

Staged Separations *

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1 Equilibrium-based Separations

Many common separation operations are based on differences in the phase equilibrium properties of the components. In a multicomponent system with N_c components, the distribution of each component i between two phases in equilibrium can be expressed in terms of its mole fractions y_i, x_i in each phase and the equilibrium mole fraction ratio K_i :

$$y_i = K_i x_i \quad i = 1, \dots, N_c \quad (1)$$

Evaluating K_i . The values $K_i = K_i(T, P, y_1, \dots, y_{N_c}, x_1, \dots, x_{N_c})$ in (1) in general are complicated functions of temperature, pressure, and composition. In practice they are obtained from thermodynamic models, typically expressed in terms of activity and/or fugacity coefficients. In the case of vapor-liquid equilibrium, for example,

$$K_i = \frac{y_i(T, P, x_1, \dots, x_{N_c}) \cdot f_i^0(T, P)}{\phi^V(T, P, y_1, \dots, y_{N_c}) \cdot P} = \frac{\phi_i^L(T, P, x_1, \dots, x_{N_c})}{\phi^V(T, P, y_1, \dots, y_{N_c})} \quad (2)$$

The equations and the component-specific parameters needed for these detailed models are contained in specialized programs such as ASPEN. However, for preliminary work it may be sufficient, and more convenient, to employ more simplified methods. If pressures are low, we may approximate $\phi_i^V \approx 1$ and $f_i^0 \approx P_i^{\text{sat}}(T)$, where $P_i^{\text{sat}}(T)$ is the vapor pressure of pure component i . Further, if the components are sufficiently similar in their intermolecular interactions, the liquid might be approximated as an ideal mixture with

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$y_i \approx 1$. Alternatively for the case of sparingly dissolved materials (e.g. light gases in liquids), $y_i f_i^0 \approx H_i(T, x_{j \neq i}) \approx \bar{H}_i(T)$. These approximations correspond to Raoult's Law and Henry's Law, respectively:

$$K_i P \doteq P_i^{\text{sat}}(T) \quad \text{or} \quad K_i P \doteq \bar{H}_i(T) \quad (3)$$

We expect the values of K_i to be strong functions of T in any case, but it is sometimes adequate to neglect the dependence on composition, as suggested by (3). The righthand side functions in (3) often are readily found in handbooks, etc.

Single separation stages. Consider first a single vapor-liquid equilibrium stage, where a feed mixture with composition mole fractions z_i , $i = 1, \dots, N_c$ has a given enthalpy such that at equilibrium it is partially vaporized as a two phase mixture. The associated mass balance is

$$F z_i = V y_i + L x_i \quad i = 1, \dots, N_c \quad (4)$$

Here F , V , and L are the total molar flowrates of the feed, vapor phase, and liquid phase respectively. Summing (4) over $i = 1, \dots, N_c$ gives the total mass balance, $F = V + L$.

The accompanying energy balance is

$$H^F = V h^V(T, P, y_1, \dots, y_{N_c}) + L h^L(T, P, x_1, \dots, x_{N_c}) \quad (5)$$

H^F is the feed total enthalpy while h^V and h^L are the vapor and liquid molar enthalpies.

If the operating pressure is given, the values of the unknown variables can be computed by simultaneous solution of (1), (4), and (5), along with either one of the following definitions:

$$\sum_{i=1}^{N_c} x_i = 1 \quad \sum_{i=1}^{N_c} y_i = 1 \quad (6)$$

Counting variables and equations shows that only one of the above relations is needed. It would be redundant to include both of them, since the values K_i used in (1) in fact ensure that the omitted relation will be satisfied anyway provided that the included relation holds.

