

Daniel Problem

Separation of Water and Isobutanol by LLE and Distillation Utilizing Stream Recycle

Abstract:

The clear presentation and solution of a problem is an effective method to teach various concepts. Formulas and concepts used as the basis for calculations and theory should be clearly stated and explained to communicate ideas clearly. A problem involving three liquid separations and two distillation processes will be analyzed in this project. This paper will attempt to solve the problem in a way that allows students to easily follow the calculations and learn how to make them on their own.

Theoretical Basis:

Calculations for liquid phase solubility were made based on a one-constant Margulies model. This model is further applied to the general form of Gibbs free energy equation to find the points at which energy of the system is minimized yielding the equilibrium point. Antoine's equation was used for calculating vapor pressures as a function of temperature. Vapor liquid equilibrium will be calculated using Raoult's law and activity coefficients from the one-constant Margulies model.

One-constant Margulies model:

$$\gamma_1 = e^{\frac{C \cdot x_2^2}{R \cdot T}}$$
$$\gamma_2 = e^{\frac{C \cdot x_1^2}{R \cdot T}}$$

Gibbs Free Energy:

$$\Delta G_{mix} = R * T * (x_1 * \ln \gamma_1 + x_2 * \ln \gamma_2)$$

Antoine's equation:

$$\log_{10}(P) = A - \frac{B}{C + T}$$

Raoult's Law

$$y_1 = x_1 * P^o_1 * \gamma_1 / P_{tot}$$
$$y_2 = (1 - x_1) * P^o_2 * \gamma_2 / P_{tot}$$

Figures 1 & 2 presented below were constructed using the above equations and are used to determine the dependence of phase equilibrium versus pressure.

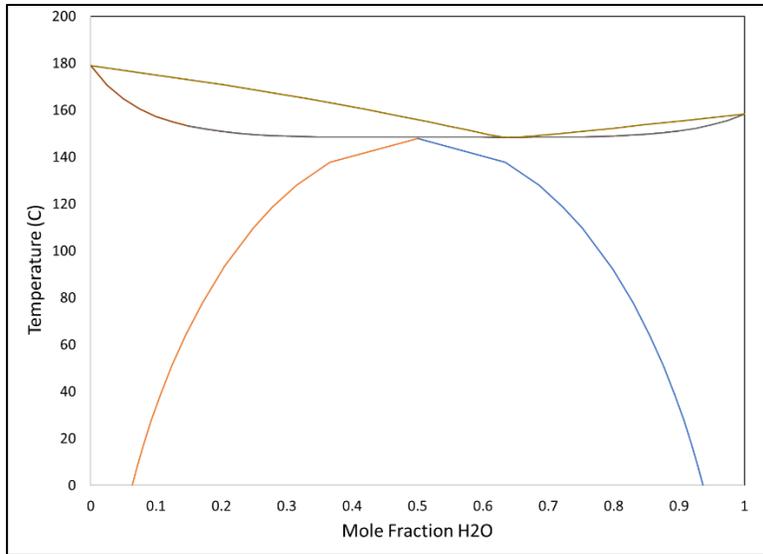


Figure 1. Water - Isobutanol equilibrium data for P = 6 bar.

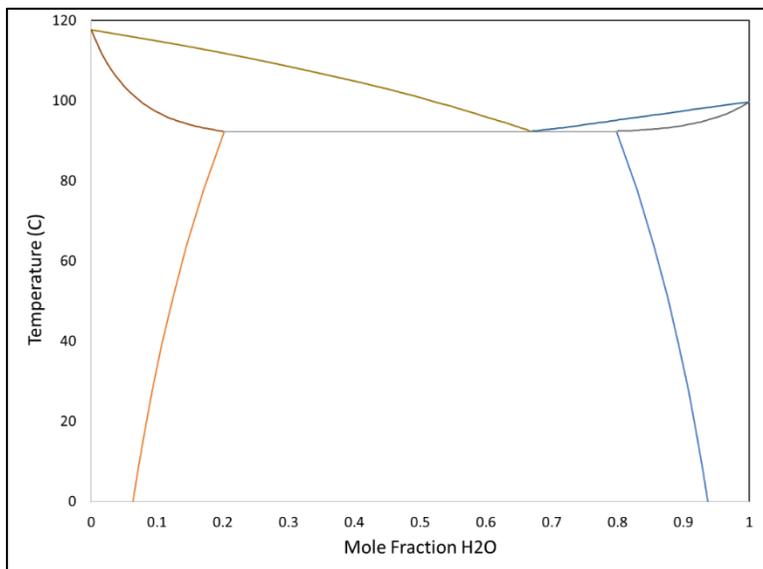


Figure 2. Water - Isobutanol equilibrium data for P = 1 bar.

