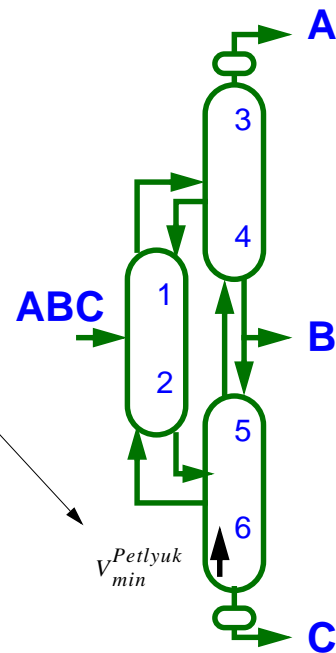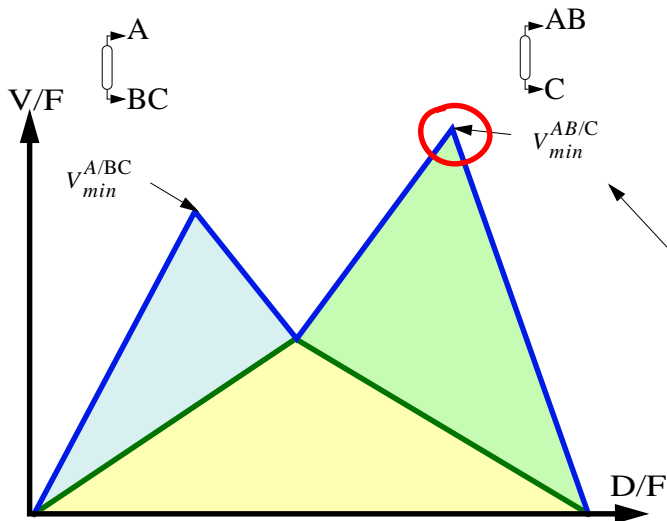# Result 1:

Visualize $V_{min}=f(D,splits)$

Result 2:
Find V_{min} for the Petlyuk column directly from the diagram:

$$V_{min}^{Petlyuk} = max(V_{min}^{A/BC}, V_{min}^{AB/C})$$

Selected references:

Classical references for multicomponent distillation

- Underwood (1946, 1948a,b), Fractional distillation of multicomponent mixtures

- Shiras (1950), Calculation of Minimum Reflux in Distillation Columns

- Franklin, Forsyth (1953), The interpretation of minimum reflux conditions in multicomponent distillation

Minimum energy expressions for Petlyuk arrangements

- Fidkowski, Krolikowski (1986), Thermally Coupled Columns: Optimization proc.

- Carlberg, Westerberg (1989) Temperature-Heat Diagrams for Complex Columns. 3. Underwood's Method for the Petlyuk Column.

Books:

- King (1980), Separation Processes.

- Stichlmair (1998), Distillation: Principles and Practice.

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Important:
The two product distillation column has only two degrees of freedom (DOF)

- Binary mixtures: #DOFs == #components:

    ==> We may specify a product completely

- Multicomponent: #DOFs < #components

    ==> We cannot specify all components in a product, just two!

Nice Implication of just two DOFs:
- Visualize the entire operating range in 2 dimensions.
- We choose the D-V plane

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Revisit of Underwood's Equations

Starting points:
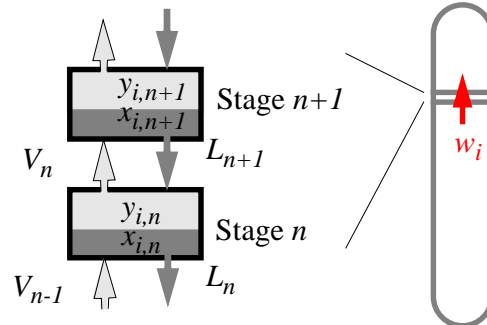
1. Net transport of a component through a stage

$$w_i = V_n y_{i,n} - L_{n+1} x_{i,n+1} \quad (1)$$

(w is defined positive upwards)

w_i is constant in a section:

Assume:

-constant molar flows
-constant relative volatility

2. Vapour liquid equilibrium (VLE):

$$y_i = \frac{\alpha_i x_i}{\sum_i \alpha_i x_i}$$

3. Divide the material balance with V, multiply with the "Underwood" factor $\alpha_i / (\alpha_i - \phi)$, and take the sum over all components:

$$\frac{1}{V} \sum_i \frac{\alpha_i w_i}{(\alpha_i - \phi)} = \frac{\sum_i \frac{\alpha_i^2 x_{i,n}}{(\alpha_i - \phi)}}{\sum_i \alpha_i x_{i,n}} - \frac{L}{V} \sum_i \frac{\alpha_i x_{i,n+1}}{(\alpha_i - \phi)} \quad (2)$$

4. The solutions for ϕ which sets the left-hand side equal to one defines the Underwood roots:

$$\text{Definition equation:} \quad V = \sum_i \frac{\alpha_i w_i}{(\alpha_i - \phi)}, \quad (3)$$

(for the top section we can also use $V^T = \sum_i \frac{\alpha_i r_{i,D} z_i}{(\alpha_i - \phi)} F = \sum_i \frac{\alpha_i x_{i,D}}{(\alpha_i - \phi)} D$)

Note the relations: $w_i = w_{i,T} = w_{i,D} = D x_{i,D} = r_{i,D} z_i F$ for the top section, and

the bottom section: $w_i = w_{i,Botoom} = w_{i,B} = (-B) x_{i,B} = (-r_{i,B}) z_i F$, where the recoveries

