

Performing Multi - Phase Mass and Energy Balances

Using thermodynamics in mass / energy balance problems means that additional equations are available for solving the required unknowns.

How can VLE calculations be used in mass balance applications?

- Solve multi - component flash distillation problems
 - Derive and use the lever - arm rule
 - Explain and sketch the basic flash distillation process [W: Ch. 2.1]
 - Derive and plot the operating equation for a binary flash distillation on a y - x diagram [W: Ch. 2.4]
 - Solve both sequential and simultaneous binary flash distillation problems.
 - Explain the difference between (and solve) binary and multi-component flash calculations [W: Ch. 2.5, 2.6]
 - Write and solve mass and energy balances for multi - stage distillation
 - Explain the connection between column and flash distillation processes [W: Ch. 3.1, 3.2]
 - Write the mass and energy balances and equilibrium expressions for any stage in a column [W: Ch. 3.4, 4.1, 4.2]
 - Explain what constant molal overflow(CMO) is, and determine if it is valid in a given situation [W: Ch. 4.2]
 - Determine the operating equations for CMO systems [W: Ch. 4.3]
 - Determine the number of stages required to achieve a separation, using the Lewis method [W: Ch. 4.3]
 - Calculate the feed quality and determine its effect on flowrates [W: Ch. 4.4]
 - Plot the feed line on a y - x diagram [W: Ch. 4.4]
 - Determine the number of stages required to achieve a separation, using the McCabe - Thiele method [W: Ch. 4.5]
 - Solve total and minimum reflux problems when CMO is valid [W: Ch. 4.5, 4.8, 4.10]
 - Explain why multicomponent distillation is trial - and - error [W: Ch. 5.1]
 - Make appropriate assumptions and make external mass balances for multicomponent distillation problems [W: Ch. 5.1]
 - Perform gas - liquid(solubility) and liquid - liquid equilibrium mass balances
 - Explain what absorption and stripping do and describe a complete gas treatment plant
 - Use the McCabe - Thiele method to analyze absorption and stripping systems for both concentrated and dilute systems
 - Solve both immiscible and partially miscible extraction problems
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Explain and sketch the basic flash distillation process

Flash Distillation

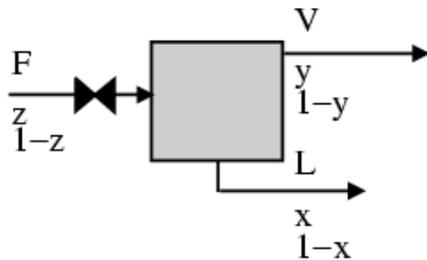
Some of the most important processes in the Chemical Process Industry are geared toward separating components from a mixture. One of the simplest ways to do this is to exploit thermodynamic differences in the phase behavior of the components.

One method of exploiting these differences is through **flash distillation**.

DEFINITION

Flash distillation is the process by which a portion of a mixture is vaporized and then the vapor and liquid phases are separated.

If our mixture is simply binary, then the Gibbs Phase rule states that ($2 + 2 - 2 = 2$) two intensive variables must be specified before we can know everything about the thermodynamic state of the system.

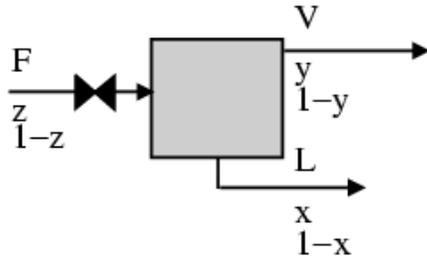


OUTCOMES:

Explain and sketch the basic flash distillation process

Analytically solve binary flash distillation problems

Binary Flash Distillation



Assuming that we choose a basis of the feed flowrate, we have 5 unknowns (the outlet flows: V , L ; and the compositions: x , y , z).

We can clearly write two material balances:

$$F = V + L$$

$$zF = yV + xL$$

We can also use K values (or a similar VLE method, like Raoult's Law) in order to relate our outlet compositions:

$$y = Kx$$

In addition to these three relations, we are often given the inlet composition, or the fraction of material vaporized (V/F). Therefore, the relations can be closed (i.e., the degrees of freedom goes to zero), if we are given more than one of these additional bits of information or if we have an adiabatic flash drum, so that we can use an energy balance as our last relation:

$$zF\hat{H}_{1F} + (1-z)F\hat{H}_{2F} = yV\hat{H}_{1V} + (1-y)V\hat{H}_{2V} + xL\hat{H}_{1L} + (1-x)L\hat{H}_{2L}$$

OUTCOMES:

Analytically solve binary flash distillation problems

Derive and plot the operating equation for a binary flash distillation

Graphical Binary Flash Distillation

It is relatively common in separations (especially when we look at **cascades** of separation units) to examine graphical approaches to solutions.