Use of mole fractions in a model formulation often makes the degrees-of-freedom accounting obscure. Formulation directly in terms of the conserved quantities may be more straightforward, since the number of physical conditions is usually easy to identify. In terms of flows $f_i = F z_i$, $v_i = V y_i$, $\ell_i = L x_i$, the single equilibrium stage may be formulated as

$$f_i = v_i + \ell_i \quad i = 1, \dots, N_c \quad (7)$$

$$y_i = K_i(T, P, y_1, \dots, y_{N_c}, x_1, \dots, x_{N_c}) \cdot x_i \quad i = 1, \dots, N_c \quad (8)$$

$$H^F = \left(\sum_j v_j \right) \cdot h^V(T, P, y_1, \dots, y_{N_c}) + \left(\sum_j \ell_j \right) \cdot h^L(T, P, x_1, \dots, x_{N_c}) \quad (9)$$

$$\text{where } y_i = \frac{v_i}{\sum_j v_j}, \quad x_i = \frac{\ell_i}{\sum_j \ell_j}$$

The $(2N_c + 1)$ physical relations are equal in number to the variables $\{v_i, \ell_i, T\}$.

Mole fractions are used in the following, since for the particular case developed it leads to a very compact formulation.

The “Constant Relative Volatility” (CRV) approximation. When considering systems of many equilibrium stages, the analysis can be simplified through the concept of “relative volatility”. This approximation is motivated by the observing that even though the $K_i P$ values are strong functions of temperature, over modest temperature ranges the curves of $\ln K_i$ vs. T for the different components i are often approximately parallel to each other. While the values of the K_i will change, their relative values K_i/K_j are then roughly constant.

Relative volatilities α_i can be defined in either of two ways. In the first way, one component $i = \text{ref}$ is selected arbitrarily and the volatilities of all components are computed relative to the reference component:

$$\alpha_i = \frac{K_i}{K_{\text{ref}}} \quad (10)$$

The second way uses a mole fraction weighted average as the reference value:

$$\alpha_i = \frac{K_i}{\sum_{j=1}^{N_c} K_j \hat{x}_j} \quad (11)$$

Note here that the selected composition \hat{x}_j used to form the weighted average must be a constant, not a variable, if the α_i are to be regarded as constants. One natural choice is to take \hat{x}_i to be the liquid composition for the particular conditions at which the K_i are evaluated. For this choice the denominator in (11) sums to unity, giving $\alpha_i = K_i$ (evaluated at fixed conditions). This choice is also convenient when using the approximations in (3), since then $\alpha_i = (K_i P)/P$. The two equations (10) and (11) give values that differ by the same constant for all components. This arbitrary scaling is usually of no consequence since only the ratios between the α_i matter in use.

Inverting (10) or (11) and combining with (1) gives

$$K_i = \frac{\alpha_i}{\sum_{j=1}^{N_c} \alpha_j x_j} ; \quad y_i = \frac{\alpha_i x_i}{\sum_{j=1}^{N_c} \alpha_j x_j} \quad (12)$$

The relative volatility form offers little advantage over (1) unless the α_i are sufficiently constant. However, when the approximation is acceptable, (12) gives a particularly simple way to compute the equilibrium of a stage.

The extent to which the α_i are actually independent of temperature (and composition) will depend on the thermodynamic characteristics of the components involved.

2 Countercurrent Cascades of Stages

The degree of separation achieved by a single equilibrium stage is limited. To achieve higher degrees of separation, stages may be cascaded in series where the liquid and vapor