$r_{i,D} = \frac{D x_{i,D}}{F z_i} = \frac{w_{i,D}}{F z_i}$ and $r_{i,B} = \frac{B x_{i,B}}{F z_i} = \frac{-w_{i,B}}{F z_i}$, and we trivially have $r_{i,B} + r_{i,D} = 1$

5. Simplify to:

$$\frac{L}{V}E(x_{n+1}, \phi) = \frac{\phi E(x_n, \phi)}{\sum_i \alpha_i x_{i,n}} \text{ where } E(x_n, \phi) = \sum_i \frac{\alpha_i x_{i,n}}{(\alpha_i - \phi)} \qquad (4)$$

6. Can derive by division of equations :

$$\left(\frac{E(x_{n+m}, \phi_k)}{E(x_{n+m}, \phi_j)}\right) = \left(\frac{\phi_k}{\phi_j}\right)^m \left(\frac{E(x_n, \phi_j)}{E(x_n, \phi_k)}\right) \text{ (compare to } \frac{x_D}{1 - x_D} = \alpha^N \frac{x_B}{1 - x_B} \text{ for binary)} \qquad (5)$$

Together with $\sum_i x_{i,n+m} = 1$, we have now N_c equations in order to compute x_{n+m}

Underwood equations can be used to relate the composition on one stage to a composition on another stage in a multicomponent separation.

Minimum energy computations: $m \to \infty$

Underwood equations for the two product column:

Definition of UW-roots in the top section: $V^T = \sum_i \frac{\alpha_i w_{i,T}}{(\alpha_i - \phi)}$ (6)

Definition of UW-roots in the bottom section: $V^B = \sum_i \frac{\alpha_i w_{i,B}}{(\alpha_i - \psi)}$ (7)

V^T

F
z,q

V^B

$V^T - V^B = (1-q)F$
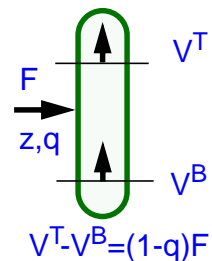
Note that $w_{i,B} = w_{i,D} - w_{i,F}$ and normally $w_{i,F} = z_i F$ (8)

For $w_{i,D} > 0$ and $w_{i,B} < 0$ the roots obey:
$$\alpha_1 > \phi_1 > \alpha_2 > \phi_3 > \ \ldots\ldots\ \ > \alpha_{Nc} > \phi_{Nc}$$
$$\psi_1 > \alpha_1 > \psi_2 > \alpha_2 > \psi_3 > \ldots \psi_{Nc-1} > \alpha_{Nc} \qquad (9)$$

Note the difference between the roots in the top (ϕ) and in the bottom (ψ)!

Underwood roots in the top and bottom approach the common roots (φ) as vapour flow is reduced

Minimum energy: $V \rightarrow V_{min} \quad \Leftrightarrow \quad \phi_i \rightarrow \psi_{i+1} \rightarrow \varphi_i$

(Infinite energy: $V \rightarrow \infty \Rightarrow \phi_i \rightarrow \alpha_i$ and $\psi_i \rightarrow \alpha_i$.)
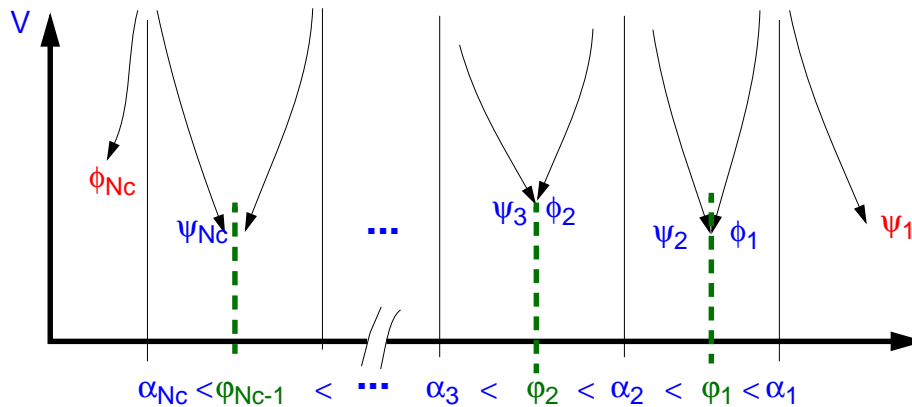
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Underwood's minimum reflux result

Underwood roots in the top and bottom sections are defined by:

$$V^T = \sum_i \frac{\alpha_i w_{i,T}}{(\alpha_i - \phi)} \text{ and } V^B = \sum_i \frac{\alpha_i w_{i,B}}{(\alpha_i - \psi)} \text{ where } w_{i,B} = w_{i,T} - z_i F \qquad (10)$$

As the vapour flow is reduced, the roots in the top section decrease, and the roots in the bottom section increase. Minimum reflux occur when the roots coincide

$$V_{min} \Leftrightarrow \phi_i = \psi_{i+1} = \varphi_i \qquad (11)$$

Recall that $V^T - V^B = (1-q)F$ where q is the liquid fraction in the feed. By subtracting equation from we obtain the well known Underwood's "feed" equation:

$$(1-q) = \sum_i \frac{\alpha_i z_i}{(\alpha_i - \varphi)} \qquad (12)$$

N_c-1 common roots obey: $\alpha_1 > \varphi_1 > \alpha_2 > \varphi_2 > \dots \varphi_{Nc-1} > \alpha_{Nc}$

Feed equation is only valid for the *active* common roots, but fortunately it can be solved once for all the *N_c-1* potential common roots, and these depend only on the feed properties: α, z, q. The actual active common roots depends on the operation.