The graphical solutions to be used always include an **operating line** and an **equilibrium curve**

DEFINITION

*The **equilibrium curve** is a plot of the composition of a component in one phase versus the composition of the same component in the other phase.*

A simple way to obtain the equilibrium curve is by using the relative volatility, which you may recall is defined as (for a binary system)

$$\alpha_{AB} = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B} = \frac{y_A(1-x_A)}{(1-y_A)x_A}$$

We can rearrange this to give:

$$y = \frac{\alpha_{AB}x}{1+(\alpha_{AB}-1)x}$$

DEFINITION

*The **operating line** is a line representing the material balance equations.*

There are several options of operating line format, but one form can be obtained, by rearranging the component mass balance for y:

$$y = -(L/V)x + (F/V)z$$

we then take the total material balance and we divide both sides by V to give:

$$(L/V) = (F-V)/V = (1-V/F)/(V/F)$$

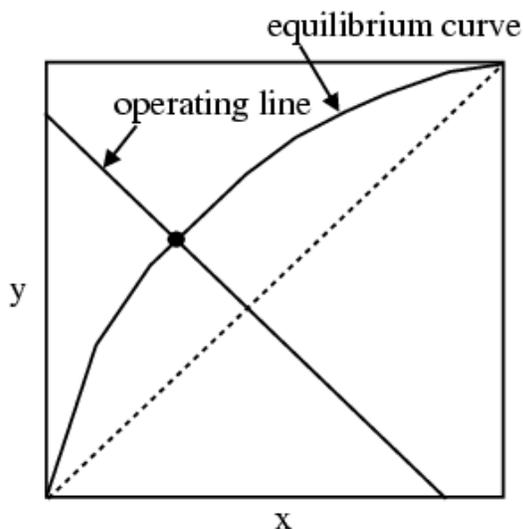
combining these two equations gives:

$$y = [(V/F-1)/(V/F)]x + (F/V)z$$

If we denote the fraction of the feed that is vaporized (i.e., V/F) as $f = V/F$, we get the operating line as:

$$y = \frac{f-1}{f}x + \frac{z}{f}$$

Plotting these two lines yields the composition of both the exiting vapor (y) and liquid (x) as the intersection of the lines.



NOTE:

The slope and intercept of the operating line are typically used to plot it in the first place. The dotted line along the diagonal is the $y=x$ line and is sometimes used to facilitate plotting the operating line (i.e., set $y=x$ in the feed line equation in order to find the location where the feed line crosses the dotted line). It has no physical significance in this application.

OUTCOMES:

Derive and plot the operating equation for a binary flash distillation on a $y-x$ diagram

Explain the difference between (and solve)
binary and multi-component flash calculations

Multi-Component Flash Distillation

If there are more than two components in the flash apparatus, a graphical procedure is no longer possible.

In order to perform our multi-component analysis for N components, we can write N balance equations. A total:

$$F = V + L$$

and N-1 component balances:

$$z_i F = y_i V + x_i L$$

We also have N equilibrium equations (using K values):

$$y_i = K_i x_i$$

In addition to the possibility of using an energy balance equation, we need to also use the physical constraints:

$$\sum_i^N y_i = 1$$

$$\sum_i^N x_i = 1$$

An efficient way of solving these equations is to first combine the total mass balance with the component equations to yield (N-1) equations of the form:

$$y_i = \frac{f-1}{f} x_i + \frac{z_i}{f}$$

we then eliminate x_i using the K_i value expressions to give:

$$y_i = \frac{K_i z_i}{K_i f - f + 1}$$

the same approach can be used to get a set of equations for x_i :

$$x_i = \frac{z_i}{K_i f - f + 1}$$

It turns out that neither of these equations, when plugged into the physical laws, yields particularly stable iterative solutions. Therefore, it is often the case that they are combined in such a way as to yield a more numerically-friendly equation

DEFINITION

*The **Rachford-Rice Equation** combines these two equations and has much nice convergence than either individually:*

$$\sum_i^N \frac{z_i (K_i - 1)}{K_i f - f + 1} = 0$$

NOTE:

This expression can be used to solve for the fraction vaporized, f . Similarly, we could have written our material balances in terms of the fraction remaining liquid, typically denoted q .