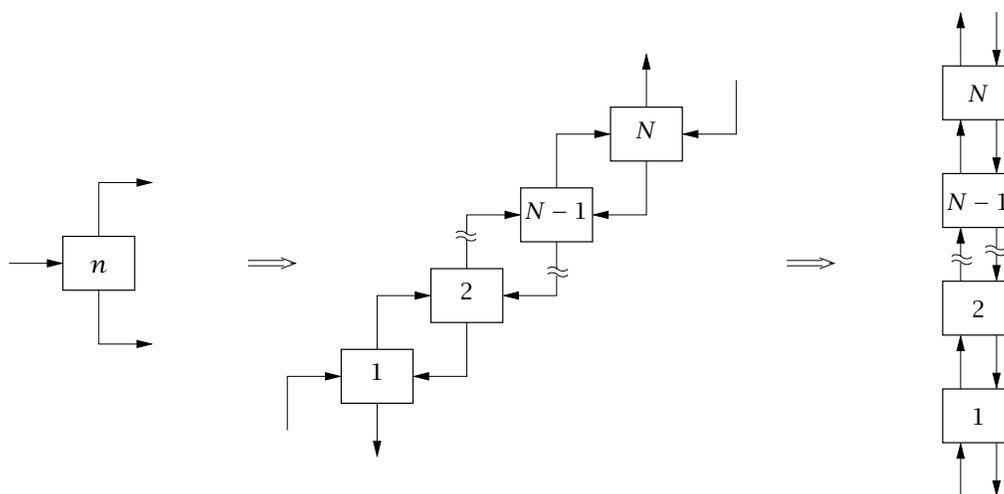


Figure 1: Countercurrent cascade of ideal stages.

streams are in countercurrent flow. Figure 1 shows the manner of interconnection of the individual stages.

The total feed entering each stage is formed by mixing the liquid stream leaving the stage above and the vapor stream leaving the stage below. (For vapor-liquid separations the stages are usually stacked vertically, and are referred to as a “column”.)

The “Constant Molar Overflow” (CMO) approximation. Usually stages operate adiabatically, and the relative amounts of vapor and liquid leaving each stage are determined by an energy balance around the stage. While the exact balance requires thermodynamic calculations of the enthalpies of the multicomponent streams, it is often adequate for initial calculations to employ the constant molar overflow assumption. This approximation ignores the sensible heat changes of the streams as their temperatures change, ignores any heat of mixing, and considers only the latent heats of vaporization or condensation. Further, it assumes the molar heats of vaporization for each component are approximately equal. The energy balance is then quite simple: The total moles of vapor leaving a stage equals the total moles of vapor entering, and the total moles of liquid leaving equals the total moles of liquid entering. Thus under the CMO assumption the total molar flowrates can be described by a single pair of variables V and L applying to every stage within the cascade.

Stage calculations. Numbering the stages in the direction of vapor flow, and using superscripts to label the stage number, the component mass balances assuming CMO around

any stage n in the cascade become:

$$V\mathcal{Y}_i^n - Lx_i^{n+1} = V\mathcal{Y}_i^{n-1} - Lx_i^n = d_i \quad (13)$$

The balance written in this way shows the net difference flow into the stage from below equals the net difference flow out from the stage to above. This difference flow must in fact be the same for all stages in the cascade, and so may be denoted by the single set of flow variables d_i .¹ Summing (13) over $i = 1, \dots, N_c$ also shows that $V = L + \sum_{i=1}^{N_c} d_i$ is not an independent quantity and may be calculated from L and d_i .

If we introduce the CRV approximation (12) into (13) and arrange x_i^{n+1} on the lefthand side we can eliminate the vapor compositions and describe the stage behavior in terms of the liquid compositions only.

$$x_i^{n+1} = \frac{V}{L} \cdot \frac{\alpha_i x_i^n}{\sum_{j=1}^{N_c} \alpha_j x_j^n} - \frac{d_i}{L} \quad (14)$$

The behavior of the cascade is given by the set of finite difference equations in (14) for $i = 1, \dots, N_c$ with n ranging over the number of stages.

3 Distillation columns

Continuous distillation is often performed in columns of countercurrent stages. The actual stages do not usually achieve complete vapor-liquid equilibrium, but nevertheless for initial design studies they may be modeled in an approximate way by using an adjusted number of equilibrium stages that is equivalent in effect to the actual number of nonequilibrium stages.

A simple distillation column has one feed and two products, and utilizes two countercurrent column sections configured in the flow pattern shown in Figure 2. The top section is termed the rectification section (R), with stages numbered upward from 1 to N_R . The bottom section is termed the stripping section (S), with stages numbered upward from $-N_S$ to -1 . The balances corresponding to the combined system are developed as follows.