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Underwood equations, examples of approach:

Binary example (N_c=2, components A,B):

There is one common root φ, easily solved from the feed eq.:
$$(1-q) = \frac{\alpha_A z_A}{\alpha_A - \varphi} + \frac{\alpha_B z_B}{\alpha_B - \varphi}$$

We can specify both product rates in the top (w_A,w_B), thus:
$$V_{min}^T = \frac{\alpha_A w_A}{\alpha_A - \varphi} + \frac{\alpha_B w_B}{\alpha_B - \varphi}$$

Ternary example (N_c=3, components A,B and C):

There are two common roots ($\alpha_A > \varphi_1 > \alpha_B > \varphi_2 > \alpha_3$), easily solved from the feed eq.

- *TRAP: There are only 2 DOFs => We cannot specify all 3 of w_A,w_B and w_C.*

Example: We specify w_A=0.9z_AF, and w_B=0.5z_BF, what is V_{min} and what is w_C?

When does φ_1 apply, and when does φ_2 apply, and do sometimes both apply?

KEY: Determine the non-distributing / distributing components!

Summary of Underwood's Equations for Minimum Energy Calculations

Feed equation gives common "V_{min}"-roots φ

Top and bottom equations gives "real" - roots ϕ and ψ

$w_{i,T}$ "Top section"
$$V^T = \sum_i \frac{\alpha_i w_{i,T}}{(\alpha_i - \phi)}$$

$w_{i,F}=Fz_{i,F}$

F,z,q

$$(1-q) = \sum_i \frac{\alpha_i z_i}{(\alpha_i - \varphi)}$$

V^T-V^B=(1-q)F

$w_{i,B}$ "Bottom section"
$$V^B = \sum_i \frac{\alpha_i w_{i,B}}{(\alpha_i - \psi)}$$

$$w_{i,B}=w_{i,T}-Fz_{i,F}$$

Underwood: When one or more pairs ϕ_i, ψ_{i+1} coincide, then $\phi_i = \psi_{i+1} = \varphi_i$, and $V=V_{min}$

How to compute:
V=?
D=?
$w_{i,T}$=?

KEY: *DISTRIBUTION*
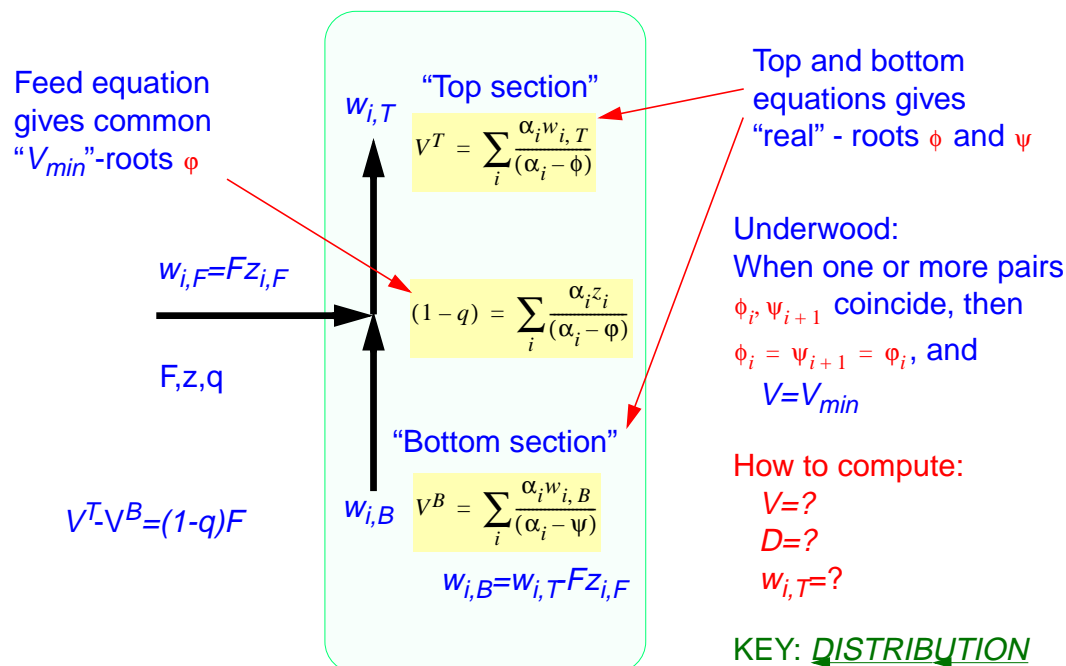
How to use Underwood's minimum energy results:

1. Compute all the *common roots* from the feed equation:

$$(1-q) = \sum_i \frac{a_i z_i}{(a_i - \phi)}$$

2. Determine the total set (N_D) of the *distributed components* (including components at the limit of being distributed)

   There will be $N_A = N_D - 1$ active Underwood roots that correspond to these distributed components.