OUTCOMES:

Explain the difference between binary and multi-component flash calculations

OUTCOMES:

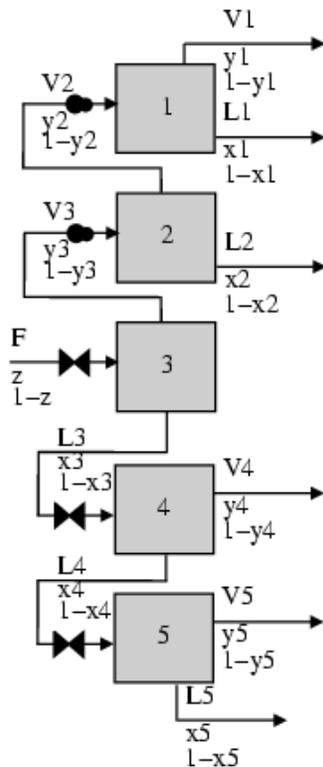
Solve both sequential and simultaneous binary flash distillation problems

Explain the connection between column and flash distillation processes

Multi-Stage Column Distillation

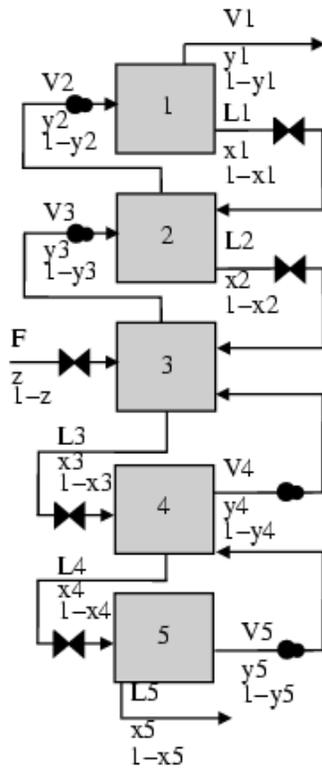
Unfortunately, unless the relative volatility of the components to be separated is vastly different from 1, a single flash operation is unlikely to achieve the required separation. (What would happen if the relative volatility was *equal to 1*?).

One option of improving the degree of separation is to use a number of flash drums in series.



In this configuration, the liquid from the flash drums "below" the main feed are partially vaporized and used as feed to yet "lower" drums, while the vapor streams "above" the main feed are partially condensed to form the feed streams in "higher" drums. This leads to a single vapor stream concentrated in the more volatile component at the "top" and a single concentrated stream of the less volatile at the "bottom"; however, we also make several streams of intermediate concentration (that might not be useful to anyone).

An alternative to this is to simply take those intermediate streams and vaporize/condense them as needed to form a second feed stream to each of the drums, as shown.



This configuration is far superior since we now get a single stream that is concentrated in each of our two components (for a binary mixture). the only small issue is that the total vapor flowrate decreases as we move "up" the column, while the total liquid flowrate decreases as we move "down" the column. A commonly used method of fixing this issue (and making design/analysis of these columns much simpler) is to use **reflux** and **boilup** streams

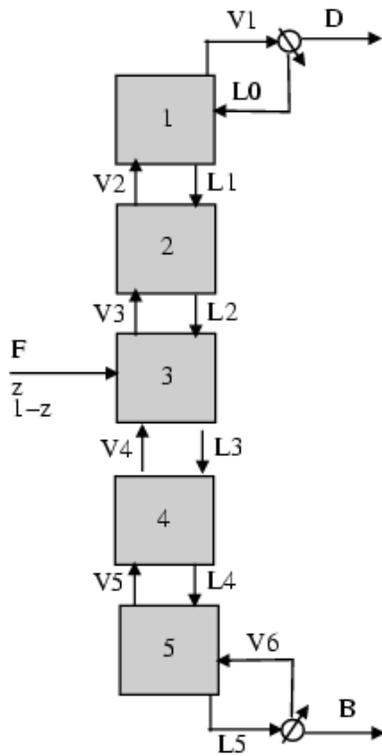
DEFINITION

A **reflux stream** is a stream that essentially recycles a portion of the vapor product stream back to the "highest" drum (stage).

DEFINITION

A **boilup stream** is a stream that essentially recycles a portion of the liquid product stream back to the "lowest" drum (stage).

A final process improvement can be made by recognizing that the energy needed to vaporize one stream can be obtained directly through the condensation of the other stream. Therefore, instead of using partial condensers/vaporizers all along the column, we simply allow the intermediate streams to physically intermix so that they can exchange energy efficiently. In this way, we change our energy requirements in such a way that we simply need a single boiler at the bottom, and a single condenser at the top. This final design is typically called a **column distillation tower** or simply a **distillation tower**:



NOTE:

Each of our "flash drums" is now called an equilibrium column stage, since they are no longer separate process units (although we will do balances as if they were).