Consider the case where the feed is a saturated liquid with flowrate F and composition x_i^F . Figure 2 shows the common case where a total condenser and a pump-through reboiler are used. The composition of the distillate (top) product equals the composition of the reflux liquid returned to the top section, and the composition of the bottoms product equals the composition of the vapor returned to the bottom column section. Also, the distillate and bottoms product flows equal the net difference flows d_i^R and d_i^S through the rectification and stripping sections, respectively. Note that the values of d_i^R are positive, but the values of d_i^S are negative, since the net flow is downward in the lower section.

¹The fact that d_i is constant throughout the cascade is true in general as a consequence of the mass balance. It does not depend on the CMO assumption.

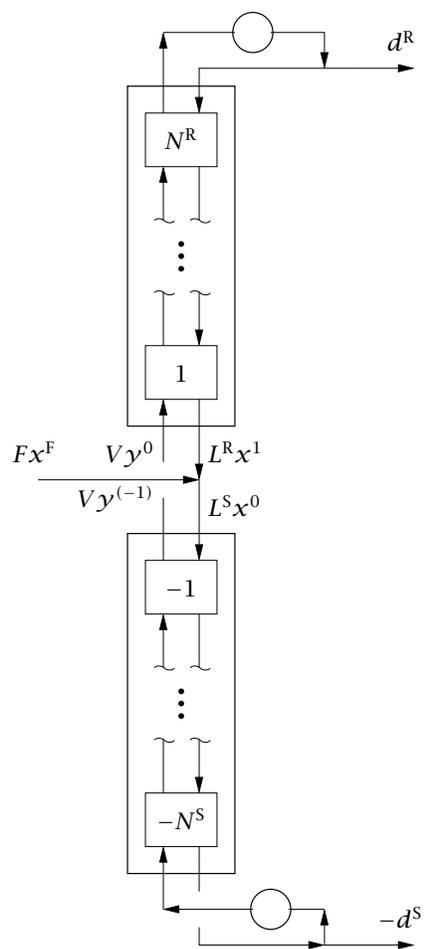


Figure 2: Flow pattern of simple one feed, two product distillation column.

The mass balances on the column as a whole are

$$Fx_i^F = d_i^R + (-d_i^S) \quad (15)$$

$$d_i^R = (V - L^R)x_i^{N_R+1} \quad (16)$$

$$d_i^S = (V - L^S)x_i^{(-N_S)} \quad (17)$$

The remaining balances are constructed around the feed addition point. In the case of saturated liquid feed, the vapor rate V is the same in both column sections, but the liquid rates L^R and L^S differ such that $L^S = L^R + F$. The balances for this case become

$$L^R x_i^1 + Fx_i^F = L^S x_i^0 \quad (18)$$

$$Vy_i^0 = Vy_i^{(-1)} \quad (19)$$

When the feed condition is specified, there are two degrees of freedom in the column remaining to be specified, corresponding to the vapor rate V generated in the reboiler and the liquid reflux rate L^R returned to the column at the top. If we set fix these two variables, the remaining variables are determined by the system of equations composed of (15), (16), (17), (18) together with a series of N_R instances of (14) for the rectification stages and a series of N_S instances of (14) for the stripping stages. Counting the variables $\{d_i^R, d_i^S, x_i^{N_R+1}, x_i^{(-N_S)}, x_i^1, x_i^0\}$, together with the $(N_R - 1)$ and $(N_S - 1)$ compositions x_i^n of the internal stages within each column section, shows that there are $(4 + N_R + N_S)N_c$ unknowns, matching the number of equations. One might then proceed to set up and solve this set of simultaneous equations, e.g. via Newton's method as discussed in Module 4 on Process Systems Steady-State Modeling and Design.

Solution via “precedence ordering” and “tearing”. While it requires the least thought to simply collect together a set of simultaneous equations and feed them directly to a solver, it often pays to analyze the algebraic structure of the problem and set up a more structured solution approach.