Note that increasing pressure increases the temperatures at which vapor-liquid equilibrium occurs but has negligible impact on the liquid-liquid equilibrium. At lower pressures the vapor-liquid equilibrium may interrupt the liquid-liquid equilibrium. This phenomenon may be used for overcoming an azeotrope that would otherwise require a pressure swing or entrainer based separation processes.

Understanding the Process:

An example of a separation for the water-isobutanol system has been presented in figure 3.

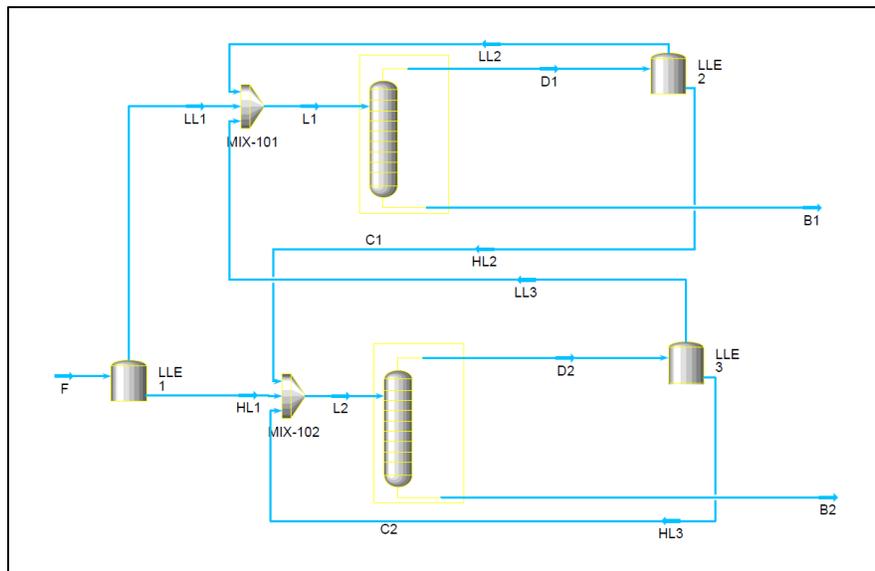


Figure 3. Water – Isobutanol separation process.

The purpose of this process is to utilize the existence of a liquid-liquid separation to assist in separating a binary system with an azeotrope. Liquid-liquid separation and distillation are necessary for this process. The attached VLE/LLE diagram shows the equilibrium separations that can be achieved by the various processes. The concentrations of effluent streams B_1 and B_2 will likely be pure ($x_{B1} \approx 0.0001$, $x_{B2} \approx 0.999$). There will be no wasted or lost product in the process. The process will be analyzed at a feed specification of $x_F = 0.5$ and $F = 100$ mol/h, although any flow rate and concentration can be used in the system. It should also be noted that any feed flow rate may be known after the calculations are made for $x_F = 0.5$ because it is an extensive property of the system. 100 mol/h was simply chosen as a standard basis for the calculations.

Figure 3 should be referenced to understand the separation setup. First, the liquid is separated at 90°C and then the light liquid from LLE1 (LL_1) and the heavy liquid from LLE1 (HL_1) are sent to columns 1 and 2 respectively. The concentrations of the column effluent must be calculated using McCabe Thiele or a linear approximation. Bottoms from both columns are taken as the product. The distillate from C1 and C2 are sent to LLE2 and LLE3 respectively. Following the liquid-liquid separation, LL_2 and LL_3 are sent back to C1 and HL_2 and HL_3 are sent back to C2.

Initial Analysis:

For the given process, there are 13 material streams, 2 distillation columns, 3 liquid-liquid extractors, 8 mass balances, 8 species balances, 5 states of equilibrium, and 2 operating equations. There are 28 unknowns, 2 unknowns for each material stream, except the feed which has been set, and the pressure of the system. The pressure of the process is set at 1 atm absolute pressure and the temperature of the LLE must be set to find the component splits. Two good options for setting of the LLE operating temperature are room temperature giving $X_I = 0.1$ and $X_{II} = 0.9$ and the bubble point giving $X_I = 0.2$ and

$x_{ii} = 0.8$. It should be noted that for LLE this system is symmetric. Once the pressure and temperatures have been set the number of unknowns drops to 24. The number of equations and variables that can be found is 28. 16 of the equations are from material balances, 2 from operating equations, and 10 variables are set when equilibrium concentrations are determined. This causes the system to be over specified by 4. This will result in the ability to solve the system and be able to check that it satisfies all equations.