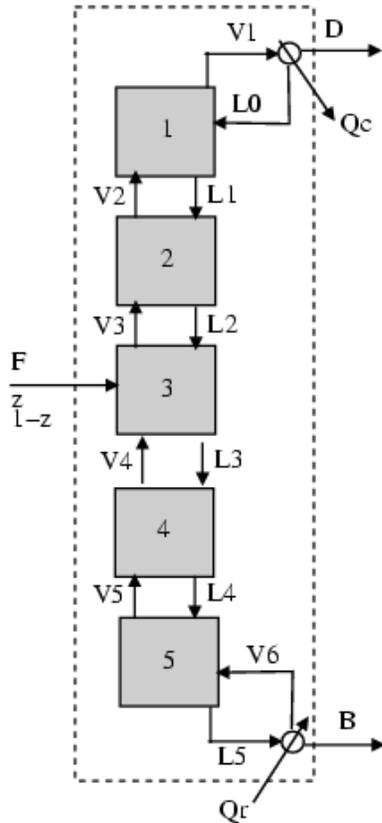
OUTCOMES:

Explain the connection between column and flash distillation processes

Write the mass and energy balances and equilibrium expressions for any stage in a column

Balances around distillation stages/column

The first step in doing solving distillation column problems is to examine the overall system (we have done this already):



We can clearly write two material balances:

$$F = B + D$$

$$zF = x_D D + x_B B$$

and an energy balance:

$$\Delta H = Q_R + Q_C$$

where Q_R is positive and Q_C is negative.

NOTE

*A critical component of solving distillation problem is knowing whether the condenser/reboiler are partial or total condensers/reboilers. Total condensers/reboilers mean that the compositions leaving the condenser/reboiler are **the same** for both streams, while partial condensers/reboilers mean the compositions leaving them are **in equilibrium***

Depending on what other information is given in the problem, these equations may need to be augmented by balances around the condenser or reboiler (if we know the reflux ratio L_0/D or the boilup ratio V_6/B).

In order to do *design* of distillation columns, we need to know the compositions at each stage (so we can determine how many to build). Doing a balance on a single stage

within a distillation column, or even a group of stages, is much like doing a balance on a single flash drum.

For reasons that will become clear in the next section, we typically write our balance equations separately for the region *above* and *below* the feed stage.

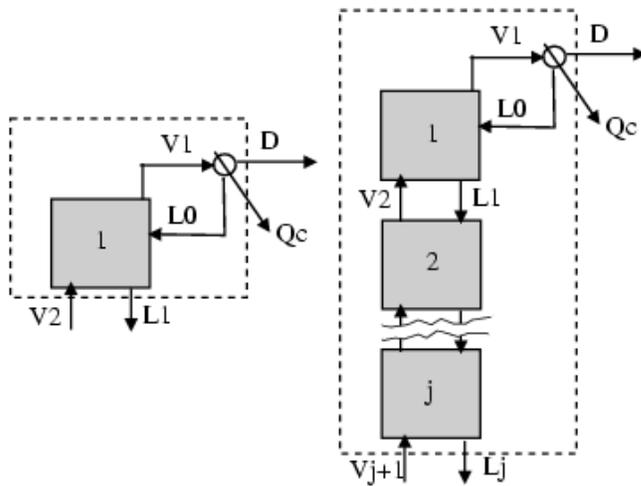
DEFINITION:

The **enriching section** or **rectifying section** of the column are the stages (and condenser) above the feed stage.

DEFINITION:

The **stripping section** of the column are the stages (and reboiler) below the feed stage.

Balances on the rectifying section,



take the form:

$$V_{j+1} = L_j + D$$

$$y_{j+1}V_{j+1} = x_jL_j + x_D D$$

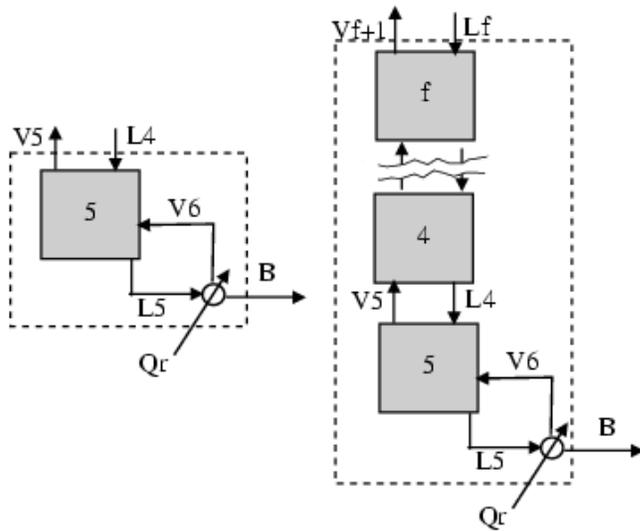
$$\Delta H = Q_c$$

NOTE

This form of the balances works even for $j=0$, the condenser. Knowing the reflux ratio (L_0/D) is very useful for that balance set.

