

SEPARATION OF N-HEPTANE-ETHYLBENZENE MIXTURE AT 1.0135 BAR

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EXECUTIVE SUMMARY

For n-heptane and ethylbenzene mixture, Van Laar and Wilson model were both used to fit the experimental data, where the latter model better fits them with lower root mean square error of 1.651. Wilson model was used in the distillation column analysis, which was performed through 3 methods; Mc-Cabe Thiele, DSTWU and RadFrac models. At the same feed stage of 7, RadFrac has a higher reflux ratio than DSTWU and Mc-Cabe, with greater condenser and reboiler heat duty than that of DSTWU. By comparing at least 5 R-N pairs generated from DSTWU, Radfrac always has a greater reflux ratio than that of DSTWU. Increasing number of stages, at fixed feed stage with the same molar recovery and purity, decreasing the reflux ratio, the condenser and reboiler heat duty, in which lowering the total cost of distilling this mixture.

INTRODUCTION

Distillation is a process where a mixture of two or more components is separated into its constituent components of the desired purity, by the application and removal of heat ^[1]. Consider a binary mixture of n-heptane (1) and ethylbenzene (2). At the distillate, a lower boiling point component (1) will be richer in composition than the other (2), where it will be less concentrated at the bottom of the distillation column. Distilling this mixture has its industrial applications, especially when separating aromatic hydrocarbon (2) from aliphatic compounds (1) in the petrochemical industry ^[2]. It is due to the high demand of aromatic compounds by the chemical industry, such as to produce paints and wood stains for arts and crafts finish ^[3]. Moreover, there are strict legal restrictions on the content of aromatics in gasoline, in order to ensure the safety of all consumers ^[2]. In the distillation analysis, it is desired to separate the mixture, with saturated liquid feed containing 0.55 mole fraction of component 1, x_{F1} , by recovering 95 % of it at the distillate with 0.95 composition, x_{D1} .

Out of all thermodynamic activity coefficient models, Wilson and Van Laar models were chosen to fit the given experimental data that was obtained at a fixed pressure of 1.0135 bar ^[4]. Van Laar took into account the more complicated systems with dissimilar molecules, where the activity coefficient for each species would not be mirror images of each other (unsymmetric). However, unlike Van Laar, Wilson acknowledged that the ratio of a species to the other molecules surrounding any molecule depends on the differences in sizes and energies of interaction of the molecules ^[5].

By using the model that best fit the experimental data, three different distillation column analysis were performed; McCabe-Thiele, DSTWU, and RadFrac. McCabe only considered binary mixture and neglected other thermodynamic effects ^[6]. Plus, it assumed that liquid and vapor always reached its phase equilibrium at each tray in the column ^[6]. DSTWU meanwhile, assumed that the relative volatilities of the pure component in the mixture and its molar overflow (L and D) remained constant ^[7]. For RadFrac, it considered the vapor and liquid to be in thermal equilibrium at each tray and neglected the dynamics of the condenser and reboiler in the column ^[8]. In the real world, a mixture is not always binary and it is hard to reach phase equilibrium at all trays in the column. There is also always some dynamic contribution from the condenser and reboiler which will affect the overall product compositions.

METHODS

For each activity coefficient model, to decide which binary parameters to specify for the regression on the experimental data, trial and error analysis was conducted multiple times on the parameters, by doing inferences based on the resulting standard deviation (SD) for each parameter. If the SD was too large compared to its value, it was removed from the specification and remained those who had it small, or add other parameters unspecified previously. The SD had an overall impact on the root mean square error (RMSE), which was a major factor in deciding which model best fit the data.