Solving Approach:

Once the problem is well understood on the surface, the general equations should be presented.

The first set of equations are the mass balances, these will be broken down in overall mass balances and one species balance. Note that $x_1 = 1 - x_2$ as an implied equation.

<u>Overall Balances:</u>		<u>Species Balances:</u>	
1. $F = LL_1 + HL_1$	(LLE1 Balance)	9. $F \cdot x_F = LL_1 \cdot x_{LL1} + HL_1 \cdot x_{HL1}$	(LLE1 Balance)
2. $D_1 = LL_2 + HL_2$	(LLE2 Balance)	10. $D_1 \cdot x_{D1} = LL_2 \cdot x_{LL2} + HL_2 \cdot x_{HL2}$	(LLE2 Balance)
3. $D_2 = LL_3 + HL_3$	(LLE3 Balance)	11. $D_2 \cdot x_{D2} = LL_3 \cdot x_{LL3} + HL_3 \cdot x_{HL3}$	(LLE3 Balance)
4. $F = B_1 + B_2$	(System Balance)	12. $F \cdot x_F = B_1 \cdot x_{B1} + B_2 \cdot x_{B2}$	(System Balance)
5. $L_1 = LL_1 + LL_2 + LL_3$	(C1 Feed Balance)	13. $L_1 \cdot x_{L1} = LL_1 \cdot x_{LL1} + LL_2 \cdot x_{LL2} + LL_3 \cdot x_{LL3}$	(C1 Feed Balance)
6. $L_2 = HL_1 + HL_2 + HL_3$	(C2 Feed Balance)	14. $L_2 \cdot x_{L2} = HL_1 \cdot x_{HL1} + HL_2 \cdot x_{HL2} + HL_3 \cdot x_{HL3}$	(C2 Feed Balance)
7. $L_1 = D_1 + B_1$	(C1 Balance)	15. $L_1 \cdot x_{L1} = D_1 \cdot x_{D1} + B_1 \cdot x_{B1}$	(C1 Balance)
8. $L_2 = D_2 + B_2$	(C2 Balance)	16. $L_2 \cdot x_{L2} = D_2 \cdot x_{D2} + B_2 \cdot x_{B2}$	(C2 Balance)

It is recommended that all Liquid-Liquid separations be carried out at the same temperature to simplify the calculations. A temperature just below the bubble temperature (92 °C) has been chosen for this analysis. Given this set of equations, the PFD, and the equilibrium data, it is possible to solve the problem.

Step 1:

Solve equations 1 and 9 at the bubble point. Using the equilibrium data from figure 1, and that $F = 100$ mol/h and $x_F = 0.5$:

The equilibrium data gives us $x_{LL1} = 0.2$ and $x_{HL1} = 0.8$.

Solving equations 1 and 9 for LL_1 and HL_1 gives us that $LL_1 = 50$ mol/h and $HL_1 = 50$ mol/h. Note that the lever rule will yield the same result, $(0.5 - 0.8)/(0.8 - 0.2) = 0.3/0.6 = 0.5 \rightarrow 0.5 \cdot 100$ mol/h = 50 mol/h.

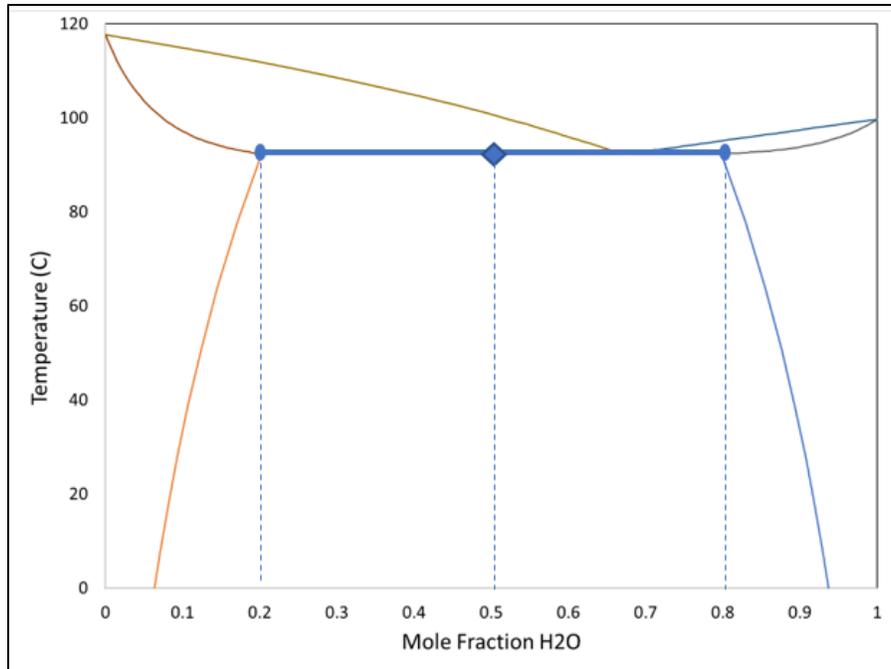


Figure 4. LLE₁ equilibrium balance.