If we start our procedure at the condenser, we know that determining whether the condensation is partial or total will allow us to relate x_D to x_0 . For each of the following stages, $j+1$, we use the previous balances (on j) to tell us x_j composition of the incoming liquid stream.

Balances on the stripping section,



take the form:

$$V'_{f+1} = L'_f - B$$

$$y_{f+1}V'_{f+1} = x_f L'_f - x_B B$$

$$\Delta H = Q_R$$

NOTE

This form of the balances works equally well for the reboiler. Knowing the boilup ratio (V_n/B) is very useful for that balance set.

If we start our procedure at the reboiler, we know that determining whether the vaporization is partial or total will allow us to relate x_B to x_6 . For each of the following stages, $f-1$, we use the previous balances (on f) to tell us x_f composition of the incoming liquid stream.

OUTCOMES:

Write the mass and energy balances and equilibrium expressions for any stage in a column

Explain what constant molal overflow (CMO) is,
and determine if it is valid in a given situation

Constant Molal Overflow (CMO)

The step-by-step procedure implied by the equations written in the previous section is laborious to solve, often involving a trial and error solution.

The solution becomes far simpler if we follow a suggestion of Lewis of assuming constant molal overflow (CMO).

DEFINITION:

Constant Molal Overflow (CMO) is the assumption that all liquid (L) and vapor (V) flows (on a molar basis) in the rectifying section are constant and that all liquid (L') and vapor (V') flows (on a molar basis) in the stripping section are constant (but not the same as those in the rectifying section).

Symbolically this means we take the following relations to be true:

$$L_1=L_2=\dots=L_j=L$$

$$V_1=V_2=\dots=V_j=V$$

$$L'_1=L'_2=\dots=L'_f=L'$$

$$V'_1=V'_2=\dots=V'_f=V'$$

The conditions under which these assumptions hold true are as follows:

- The column (except the reboiler and condenser) is adiabatic
- Enthalpic contributions due to temperature changes are negligible relative to those due to phase change
- The heat of vaporization per mole is not concentration dependent (i.e., the two components have similar heats of vaporization)

NOTE

*It is possible that constant **mass** overflow is valid (instead of molal), if the third condition holds true on a mass basis, rather than a molar basis (which is sometimes true for hydrocarbon mixtures).*

OUTCOMES:

Explain what constant molal overflow (CMO) is, and determine if it is valid in a given situation

Determine the operating equations for CMO systems

Operating equations for CMO distillation

Much like in flash distillation, it is useful to recast our material balance expressions in the form $y = F(x)$ (to facilitate future graphical solutions).

DEFINITION

*Assuming CMO in order to perform distillation calculations is often called the **Lewis Method**.*

In order to obtain these operating lines, we recall the generic balance equations for each section of the column. For the rectifying section, we have:

$$V_{j+1} = L_j + D$$

$$y_{j+1}V_{j+1} = x_jL_j + x_D D$$

Applying the assumption of CMO, these become:

$$V = L + D$$

$$y_{j+1}V = x_jL + x_D D$$

Combining them, we get the rectifying section operating equation:

$$y_{j+1} = x_j(L/V) + x_D(1-L/V)$$

For the stripping section,

$$V' = L' - B$$

$$y_{f+1}V' = x_fL' - x_B B$$

which gives us the stripping section operating equation as:

$$y_{f+1} = x_f(L'/V') - x_B(L'/V'-1)$$

NOTE

*L does **not** generally equal L'.*

OUTCOMES:

Determine the operating equations for CMO systems

Calculate the feed quality and determine its effect on flowrates

Feed Quality and the Feed Line

Before we try to combine the use of the rectifying and stripping operating equations and analyze how many stages a given separation should take, we must first look at how the feed affects our calculations:

There are five possibilities for how the feed could impact the column flows:

- Feed is a saturated liquid (so it simply increases L')
- Feed is a saturated vapor (so it simply increase V)
- Feed is a subcooled liquid (so it *condenses* some of V and increases L' significantly)
- Feed is a superheated vapor (so it *evaporates* some of L' and increases V significantly)
- Feed is a mixture of vapor and liquid (both L' and V increase)