3. Apply the set of definition equations (in the top or in the bottom) corresponding to each active root.

   This gives N_A equations and N_A unknowns when we specify 2 DOFs. (The non-distributed components have recoveries of either 1 or 0)

$$V_{min}^T = \sum_{i=1}^{N_c} \frac{a_i r_{i,D} z_i}{(a_i - \phi_{a1})}$$

$$\bullet$$
$$\bullet$$

$$V_{min}^T = \sum_{i=1}^{N_c} \frac{a_i r_{i,D} z_i}{(a_i - \phi_{aN_a})}$$

Visualisation of minimum energy and component distribution for the ternary example (feed components ABC)

$V > V_{min}$ above the "mountains"

$V = V_{min}$ in the "mountain-sides" and below

Note:
$V_{min} = f(spec.)$
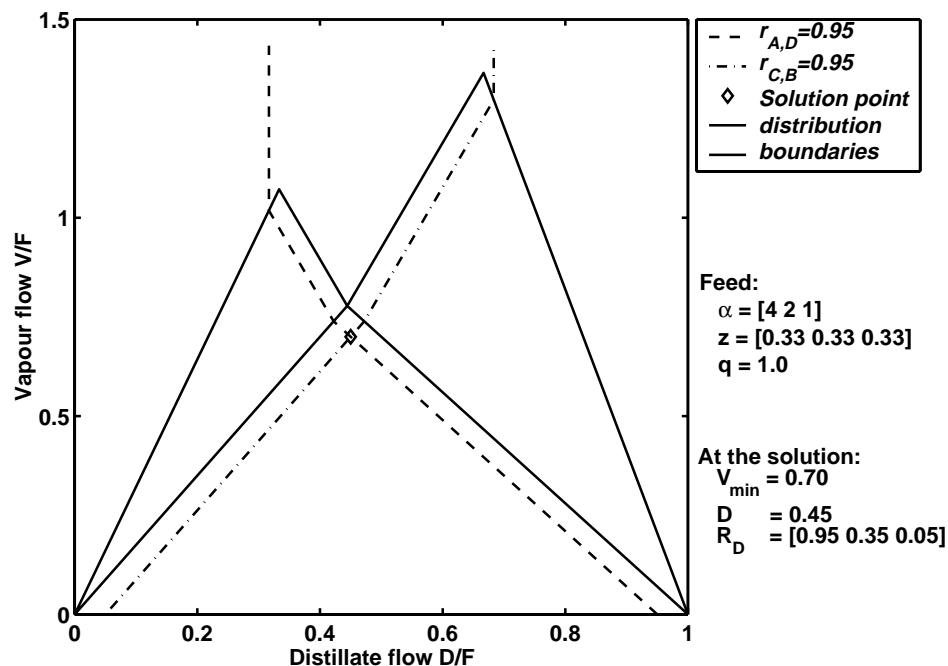
$\alpha_A > \phi_1 > \alpha_B > \phi_2 > \alpha_C$
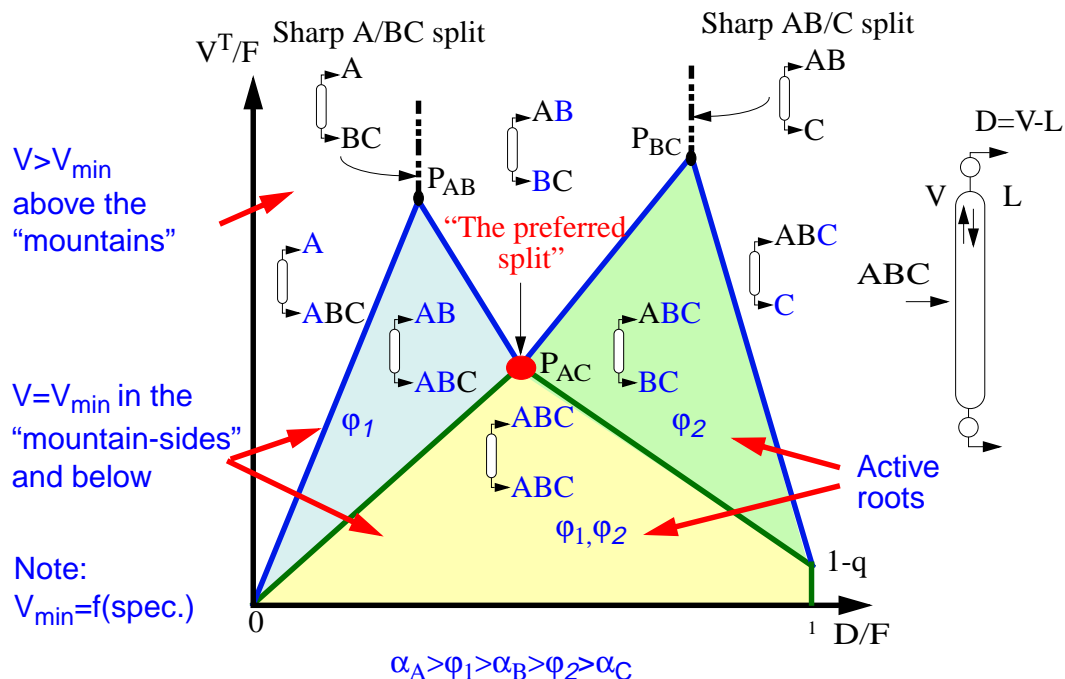
Visualization of the operation in the D-V plane

- Any feasible point in the 2-dimensional plane spanned by 2 independent DOFs (here D,V) determines the operation completely.

- In every polygon region, a particular set of components distribute.

- The "active Underwood roots" are always adjacent, and are in the set laying between the volatilities of the distributed components. Thus each polygon region corresponds to a set of active Underwood roots.

- On the straight line boundaries between the polygon regions, one particular component is at the limit of being distributed to both products.