For Mc-Cabe analysis, the x-y plot from both models were generated. The molar ratio (1) at distillate, x_{D1} and bottom, x_{B1} were determined to be 0.95 and 0.061 respectively from mass balance. An infinite reflux ratio (R^∞) with a minimum number of stages (N_{min}) column has the rectification (C) and stripping (S) operating line overlapping the $y = x$ line. To determine N_{min} , a horizontal line from x_{D1} at $y = x$ line was drawn until it touched the equilibrium curve, continued with a vertical line until it reached back the $y = x$ line. Multiple of these steps were performed until it immediately passed through x_{B1} , where the number of ‘square hoops’ represented the number of stages. For other R values, the vertical lines of the ‘square hoops’ instead were drawn until they reached C and S lines that could be determined from Eq. 1 and 2, which no longer overlapped the $y = x$ line, before and after x_{F1} of 0.55, respectively. The feed stage was determined from the location of ‘square hoops’ where it started to change from the C to S line. For a saturated liquid feed, a vertical line (q line) was drawn from the feed line after passing through the $y = x$ line, as a divider for other C and S lines ^[10]. A pinch point at the equilibrium curve, from the intersection of S, C, and q line was identified for N^∞ condition, by interpolating the C-line’s intercept and equating it to the intercept equation in Eq. 1 to find R_{min} . For this particular analysis, R was chosen to be $1.2R_{min}$.

$$^{[5]} \text{ C line : } y_{i+1} = \frac{x_D}{1+R} + \frac{R}{1+R}x_i, \text{ intercept} = \frac{x_D}{1+R}, \text{ slope} = \frac{R}{1+R} \quad (\text{Eq. 1})$$

$$^{[5]} \text{ S line : } y_I = \frac{R + \frac{E}{D}}{1+R}x_{I+1} - \frac{\frac{E}{D} - 1}{1+R}x_B, \text{ intercept} = -\frac{\frac{E}{D} - 1}{1+R}x_B, \text{ slope} = \frac{R + \frac{E}{D}}{1+R} \quad (\text{Eq. 2})$$

DSTWU analysis was performed in ASPEN, by setting up the simulation with the same constraints as mentioned previously in Mc-Cabe. The R and N values from DSTWU were then used as initial guesses for RadFrac analysis. The desired recovery and purity were set up and the reflux ratio was varied within a specified interval (at least $-2R_{guess} \leq R \leq 2R_{guess}$) to generate a new reflux ratio with a fixed feed stage value and number of stages as that of DSTWU.

RESULTS AND DISCUSSION

^[11] **Wilson model:**

$$\ln \gamma_i = 1 - \ln \left(\sum_j^c A_{ij} x_j \right) - \sum_j^c \frac{A_{ji} x_j}{\sum_k^c A_{jk} x_k}$$

$$\ln A_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij} T + \frac{e_{ij}}{T^2}$$

$a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij}$ are unsymmetrical

$$b_{ij/ji} = d_{ij/ji} = e_{ij/ji} = 0, a_{12} = -0.467 \pm 7.808, a_{21} = 2.729 \pm 2.908$$

$$c_{12} = -0.00093 \pm 1.30112 K, c_{21} = 0.0025 \pm 0.4868 K, \text{RMSE} = 1.651$$

^[11] **Van Laar model:**

$$\ln \gamma_i = A_i (1 - z_i)^2 \left[1 + C_i z_i \left(z_i - \frac{2}{3} \right) + 2z_i \left(\frac{A_i B_i}{|A_i B_i|} - 1 \right) \right]$$

$$z_i = \frac{|A_i| x_i}{|A_i| x_i + |B_i| (1 - x_i)}$$

$$A_i = \frac{\sum_j^c x_j A_{ij}}{(1 - x_i)}, B_i = \frac{\sum_j^c x_j A_{ji}}{(1 - x_i)}, C_i = \frac{\sum_j^c x_j C_{ij}}{(1 - x_i)}$$

$$A_{ij} = a_{ij} + \frac{b_{ij}}{T}, C_{ij} = c_{ij} + \frac{d_{ij}}{T}, C_{ij} = C_{ji}, A_{ii} = B_{ii} = C_{ii} = 0$$