Performing a balance on the feed stage, we can see how these options affect column operation:

$$F + V' + L = V + L'$$

Recalling that the rectifying and stripping sections meet at the feed stage, we can envision either plotting the lines and finding where they intersect (i.e., where $x_{rectifying} = x_{stripping}$ and $y_{rectifying} = y_{stripping}$) or thinking of the column as a continuum and doing out balance on a tiny slice of column right where the feed stage would go (but currently is not, yet). This would give us for the stripping section:

$$yV' = xL' - x_B B$$

and for the rectifying section:

$$yV = xL + x_D D$$

We can subtract the operating equation for the stripping section from the rectifying section, to get:

$$y(V-V') = x(L-L') + x_D D + x_B B$$

From an overall column balance we have:

$$zF = x_D D + x_B B$$

so:

$$y(V-V') = x(L-L') + zF$$

which is essentially a component balance on the feed "slice" discussed above. Similarly, a total balance on this slice yields:

$$(V-V') = (L-L') + F$$

DEFINITION:

The feed quality, q is the fraction of the feed that is liquid (just like it was for our flash calculations), or:

$$q = (L'-L)/F$$

Rearranging our total balance on the feed stage/slice and dividing by F , we get:

$$F/F = 1 = (L'-L)/F + (V-V')/F$$

or

$$1-q = (V-V')/F$$

Dividing our component feed stage/slice balance also by F , and using this relation for $(V-V')/F$, we get

$$y(1-q) = -xq + z$$

solving for y , gives us the feed equation as:

$$y = \frac{xq}{(q-1)} - \frac{z}{(q-1)}$$

Returning to our five feed types we see:

- If feed is a saturated liquid, $q=1$ (i.e., the difference in liquid flows is purely due to the feed: $L'-L=F$), "slope" of feed equation is infinite
- If feed is a saturated vapor, $q=0$ (i.e., the difference in vapor flows is purely due to the feed: $V-V'=F$), "slope" of feed equation is zero
- If feed is a subcooled liquid, $q>1$ (i.e., L' augmented by vapor condensation), "slope" of feed equation is positive
- If feed is a superheated vapor, $q<0$ (i.e., L' decreased evaporation), "slope" of feed equation is positive
- If feed is a mixture of vapor and liquid, q is between 0 and 1, "slope" of feed equation is negative

Combining this feed information with our equations for the rectifying and stripping sections allows us to analytically determine the number of stages necessary to achieve a particular outlet concentration.

OUTCOMES:

Calculate the feed quality and determine its effect on flowrates

OUTCOMES:

Determine the number of stages required to achieve a separation, using the Lewis method

Determine the number of stages required to achieve a separation at total reflux

McCabe-Thiele Analysis

In order to determine the number of stages necessary for a given separation (i.e., known feed composition, bottoms composition, and distillate composition), we could analytically solve stage-wise balance equations starting from the top (with the rectifying equations) and switching over to the stripping equations, once we reach the feed composition. A simpler technique, however, involves a graphical approach. We already have two operating equations (lines), an equilibrium expression (line) using the relative volatility, and a feed expression (line).

$$\text{EQUILIBRIUM LINE: } y = \frac{\alpha_{AB}x}{1+(\alpha_{AB}-1)x}$$

$$\text{RECTIFYING LINE: } y = xL/V + x_D(1-L/V)$$

$$\text{STRIPPING LINE: } y = xL'/V' - x_B(L'/V'-1)$$

$$\text{FEED LINE: } y = xq/(q-1) - z/(q-1)$$

DEFINITION:

The McCabe-Thiele method is a graphical separations procedure that exploits the fact that a separation stage involves interaction between the mass balance and vapor-liquid equilibrium.

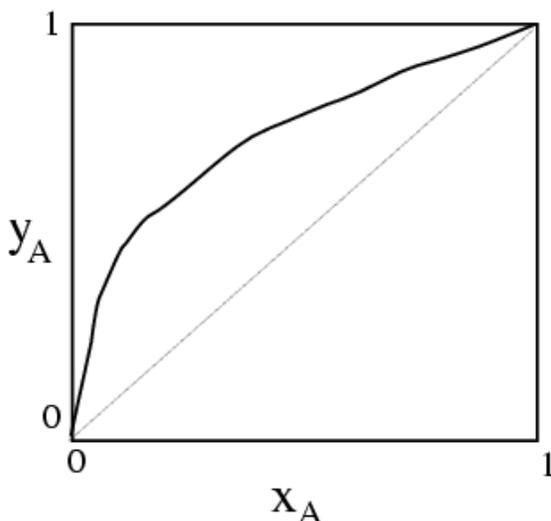
The simplest example of a McCabe-Thiele analysis involves the special case of no material being removed from the top or the bottom, so that the $L=V=L'=V'$ and both the stripping and rectifying lines reduce to:

$$y = x$$

NOTE

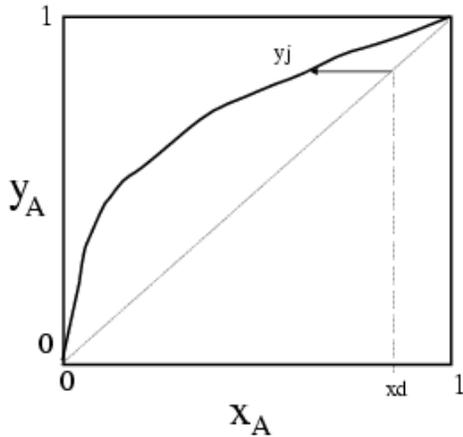
This operating condition corresponds to a reflux ratio (L/D) and boil-up ratio (V/B) of infinity. The feed line is useless in this case.