Steps 2-5 Overview:

Steps 2-5 will differ based on the method that is selected to solve the system.

The first method requires solving equations 5 and 13, however, since LL_2 and LL_3 are both unknown quantities, they must be guessed and through the process of trial and error the actual values can be found that result in little variation in the final answer.

The second method for solving the problem would be to solve the system balances (equations 4 & 12) first, given the design parameters, and work back to find the feed concentration for the two columns.

For this paper, both methods will be described and compared.

Method 1:

Step 2:

This method will require multiple iterative steps to arrive at the final solution. The first of these steps will be to assume no recycle coming into the system initially, until those values are calculated. That is, for equations 5 and 13, LL_2 and LL_3 are zero, likewise for equations 6 and 14 HL_2 and HL_3 are zero.

Therefore:

$$L_1 = LL_1 \rightarrow \underline{L_1 = 50 \text{ mol/h}}, L_2 = HL_1 \rightarrow \underline{L_2 = 50 \text{ mol/h}}$$

Step 3:

The next step is to determine the outlet concentrations of the two columns. This may be done using McCabe Thiele analysis based on a given boil-up rate. The operating lines have been set as $L_1/V_1 = 1.667$ and $L_2/V_2 = 1.11$. Given these operating lines, the vapor-liquid equilibrium, and stream flow rates and compositions the flow rate and composition may be obtained.

A McCabe Thiele analysis can be approximated for systems that are either low concentrations or can be reasonably approximated using a linear vapor-liquid equilibrium line. For such a case, the equation to do so is presented below.

$$x_n = \left\{ \left(\frac{m * V}{L} \right)^n + \left(\left(\frac{m * V}{L} \right)^{n-1} + \dots + 1 \right) \left(1 + \frac{V}{L} \right) \right\} * x_B$$

The following equation is used to determine the geometric series where $a = m * V / L$.

$$1 + a + a^2 + a^3 + \dots + a^{n-1} = \frac{a^n - 1}{a - 1}$$

This results in the following equation.

$$x_n = \left\{ \left(\frac{m * V}{L} \right)^n + \left(\frac{\left(\frac{m * V}{L} \right)^n - 1}{\left(\frac{m * V}{L} \right) - 1} \right) \left(1 + \frac{V}{L} \right) \right\} * x_B$$

Where m is the slope of a line that is used to approximate the equilibrium curve, V is the vapor flow rate, L is the liquid flow rate, n is the stage of interest, and x_B is the bottoms concentration.