In many problems a simple counting of equations and variables does not guarantee a valid formulation. This potential difficulty may be seen in the present problem. Observe that the set of mass balance equations in (19) were omitted from the collected system of equations described above. Why omit this particular set, and not, for instance, omit the set in (15) instead? (We could do this by including the set of variables y^0 and $y^{(-1)}$, along with two more sets of equations in the form of (12). This would add $2N_c$ more variables and $2N_c$ more equations to the problem. Equivalently, we could use (12) twice to eliminate y^0 and $y^{(-1)}$ from (19), ending up with a version containing only x^0 and $x^{(-1)}$.)

In this example, we could successfully exchange (19) for (15) in the collected system. In contrast, exchanging (19) for either (16) or (17) or (18) will *not* work. The resulting system of equations would be “singular” because the selected equations are not all independent, leaving the variables underdetermined. Passing such a system to a nonlinear solver such as fsolve will end in a convergence failure, with little clue as to the source of the difficulty.

One approach to avoiding such potential traps is to break the equations into smaller sets which are then solved sequentially. This “hands on” approach can make it easier to see how the degrees of freedom are structured, so that a workable solution procedure will be obtained. It is much like the process one would use in organizing a problem to solve equations on paper. The main idea is to view each set of equations in terms of its possible sets of “output variables”, i.e. variables that the equations could be solved for, if values for the other variables were given as inputs. A sequence is then figured out where at each step an equation set is solved to produce outputs, which then can be used as inputs for other equation sets in later steps.

For the present problem, we can begin by treating the finite difference equations in (14) over a column section as one such equation set. Given values for the input variables x^1 , the equations can be computed in sequence to produce the output variables x^{N+1} . This computation is performed by the function cascade developed in Exercise 1.

The structure of the rest of the problem can be seen by constructing the following table of equations and variables.

Eqn.	d^R	d^S	x^{N_R+1}	$x^{(-N_S)}$	x^1	x^0
(15)	⊗	⊗				
(16)	⊗		⊗			
(17)		⊗		⊗		
(18)				⊗	⊗	⊗
R-cascade	×		⊗		×	
S-cascade		×		×		⊗

Here an \times indicates the incidence of a variable in an equation such that it is a required input. An \otimes indicates those variables that could be assigned as the output from the equation², while if not so assigned they remain as inputs.

Sequential solution requires a precedence order such that at each step, calculated values are known for all inputs to the next equation. One such ordering is show in Figure 3. Each of the equations in the sequence requires inputs, so there is no simple “once-through” sequence for this problem. An iterative solution method is required. The approach is to pick a variable or set of variables such that the remaining other variables can then be obtained as outputs by following a calculation sequence. The selected variables are termed “tear” variables, since by “tearing” the connection arrows going into them in Figure 3 the result gives a once-through calculation. This once-thorough calculation takes values for the tear variables as input and produces values for the tear variables as output. The once-through calculation for the overall system can be written

$$X_{\text{out}}^{\text{tear}} = F_{\text{overall}}(X_{\text{in}}^{\text{tear}}) \quad (20)$$

²Here we have elected to consider only output variables that could be obtained explicitly by algebraic rearrangement of the equation. The approach may be extended if desired to outputs obtained numerically by iterative solutions of the individual equation sets. This is not needed here for the CRV-CMO version of the model. Also see Exercise 7.

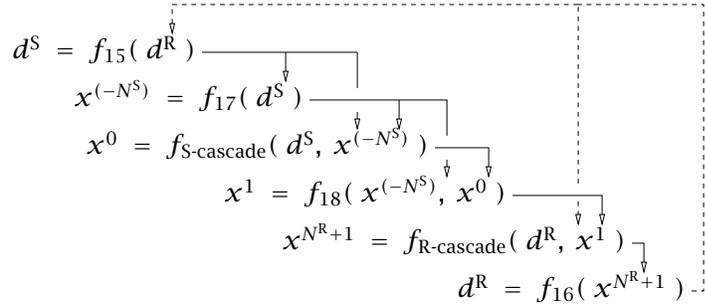


Figure 3: Precedence-ordered sequence. $f_k(\cdot)$ denotes the use of equation k to obtain the output variable.