- The "mountain" tops: Sharp splits between adjacent key components (neighbours i relative volatility)

- Minimum points: "Preferred split", or optimal distribution of intermediate components.

Ternary Example: Specification of 95% recovery of light and heavy components in the products

Legend:
- $r_{A,D} = 0.95$
- $r_{C,B} = 0.95$
- ◇ Solution point
- distribution
- boundaries

Feed:
$\alpha = [4\ 2\ 1]$
$z = [0.33\ 0.33\ 0.33]$
$q = 1.0$

At the solution:
$V_{min} = 0.70$
$D = 0.45$
$R_D = [0.95\ 0.35\ 0.05]$

Axes: Vapour flow V/F (vertical), Distillate flow D/F (horizontal)

5-Component example:

P_{ij} marks V_{min} for sharp split of keys i, j.
$V > V_{min}$ all above the "mountains"

All computations are generalized and is valid for any number of components.

Ternary example: Composition Profile Behaviour

Preferred split

Sharp A/C to the right of preferred split

Sharp A/BC split

Sharp A/BC split

Example of computation:
Procedure for sharp split between adjacent components
(the mountain tops):

Key components *j* and *j+1* ($r_{j,D} = 1$ and $r_{j+1,D} = 0$). The procedure is then simply:

1. Compute the common root (φ_j) for which $\alpha_j > \varphi_j > \alpha_{j+1}$

   from the feed equation: $(1 - q) = \sum_i \dfrac{a_i z_i}{(a_i - \varphi)}$

2. Compute the minimum energy by applying the definition equation for φ_j.

$$\frac{V_{min}^T}{F} = \sum_{i=1}^{j} \frac{a_i z_i}{(a_i - \varphi_j)}.$$

   Note that the recoveries $r_{i,D} = \begin{cases} 1 & \text{for } i \le j \\ 0 & \text{for } i > j \end{cases}$

Example of computation:
Procedure for the "preferred split", i.e.
when all components distribute:

1. Compute all the N_c-1 common roots (φ) from the feed equation.

2. Set $r_{1,D} = 1$ and $r_{N_c,D} = 0$ and solve the following linear equation set ($N_c - 1$ equations) with respect to $V^T, r_{2,D}, r_{3,D} \cdots r_{N_c-1}$ ($N_c - 1$ variables):

$$V^T = \sum_{i=1}^{N_c} \frac{a_i r_{i,D} z_i}{(a_i - \varphi_1)}$$

$$\bullet$$
$$\bullet$$
$$\bullet$$

$$V^T = \sum_{i=1}^{N_c} \frac{a_i r_{i,D} z_i}{(a_i - \varphi_{N_c-1})}$$

(13)

Simple Matlab™ function prototypes

$[\varphi]$ $\quad$ =UWroots(α,z,q) $\qquad$ Compute the common roots from the feed equation

[Vs,Ds,Rs]=UWmulti(α,z,q) $\qquad$ Compute all the polygon points in the D-V plane

[V,D,R]=UWrspec(α,z,q,ri,rj) $\quad$ Compute an operation point from
$\qquad\qquad\qquad\qquad\qquad\qquad$ specification the recoveries (r) of keys i,j

[V,D,R]=UWxspec(α,z,q,xi,xj) Compute an operation point from
$\qquad\qquad\qquad\qquad\qquad\qquad$ specification the product composition (x) of keys i,j

$[R]$ $\quad$ =UWvdspec(α,z,q,V,D) Compute all recoveries R as function of V and D

V: Normalized top section vapour flow (F=1)
D: Normalized distillate product flow (F=1)
R: All component recoveries $R=[r_1,r_2,r_3,....r_{Nc}]$ (in the distillate product)
α: Relative volatilities $\qquad \alpha=[\alpha_1,\alpha_2,\alpha_3,....\alpha_{Nc}]$
z : Feed composition $\qquad\quad z=[z_1,z_2,z_3,....z_{Nc}]$
q : Feed liquid fraction
Note that the distillate flow $D=FRz^T$, and the top composition $x_{i,D}=r_i z_i/(D/F)$

PART 2: Underwood equations for fully thermally coupled columns:

Recall that we only use the net material flow *w* the definition of the Underwood roots, thus the equations can also be applied for fully thermally coupled sections[1]:

Ordinary 2-product · condenser · reboiler · Or for structures like these: · PETLYUK · Modified

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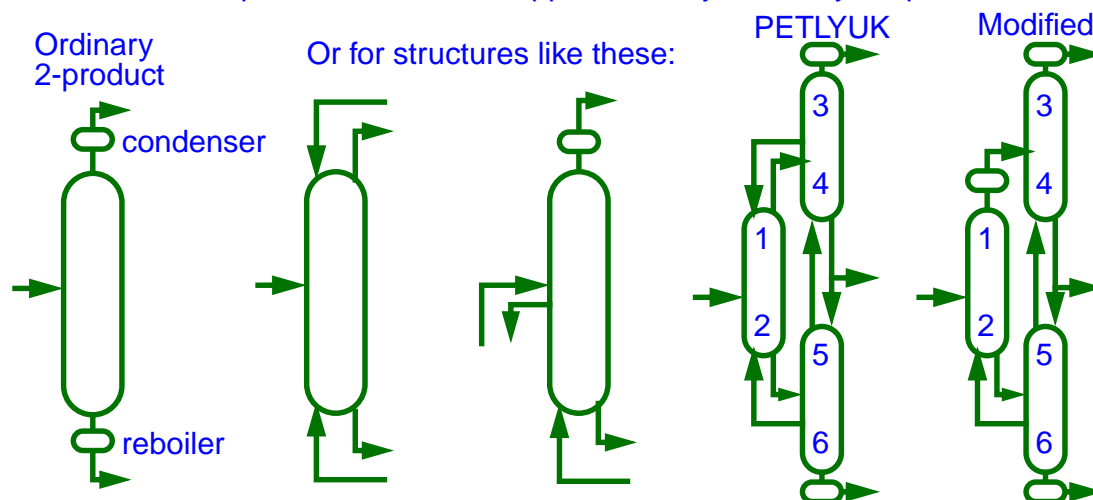
1. In this case we cannot ensure that the net material flow from the feed to the top always is positive. We may have situations with "reverse" transport of some components. This may lead to some special treatment of the equations, but Underwood's equations are still useful as they are based on the true material balance.