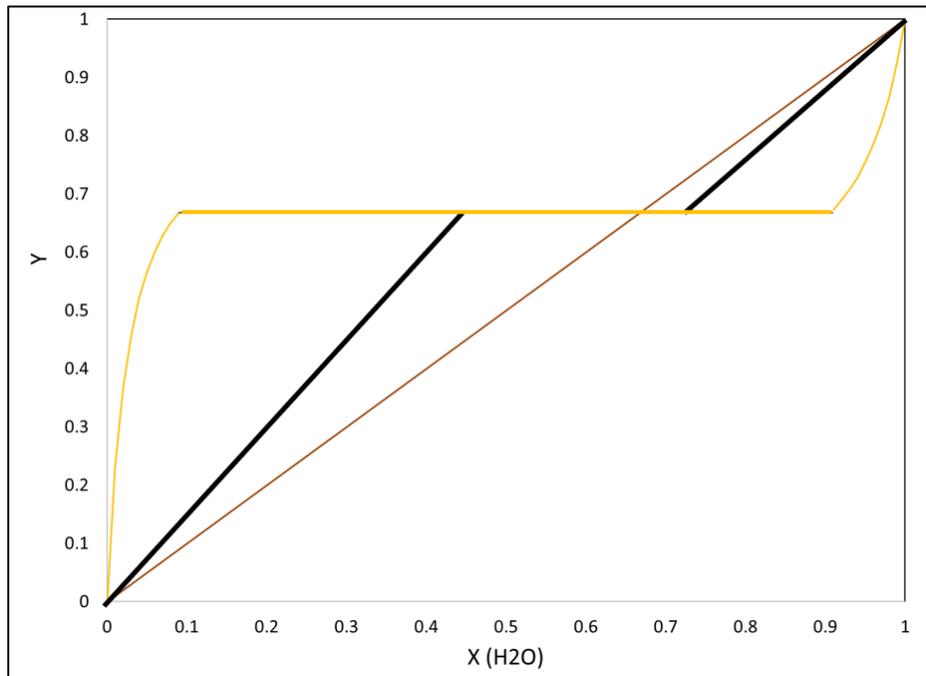


Figure 5. X-Y diagram for Water – Isobutanol system.

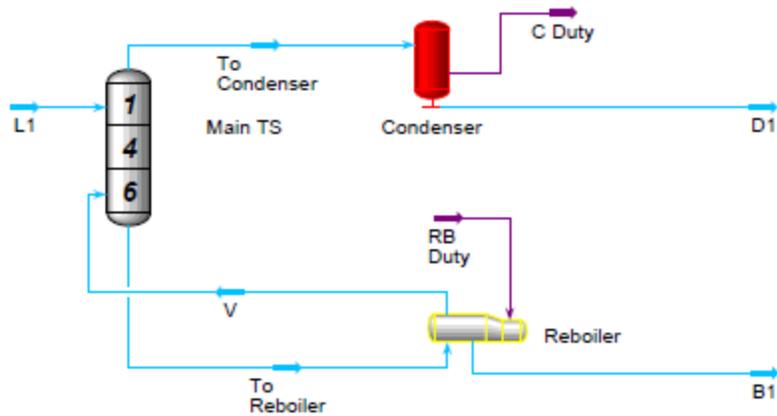


Figure 6. Distillation column 1.

Equations 7 and 15 were used for column 1 (C1) and 8 and 16 for column 2 (C2). The set L/V was also used to determine the outlet stream. Note that V and D are the same.

$$7. L_1 = D_1 + B_1 \quad (\text{C1 Mass Balance})$$

$$15. L_1 \cdot x_{L1} = D_1 \cdot x_{D1} + B_1 \cdot x_{B1} \quad (\text{C1 Species Balance})$$

$$L_1/V_1 = 1.667 \quad (\text{C1 Reflux Ratio})$$

$$8. L_2 = D_2 + B_2 \quad (\text{C2 Mass Balance})$$

$$16. L_2 \cdot x_{L2} = D_2 \cdot x_{D2} + B_2 \cdot x_{B2} \quad (\text{C2 Species Balance})$$

$$L_2/V_2 = 1.11 \quad (\text{C2 Reflux Ratio})$$

The balance yields the flow rates and concentrations of the distillate and bottoms for each column.

$$L_1 = 50 \text{ mol/h} \ \& \ L_1/V_1 = 1.667 \ \rightarrow \ \underline{V_1 = 30 \text{ mol}}$$

$$L_1 = D_1 + B_1 = V_1 + B_1 \ \rightarrow \ B_1 = L_1 - V_1 = (50 \text{ mol/h}) - (30 \text{ mol/h}) \ \rightarrow \ \underline{B_1 = 20 \text{ mol/h}}$$

These values can now be used to solve equation 15.

Staging trial and error will yield negligible amounts of water in the bottoms for the first column meaning that this assumption can be used to calculate the composition of the distillate.

$$L_1 \cdot x_{L1} = D_1 \cdot x_{D1} + B_1 \cdot x_{B1} \ \rightarrow \ (50 \text{ mol/h}) \cdot (0.2) = (30 \text{ mol/h}) \cdot x_{D1} + (20 \text{ mol/h}) \cdot (\sim 0) \ \rightarrow$$

$$x_{D1} = (50 \text{ mol/h}) \cdot (0.2) / (30 \text{ mol/h}) \ \rightarrow \ \underline{x_{D1} = 0.33}$$

The linear approximation equation can be used to determine the precise concentration of x_B .

$$\text{For 6 stages, } L/V = 1.667, \text{ and } m = 6, \ \underline{x_{B1} = 5.9 \cdot 10^{-6}}$$

For the precision necessary for these calculations, $x_{B1} = 5.9 \cdot 10^{-6}$ is equal to 0, as originally estimated.