In Figure 3, if we tear on variables d^R , the remaining sequence can be computed. Given an input value d_{in}^R , the calculation produces output values for all variables, including d_{out}^R .

With $F_{overall}$ constructed, the solution procedure is completed by solving (20) to find values $X_{out}^{tear} = X_{in}^{tear}$, i.e.

$$X^{tear} = F_{overall}(X^{tear}) \quad (21)$$

Certain numerical methods specifically treat equations in this “fixed point” form, but by simply rearranging

$$[F_{overall}(X^{tear}) - X^{tear}] = f_{overall}(X^{tear}) = 0 \quad (22)$$

we can apply a general nonlinear equation solver.

Thus the overall distillation column model can be solved by numerical solution of $f_{overall}(d^R) = 0$. There are only N_c variables to be iterated upon by the solver. It will be much easier to provide initial guesses for this smaller number of variables, compared to a simultaneous solution which would need initial guesses for every variable in the problem. Also, we have some notion of what variable values are “reasonable” for d_i^R , since these equal the distillate product component flows, which we know are some recovery fraction times the feed flows. It is also worth noting that in many cases narrowing down the number of variables to be given to the nonlinear iterative solver can improve the chances that it will converge.

Finally, the above procedure may actually still be quite useful even if it is decided to solve the entire equation set with a simultaneous solver. It offers a means to verify that the proposed system of equations are independent and sufficient, and a way to identify the required input parameters.

4 Exercises

Exercise 1

Write a MATLAB function that calculates the liquid compositions x_i^n on each stage of a countercurrent column section according to (14), for stages numbered from 1 to N and including the inlet composition x_i^{N+1} . The function will take as inputs the liquid composition x_i^1 exiting stage 1, the difference flows through the cascade d_i , V , the relative volatilities α_i , and the total number of stages N . The function will return the liquid composition profile x_i^n in the column section:

function X = cascade(x1, d, V, alpha, N)

Use the function to prepare a plot of the liquid composition for the following column section case:

i	x_i^1	d_i	α_i
1	0.34	0.75	2.0
2	0.25	0.22	1.5
3	0.18	0.02	1.0
4	0.13	0.002	0.67
5	0.10	0.0002	0.50
$L = 2.0$			
$N = 8$			

Exercise 2

Construct a MATLAB function

function dR = distil (feed, V, LR, NR, NS)

to execute the solution procedure for the CRV-CMO distillation column model based on the tearing and precedence-ordering scheme in Figure 3. Using the cascade function you developed in Exercise 1 as a building block, write function resid = foverall(dR) to compute $f_{\text{overall}}(d^R)$. Use fsolve to solve the model.

Apply the procedure to solve the following problem, determining the flowrates for each component in the distillate product. This example takes a feed mixture of ethane, propane, n-butane, n-pentane, and naphtha, and separates it into a C_3 - stream and C_{5+} stream. Molar flowrates are given for the feed. Relative volatilities were computed at the conditions of the feed stream as a saturated liquid.

i	Component	Fx_i^F	α_i
1	C ₂	5	3.2
2	C ₃	9	1.9
3	C ₄	6	1.0
4	C ₅	4	0.58
5	C ₆₊	76	0.25

$V = 35$
$L^R = 21$
$N_R = 4$
$N_S = 5$

Try different initial guesses as follows:

1. Devise an initial guess on your own.
2. Use $(d^R)^0 = [4, 8, 2, 0, 0]$.
3. Use $(d^R)^0 = [5, 9, 0, 0, 0]$.
4. Use $(d^R)^0 = [5, 8, 1, 0, 0]$.
5. Use $(d^R)^0 = [2.8, 2.8, 2.8, 2.8, 2.8]$.
6. Use $(d^R)^0 = D \cdot \frac{\alpha_i x_i^F}{\sum_{i=1}^{N_C} \alpha_i x_i^F}$ where $D = V - L^R$. (This uses the known total moles of distillate and the vapor composition y_i^F in equilibrium with the feed.)