This condition leads to a plot that involves the equilibrium curve and a 45 degree operating line

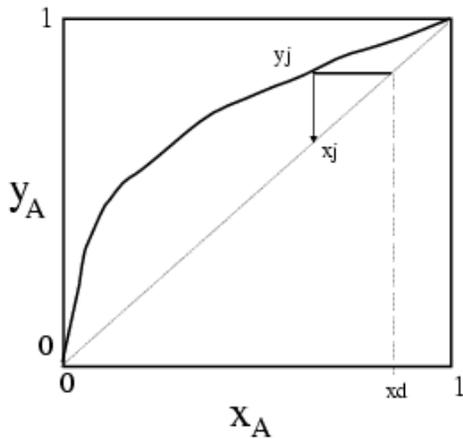


If we start at the desired distillate composition x_D , and recalling that we need to use a total condenser if $D=0$, we note that the vapor composition y_j coming off the top stage

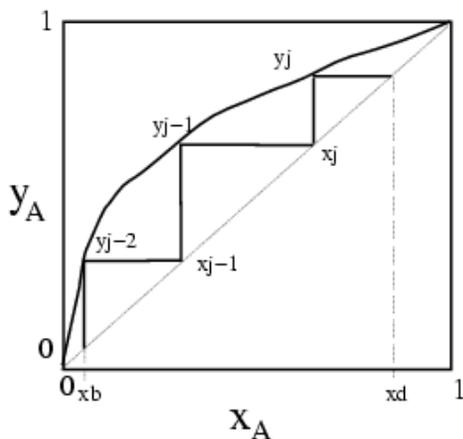
of the column is the same as x_D (as is the liquid composition returning to the column x_0). The 45 degree line, therefore, shows what the composition y_j actually is.



The composition of the liquid in equilibrium with that vapor (i.e., the one with composition x_j) can be determined by looking vertically at the x value of the curve at that point y_j .



Our material balance (operating line) tells us the relationship between the current vapor composition and the composition of the next vapor stage. We, therefore, "perform" our material balance by first moving vertically (down) to the operating line (in this case the $y=x$ line) then moving horizontally (left) to the equilibrium line, to tell us the y composition of the next lower stage. In order to solve the remainder of the problem, we continue with stage-wise stepping until we reach the bottoms composition:



NOTE

Each stair-step represents a stage within the column. This example, therefore, involved 3 stages.

OUTCOMES:

Determine the number of stages required to achieve a separation at total reflux using the McCabe-Thiele method

Determine the number of stages required to achieve a separation at minimum or higher reflux ratios u

McCabe-Thiele Analysis

McCabe-Thiele analysis for (almost) arbitrary reflux ratios is similar to total reflux, if slightly harder.

In this case the two operating equations (lines), an equilibrium expression (line) using the relative volatility, and a feed expression (line) do not simplify, and thus must be used in their normal forms:

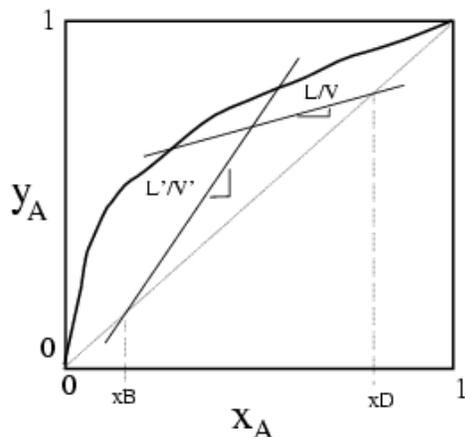
EQUILIBRIUM LINE: $y = \frac{\alpha_{AB}x}{1+(\alpha_{AB}-1)x}$