Application to Petlyuk Arrangements
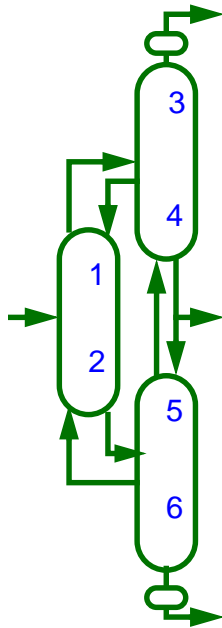
$V^{S3} - V^{S4} = V^{S1}$ => The "feed" equation for column (34) equals the "top" equation for column (12) thus the roots $\varphi_i^{S34} = \phi_i^{S1}$
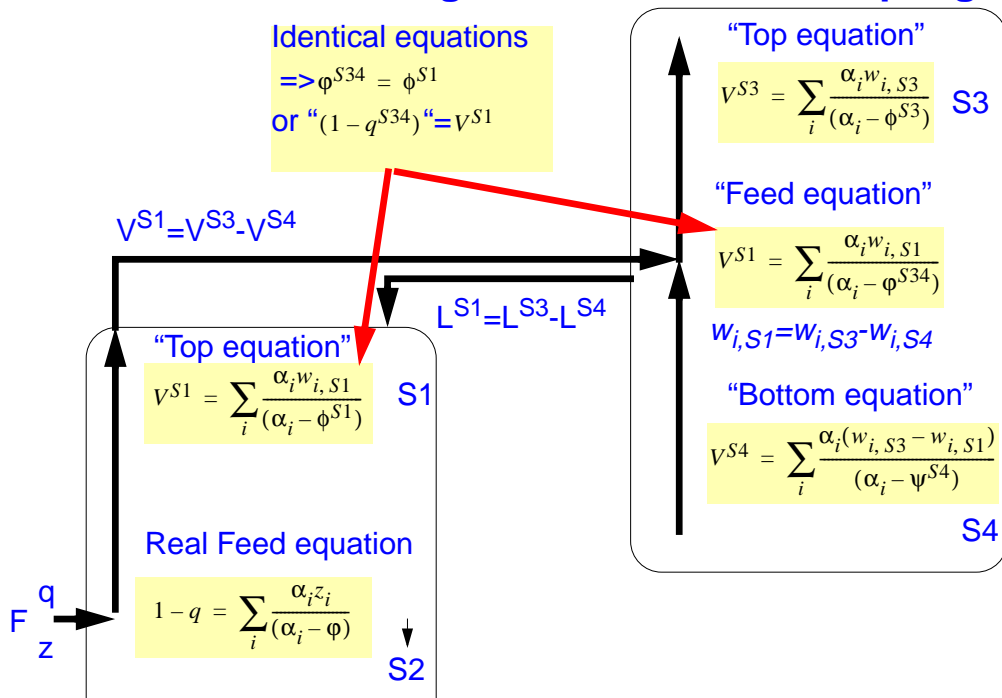
$V^{S6} - V^{S5} = V^{S2}$ => The "feed" equation for column (56) equals the "bottom" equation for column (12) thus the roots $\varphi_i^{S56} = \psi_i^{S2}$

Assume operation at the "Preferred split" for the prefractionator.

- Then all roots of the feed-equation in (12) are also roots of the top and bottom equations of (12) $\varphi_i^{S12} = \phi_i^{S1} = \psi_{i+1}^{S2}$

- Then all roots also carry over as the minimum energy roots for column (34) and (56)

Illustration of how Underwood roots carry over to the next column through the full thermal coupling

Identical equations

=> $\varphi^{S34} = \phi^{S1}$

or "$(1 - q^{S34})$" = V^{S1}

"Top equation"

$$V^{S3} = \sum_i \frac{\alpha_i w_{i,S3}}{(\alpha_i - \phi^{S3})} \quad S3$$

$V^{S1} = V^{S3} - V^{S4}$

$L^{S1} = L^{S3} - L^{S4}$

"Feed equation"

$$V^{S1} = \sum_i \frac{\alpha_i w_{i,S1}}{(\alpha_i - \varphi^{S34})}$$

$w_{i,S1} = w_{i,S3} - w_{i,S4}$

"Top equation"

$$V^{S1} = \sum_i \frac{\alpha_i w_{i,S1}}{(\alpha_i - \phi^{S1})} \quad S1$$

"Bottom equation"

$$V^{S4} = \sum_i \frac{\alpha_i (w_{i,S3} - w_{i,S1})}{(\alpha_i - \psi^{S4})}$$

S4

Real Feed equation

$$1 - q = \sum_i \frac{\alpha_i z_i}{(\alpha_i - \varphi)}$$

S2

F q z

Minimum vapour flow in the upper part of the main column (34):

Prefractionator at its preferred split implies: All roots "carry over" to the main column:

$$V_{min}^{S3} = \sum_i \frac{\alpha_i w_i^{S3}}{\alpha_i - \varphi^{S34}} = \sum_i \frac{\alpha_i w_i^{S3}}{\alpha_i - \varphi^{S12}} \tag{14}$$

Example: Normalized ternary feed (F=1, $\alpha = [\alpha_1, \alpha_2, 1]$).
Pure top product implies: $w_1^{S3} = z_1$, and $w_2^{S3} = w_2^{S3} = 0$.