This process is the same for determining the outlet stream for the second column.

$$L_2 = 50 \text{ mol/h} \ \& \ 2_1/2_1 = 1.11 \ \rightarrow \underline{V_2 = 45 \text{ mol}}$$

$$L_2 = D_2 + B_2 = V_2 + B_2 \ \rightarrow \ B_2 = L_2 - V_2 = (50 \text{ mol/h}) - (45 \text{ mol/h}) \ \rightarrow \underline{B_2 = 5 \text{ mol/h}}$$

This information can now be used to solve equation 15.

Staging trial and error will yield negligible amounts of isopropanol in the bottoms for the second column. As in column 1, this fact is used to find x_{D2} .

$$L_2 * x_{L2} = D_2 * x_{D2} + B_2 * x_{B2} \ \rightarrow \ (50 \text{ mol/h}) * (0.8) = (45 \text{ mol/h}) * x_{D1} + (5 \text{ mol/h}) * (\sim 1) \ \rightarrow$$

$$x_{D1} = [(50 \text{ mol/h}) * (0.8) - (5 \text{ mol/h})] / (45 \text{ mol/h}) \ \rightarrow \underline{x_{D2} = 0.78}$$

A check of the approximation that $x_{B2} = 1$ requires solving the linear approximation for $n = 6$, $L/V = 1.111$, and $m = 3$ yields $x_{B2} = 0.99982$. Rounding to 2 sig figs results in $\underline{x_{B2} = 1.0}$

Step 4:

Once that the first iteration of the distillation columns was done, a balance may be conducted of the liquid-liquid extraction to determine the feed flow rates for the subsequent iteration of the distillation columns.

For LLE2 and LLE3 the governing equations are presented below.

$$2. \ D_1 = LL_2 + HL_2 \quad (\text{LLE2 Mass Balance})$$

$$10. \ D_1 * x_{D1} = LL_2 * x_{LL2} + HL_2 * x_{HL2} \quad (\text{LLE2 Species Balance})$$

$$3. \ D_2 = LL_3 + HL_3 \quad (\text{LLE3 Mass Balance})$$

$$11. \ D_2 * x_{D2} = LL_3 * x_{LL3} + HL_3 * x_{HL3} \quad (\text{LLE3 Species Balance})$$

Solving 2 and 10 simultaneously yields

$$30 = LL_2 + HL_2 \ \rightarrow \ LL_2 = 30 - HL_2 \ \text{plugging this into eq. 10}$$

$$30 * (0.333) = (30 - HL_2) * (0.2) + HL_2 * (0.8)$$

$$\text{This equation simplifies to } HL_2 = 30 * (0.333 - 0.2) / (0.8 - 0.2) \ \rightarrow \underline{HL_2 = 6.67 \text{ mol/h}}$$

$$\text{And } LL_2 = 30 - 6.67 \ \rightarrow \underline{LL_2 = 23.3 \text{ mol/h}}$$

The same process is used for equations 3 and 11 yielding $\underline{HL_3 = 43.3 \text{ mol/h}}$ and $\underline{LL_3 = 1.67 \text{ mol/h}}$

The equilibrium balances for LLE2 and LLE3 are presented below in figures 7 and 8 respectively.

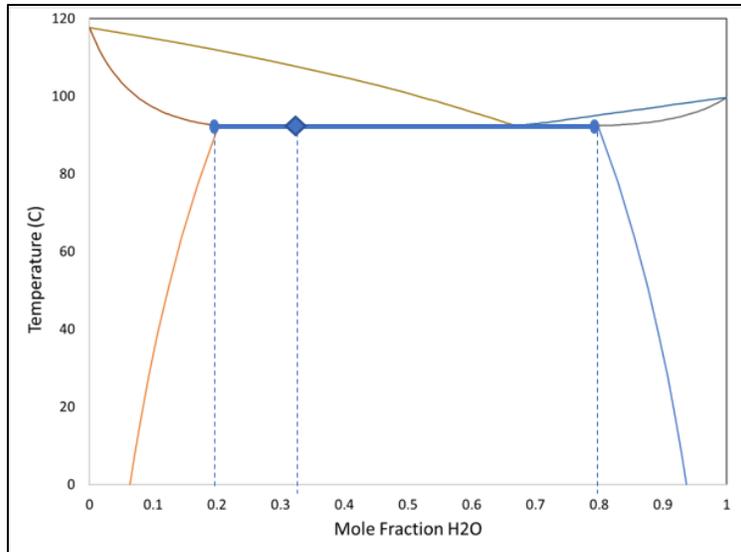


Figure 7. LLE₂ equilibrium balance.