RECTIFYING LINE: $y = xL/V + x_D(1-L/V)$

STRIPPING LINE: $y = xL'/V' - x_B(L'/V'-1)$

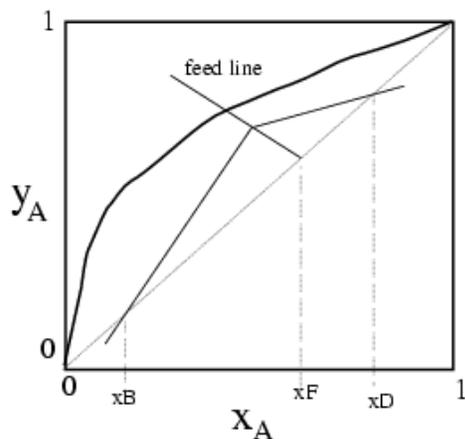
FEED LINE: $y = xq/(q-1) - z/(q-1)$

We first plot the equilibrium line on an x - y diagram. We then plot the rectifying and stripping operating lines -- using the x_D and x_B points on the $y=x$ line as our first points and the slopes L/V and L'/V' , respectively.

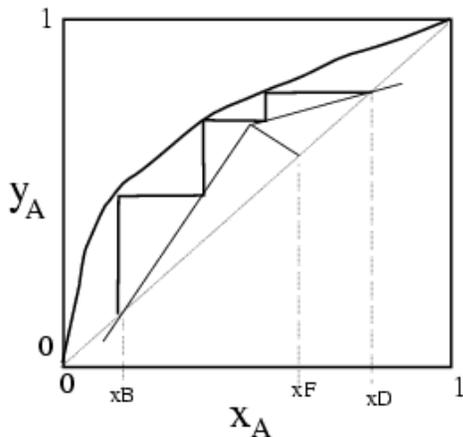


NOTE

The feed line will start at the x_F composition on the $y=x$ line and go to the intersection of the two operating lines. It is possible that we might need to use this info rather than the distillate and bottoms compositions and slopes. One option would be to set the feed equation equal to one of the other operating equations to analytically find the intersection point.



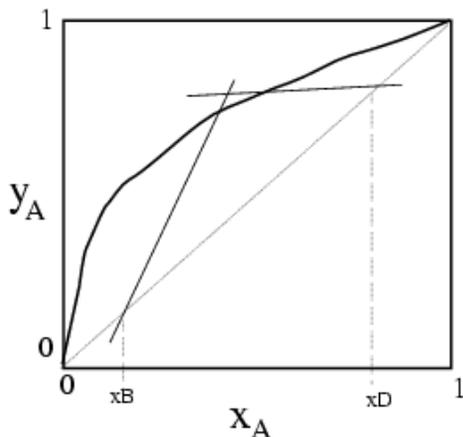
The steps in this case still go horizontally (left) for equilibrium, but now when we go vertically (down) for our material balance, we go to the rectifying operating line (prior to the intersection point) and down to the stripping operating line (after the intersection point):



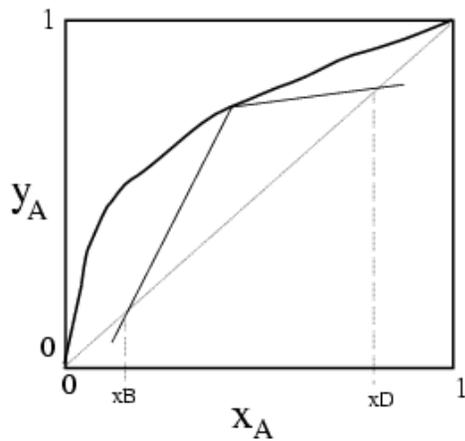
NOTE

It is possible that we will not match our distillate and bottoms compositions both exactly. In this case, we say we need 2.9 stages, for example. In reality we obviously can only have an integer number of stages (but would achieve a better separation than expected).

If we think about it, we can see that there is a limit to how small our reflux ratio (L/D) can be. As L/D decreases, we also decrease our slope L/V (prove this to yourself with an overall material balance on the rectifying section). In this case, we might obtain a graph like the following:



Clearly we cannot operate the column in this way, as we would need to move horizontally **beyond the equilibrium point**, which is physically impossible. Instead there is a minimum value of the reflux ratio that can be determined by finding the conditions under which the intersection point *just* "pinches" the equilibrium line:



DEFINITION:

The **minimum reflux ratio** is the ratio of L/D that leads to the intersection of the rectifying and stripping operating lines falling on the equilibrium curve (rather than inside it).

This condition, however, would require an infinite number of stages (can you see why?).

NOTE

In reality, each stage will not quite achieve the equilibrium compositions (due to poor mixing, or finite contact times), therefore our predictions from a McCabe-Thiele analysis will be slightly low relative to the actual number of stages required.

OUTCOMES:

Determine the number of stages required to achieve a separation at minimum or higher reflux ratios using the McCabe-Thiele method