This is a sharp A/BC split and a point P_{AB} in a DV-plane for column (34).

Identical UW-roots implies identical V_{min}-expression as at P_{AB} the DV-plane for the prefractionator column (12).

At P_{AB} φ_1^{S12} is the only active root (omit superscript $\varphi^{S12} = \varphi$):

$$V_{min}^{S3} = \frac{\alpha_1 z_1}{\alpha_1 - \varphi_1} \text{ which is identical to } V_{min}^{A/BC} \text{ for prefractionator!} \tag{15}$$

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Minimum energy for the Petlyuk column, sharp product splits:

$$V_{min}^{Petlyuk} = min(V^{S6}), \text{ subject to product purity specifications} \tag{16}$$

There are several degrees of freedom in operation, but it can be shown (e.g. Fidkowski (1986)) that when the prefractionator is operated at the preferred split, the optimum can be expressed as[1]:

$$V_{min}^{Petlyuk} = max(V_{min}^{S3} - (1-q), V_{min}^{S6}), \text{ (note that } V^{S6} = V^{S3} - (1-q)) \tag{17}$$

Similarly as for V_{min}^{S3}, we find: $V_{min}^{S6} = \frac{\alpha_3 z_3}{\alpha_3 - \varphi_2} = V_{min}^{AB/C}$ for prefractionator! (18)

For our ternary example, and sharp product splits we obtain:

$$V_{min}^{Petlyuk} = max\left(\frac{\alpha_1 z_1}{\alpha_1 - \varphi_1} - (1-q), \frac{\alpha_3 z_3}{\alpha_3 - \varphi_2}\right) \tag{19}$$

This result is identical to the minimum reflux result of Fidkowski (1986).(for q=1)

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1. The optimum is really flat for operation in a region on one side of the preferred split, always including the preferred split point, but let us skip that here.

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Non-sharp product splits:

With our approach we can very easily put up the expression for non-sharp products too.

Assume we specify small amounts of the intermediate component 2 in both top and bottom, and that the recoveries of light and heavy keys in the top and bottom in slightly less than one. (Then the side-stream i also defined).

We can assume that the same UW-roots will apply since we are not far from the sharp split points, and the result can be written directly from our knowledge of the definition equations for the Underwood roots for sections 3 and 6:

$$V_{min}^{Petlyuk} = max\left(\frac{\alpha_1 r_1^{S3} z_1}{\alpha_1 - \phi_1} + \frac{\alpha_2 r_2^{S3} z_2}{\alpha_2 - \phi_1} - (1-q), \frac{r_3^{S6} z_3}{1 - \phi_2} + \frac{\alpha_2 r_2^{S6} z_2}{\alpha_2 - \phi_2}\right) \qquad (20)$$

The expression is exact for $r_1^{S3} \approx 1$, $r_2^{S3} \approx 0$ and $r_3^{S6} \approx 1$, $r_2^{S6} \approx 0$

Note, if $V_{min}^{Petlyuk} = V_{min}^{S6} => V^{S3} > V_{min}^{S3}$, and $r_1^{S3} < 1$ may be infeasible![1]

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1. This example shows that some product specifications are infeasible to combine with minimum energy operation.

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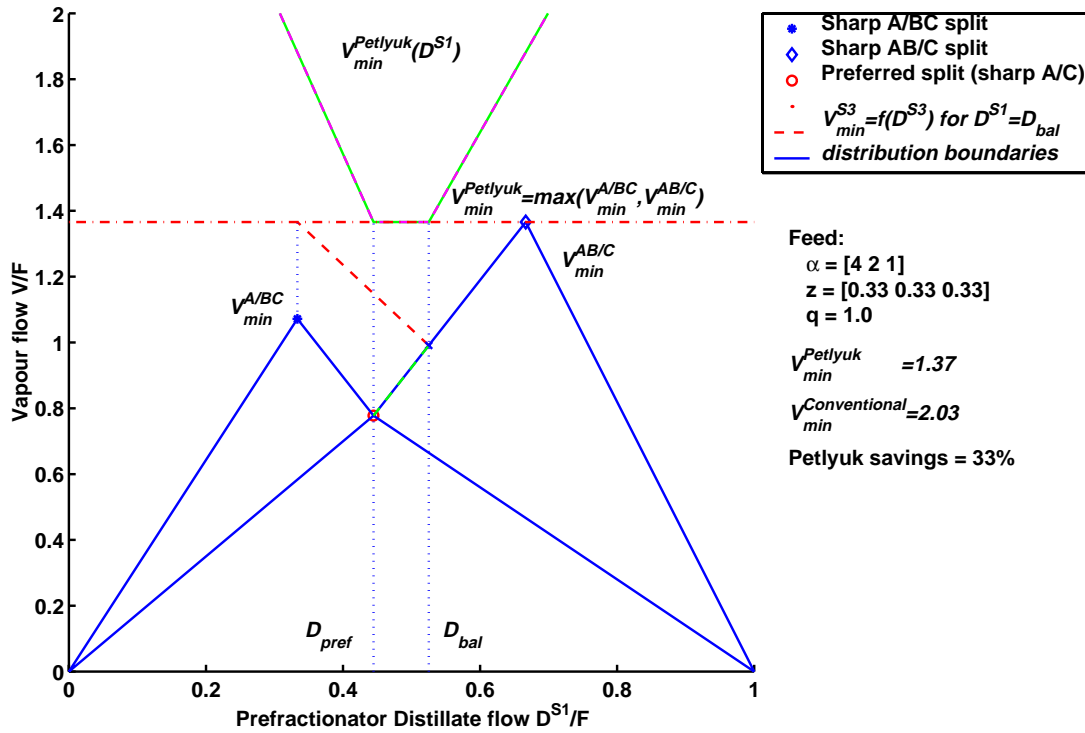AIChE Annual Meeting 1999, Dallas TX, 31. October-5. November