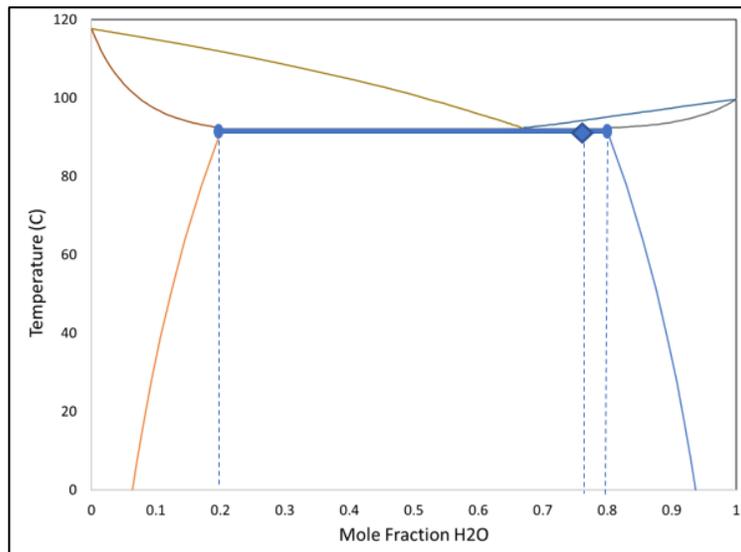


Figure 8. LLE₃ equilibrium balance.

Step 5:

Equations 5, 13, 6 and 14 may now be solved to determine the new feed flow rates to the two distillation columns.

5. $L_1 = LL_1 + LL_2 + LL_3$ (C1 Feed Balance)

13. $L_1 \cdot x_{L1} = LL_1 \cdot x_{LL1} + LL_2 \cdot x_{LL2} + LL_3 \cdot x_{LL3}$ (C1 Feed Balance)

6. $L_2 = HL_1 + HL_2 + HL_3$ (C2 Feed Balance)

14. $L_2 \cdot x_{L2} = HL_1 \cdot x_{HL1} + HL_2 \cdot x_{HL2} + HL_3 \cdot x_{HL3}$ (C2 Feed Balance)

The decision to run the LLE at the same temperature simplifies the equations and allows flow rates and concentrations to be obtained quickly.

$$L_1 = 50 \text{ mol/h} + 23.3 \text{ mol/h} + 1.67 \text{ mol/h} \rightarrow \underline{L_1 = 75 \text{ mol/h}}$$

$$x_{L1} = (LL_1 * x_{LL1} + LL_2 * x_{LL2} + LL_3 * x_{LL3}) / L_1 = (50 \text{ mol/h} * (0.2) + 23.3 \text{ mol/h} * (0.2) + 1.67 \text{ mol/h} * (0.2)) / 75 \text{ mol/h}$$

$$\underline{x_{L1} = 0.2}$$

The same process is done for equations 6 and 14 yielding $\underline{L_2 = 100 \text{ mol/h}}$, $\underline{x_{L2} = 0.8}$

These flow rates are significantly different from the previous feed rate which shows that further iteration is necessary.

32 iterations yield feed flow rate differences of less than 1 mol/h.

50 iterations yield feed flow rate differences of less than 0.1 mol/h.

The results after 50 iterations are summarized in table 1 below.

	C1	C2
L	125	500
V	75	450
B	50	50
L/V	1.67	1.11
x_D	0.334	0.778
x_B	0	1
HL	16.7	433.5
LL	58.3	16.7

Table 1. Method 1 distillation stream flow rates, operating conditions and compositions.

Method 2:

Step 2:

As previously described, the first equations that must be solved are equations 4 and 12. This will yield an understanding of an expected final solution that will be confirmed in later calculations.

Equation 4:

$$F = B_1 + B_2 \rightarrow 100 \text{ mol/h} = B_1 + B_2$$

Equation 12:

$$F * x_F = B_1 * x_{B1} + B_2 * x_{B2} \rightarrow 100 * (0.5) = B_1 * (0.0001) + B_2 * (0.999)$$

Solving these two equations and two unknowns yields $B_1 = 50 \text{ mol/h}$ and $B_2 = 50 \text{ mol/h}$.

Step 3:

Given the flow rates and concentrations in the bottoms products and being able to set a reflux ratio for both columns, the feed flow rate and distillate flow rates can be solved. Figure 5 and equations 2, 3, 10, and 11 can be used to determine the outlet concentration and flow rate of the distillate. The operating lines have been set as $L_1/V_1 = 1.667$ and $L_2/V_2 = 1.11$. Staging for both columns yields the desired concentrations in 6 stages plus RB. Both columns have been designed with 6 stages which will be sufficient in obtaining pure bottoms product streams.