Exercise 3

Modify your code in Exercise 2 so that distil also outputs profiles of the compositions of each component on each stage in the column. Plot these profiles as curves of stage number vs. liquid mole fraction, where the stage number ranges from $(-N_S)$ to $(N_R + 1)$.

Exercise 4

Algebraic models involving several variables quite often will have more than one mathematical solution. Even if a numerical method succeeds at converging to a solution x satisfying $f(x) = 0$, that might not be the solution desired. For the distillation model in Exercise 2, there is another (mathematical, not physical) solution having some negative flowrates.

Sometimes the iterative calculation can be steered to the desired solution by using transformations on the variables. The goal is to keep each actual variable within its desired domain (e.g. positive) by giving the solver a surrogate variable η_i to manipulate as it wishes. However, the surrogate variable is mapped onto the actual variable in such a way that the actual variable will never be given a value outside of its desired domain. For the distillation model, the actual variables d^R and $-d^S$ both need to remain positive. We can accomplish

this if we keep the distillate fractional recoveries ξ_i for each component within the range $0 < \xi_i < 1$.³ We can use the following variable transformation:

$$\eta_i \rightarrow \xi_i = \begin{cases} \left[\frac{1 + \eta_i}{2 + \eta_i} \right] & (\eta_i \geq 0) \\ \left[\frac{1}{2 - \eta_i} \right] & (\eta_i < 0) \end{cases} \rightarrow d_i^R = (F x_i^F) \cdot \xi_i \quad (23)$$

$$d_i^R \rightarrow \xi_i = d_i^R / (F x_i^F) \rightarrow \eta_i = \begin{cases} \left[\frac{1}{1 - \xi_i} - 2 \right] & (\frac{1}{2} \leq \xi_i < 1) \\ \left[2 - \frac{1}{\xi_i} \right] & (0 < \xi_i < \frac{1}{2}) \end{cases} \quad (24)$$

Here η_i can be allowed to range over the entire real line, but ξ_i will always be kept within the range $0 < \xi_i < 1$. The pair d_i^R, η_i are one-to-one for fixed feed, so either version can readily be converted to the other via (23, 24).

Write MATLAB functions `diR = map(etai, feedi)` and `etai = unmap(diR, feedi)` to perform the mappings in Equations (23,24). Plot each mapping function to test.

Modify your function `foverall` from Exercise 2 to use these mapping functions so that `fsolve` iterates on the values of η instead of d^R . Run the model using the various starting points tried before in Exercise 2.

Exercise 5

Write a function of the form

```
function LR = reflux( feed, V, key, dkeyR )
```

that uses your function `distil` from Exercise 2 to solve for the value of the reflux flowrate L^R needed to obtain a product flowrate for component $i = \text{key}$ of value d_{key}^R . Solve the case in Exercise 2 for `key = 4`, $d_4^R = 0.15$. Repeat for $d_4^R = 0.08$.

Exercise 6

The reflux rate L^R is an important decision parameter in distillation design. For a given separation, there exists a tradeoff between the number of stages used and the amount of reflux employed.

The “reflux ratio” $R = L^R / \sum_{i=1}^{N_c} d_i^R$ is a convenient dimensionless measure of the reflux rate. Consider again the separation in Exercise 5 specified by `key = 4`, $d_4^R = 0.12$. Consider a total number of stages $N_{\text{tot}} = N_R + N_S$ taking $N_S = N_R$. Using the function `reflux` developed in Exercise 5, prepare a plot of required R vs. N_{tot} . Consider the range $6 \leq N_{\text{tot}} \leq 30$.

Exercise 7

Show how the finite difference equations in (14) can be inverted algebraically to obtain the explicit output of the variables x_i^n , taking x_i^{n+1} and d_i as inputs.

³With a finite number of stages the recovery values can never completely reach either zero or one.

References

W. L. McCabe, J. C. Smith, and P. Harriott. *Unit Operations of Chemical Engineering*. McGraw-Hill, New York, seventh edition, 2005.