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Super-simple procedure for the minimum energy requirement for 3 product Petlyuk Column

1. Compute the Minimum energy "mountains" for the feed to the prefractionator

2. Compute the energy requirement to produce the Petlyuk top product specification in a single column, and plot it into the diagram ($V_{min}^{A/BC}$)

3. Compute the energy requirement to produce the Petlyuk bottom product specification in a single column and plot it into the diagram ($V_{min}^{AB/C}$)

4. The minimum energy requirement for the Petlyuk column is simply the maximum value of 2 and 3 (adjusted for 1-q): $V_{min}^{Petlyuk} = max(V_{min}^{A/BC}, V_{min}^{AB/C})$

5. This also gives us information of the extent of the flat region. If the difference is large, there is a large flat region.

This procedure also holds for non-sharp splits, and even for any multicomponent feed mixture (Nc>3).

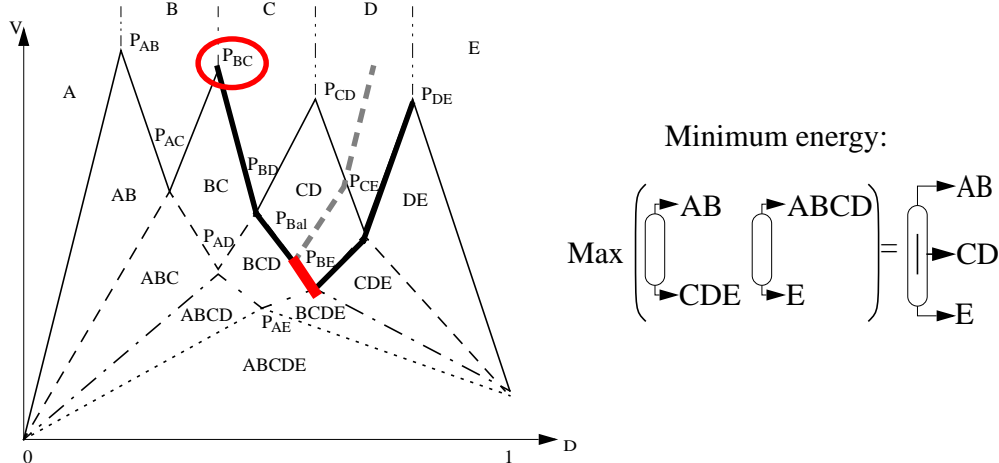**NTNU Department of Chemical Engineering**

AIChE Annual Meeting 1999, Dallas TX, 31. October-5. November

Example: Application to a 3 product Petlyuk Column:

Legend:
- Sharp A/BC split
- Sharp AB/C split
- Preferred split (sharp A/C)
- $V_{min}^{S3}=f(D^{S3})$ for $D^{S1}=D_{bal}$
- distribution boundaries

$V_{min}^{Petlyuk}(D^{S1})$

$V_{min}^{Petlyuk}=max(V_{min}^{A/BC},V_{min}^{AB/C})$

$V_{min}^{AB/C}$

$V_{min}^{A/BC}$

D_{pref} D_{bal}

Vapour flow V/F

Prefractionator Distillate flow D^{S1}/F

Feed:
α = [4 2 1]
z = [0.33 0.33 0.33]
q = 1.0

$V_{min}^{Petlyuk}$ = 1.37

$V_{min}^{Conventional}$ = 2.03

Petlyuk savings = 33%

Example: application to 3-product Petlyuk arrangement with 5-component feed

We want pure A+B in the top, and pure C+D in the side and pure E in the bottom

Minimum energy:

$$Max\begin{pmatrix} \nearrow AB & \nearrow ABCD & \nearrow AB \\ & & = & \searrow CD \\ \searrow CDE & \searrow E & \searrow E \end{pmatrix}$$

Solution: Operate the prefractionator between P_{Bal} and P_{BE}
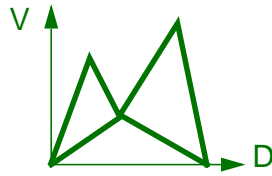
The energy requirement to the Petlyuk column is found as $max(P_{BC},P_{DE})=P_{BC}$

Conclusions

- Underwood's equations are very useful for minimum energy calculations
- Results can be visualized in the D-V plane as a set of informative "mountain" regions.

- Underwood roots can "carry" over to the next column.
- Determine minimum energy requirements for Petlyuk column with a quick glance at the D-V plane plots.