To find the feed and distillate flow rates, the first assumption is that all feed concentrations to C1 and C2 are $x_{L1} = 0.2$ and $x_{L2} = 0.8$. This is a valid assumption if all liquid separations are carried out at atmospheric pressure and just below saturated liquid temperatures (from equations 13 and 14).

Mass and species balances must be done on the distillation columns to solve for the unknowns.

Equations for the columns are as follows:

$$L_1/V_1 = 1.667$$

$$L_1 = V_1 + B_1$$

$$L_1 * x_{L1} = D_1 * x_{D1} + B_1 * x_{B1}$$

Solving equations 7 and 15 via the predictive method yields:

$$1.667 * V_1 = B_1 + V_1 \rightarrow V_1 = (50 \text{ mol/h}) / 0.667 = 75 \text{ mol/h meaning } \underline{D_1 = 75 \text{ mol/h}} \text{ and } \underline{L_1 = 125 \text{ mol/h}}$$

This yields $\underline{x_{D1} = 0.333}$ and $\underline{x_{B1} = 5.9 * 10^{-6}}$ thus confirming the assumptions made to solve the equations.

Similarly, solving equations 19, 20, 23, 24 with $L_2/V_2 = 1.11$

$$1.11 * V_1 = B_1 + V_1 \rightarrow V_1 = (50 \text{ mol/h}) / 0.11 = 450 \text{ mol/h meaning } \underline{D_1 = 450 \text{ mol/h}} \text{ and } \underline{L_1 = 500 \text{ mol/h}}$$

Similarly yielding $\underline{x_{D2} = 0.778}$ and $\underline{x_{B2} = 1.0}$.

Step 4:

Next, the equilibrium balances for LLE₂ & LLE₃ must be solved. Given that $D_1 = 125$ & $D_2 = 450$, the variables LL₂, HL₂, LL₃, and HL₃ can be solved using equilibrium balances for LLE₂ and LLE₃. The equilibrium balances are shown in figures 7 and 8 above in method 1.

Equations 2, 3, 10, and 11 are used to solve the two liquid-liquid equilibrium equations.

$$2. D_1 = LL_2 + HL_2 \quad (\text{LLE2 Balance})$$

$$10. D_1 * x_{D1} = LL_2 * x_{LL2} + HL_2 * x_{HL2} \quad (\text{LLE2 Balance})$$

$$3. D_2 = LL_3 + HL_3 \quad (\text{LLE3 Balance})$$

$$11. D_2 * x_{D2} = LL_3 * x_{LL3} + HL_3 * x_{HL3} \quad (\text{LLE3 Balance})$$

Solving 2 and 10 simultaneously yields

$125 = LL_2 + HL_2 \rightarrow LL_2 = 125 - HL_2$ plugging this into eq. 10

$$125*(0.333) = (125 - HL_2)*(0.2) + HL_2*(0.8)$$

This equation simplifies to $125*(0.333 - 0.2)/(0.8 - 0.2) = HL_2 = 16.625$ mol/h

And $LL_2 = 125 - 16.625 - 58.33$ mol/h.

The same process is used for equations 3 and 11 yielding $HL_3 = 433.35$ mol/h and $LL_3 = 17.1$ mol/h

Step 5:

The final step in the process is to check the assumptions that were made and evaluate their validity.

L_1 was found by assuming $B_1 = 50$ mol/h if the assumption is correct, then equations 5 and 6 will be balanced.

$$L_1 = LL_1 + LL_2 + LL_3$$

$$L_2 = HL_1 + HL_2 + HL_3$$

$$L_1 = 125 \text{ mol/h}, LL_1 + LL_2 + LL_3 = 50 \text{ mol/h} + 58.3 \text{ mol/h} + 17.1 \text{ mol/h} = 125.4$$

$125 \text{ mol/h} \sim 125.4 \text{ mol/h}$ therefore the first set of assumptions is valid.

$$L_2 = 500 \text{ mol/h}, HL_1 + HL_2 + HL_3 = 50 \text{ mol/h} + 16.6 \text{ mol/h} + 433.4 \text{ mol/h} = 500 \text{ mol/h}$$

$500 \text{ mol/h} = 500 \text{ mol/h}$ therefore the second set of assumptions is valid.

The results are summarized below.

	C1	C2
L	125	500
V	75	450
B	50	50
L/V	1.67	1.11
x_D	0.334	0.778
x_B	0	1
HL	16.7	433.5
LL	58.3	16.7

Table 2. Method 2 distillation stream flow rates, operating conditions and compositions.

It should be noted that both methods yield the same results as expected.