a_{ij}, b_{ij} are unsymmetrical

$$b_{ij/ji} = d_{ij} = 0, a_{12} = -2.106 \pm 0.029, a_{21} = 8.011 \pm 0.077$$

$$c_{12} = c_{21} = 4.104 \pm 0.865, \text{RMSE} = 6.180$$

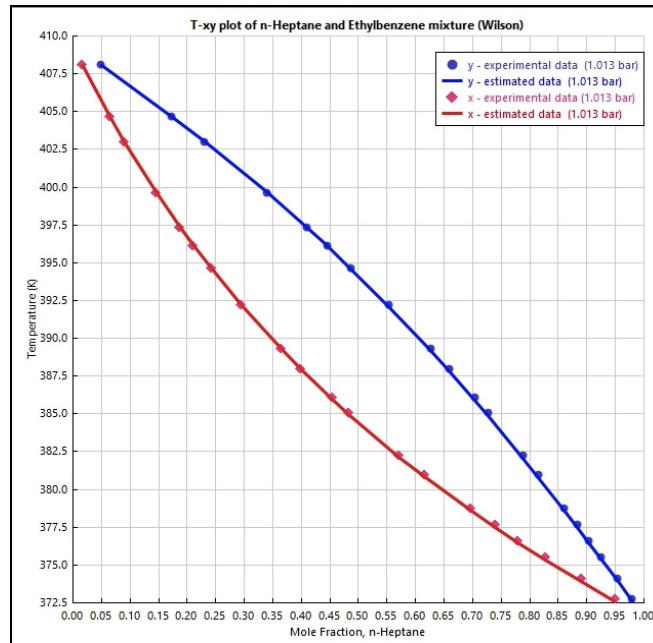


Figure 1: T-xy plot of Wilson Model at 1.0135 bar

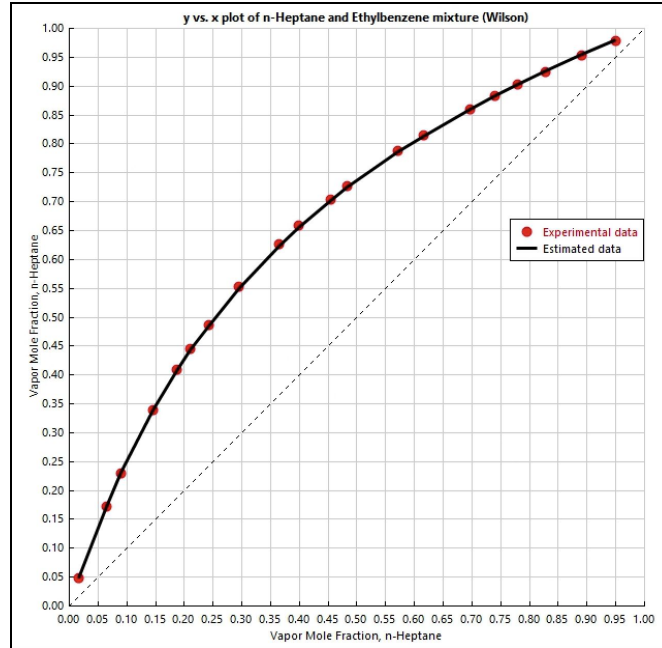


Figure 2: Equilibrium plot with Wilson Model at 1.0135 bar

From both of the regression models with the specified parameters mentioned above, the RMSE obtained was 1.651 and 6.180, for Wilson and Van Laar models respectively. RMSE value indicates how well the model fits the experimental data, where the lower the RMSE value is, the better the given model fits, as the data is closely aligned with the regression fit^[9]. It could be seen that Wilson has a lower RMSE value than Van Laar, and thus has a better fitting on the data. Figure 1 and 2 also suggest the same finding, where the fitting line from the Wilson model closely fits the experimental data.

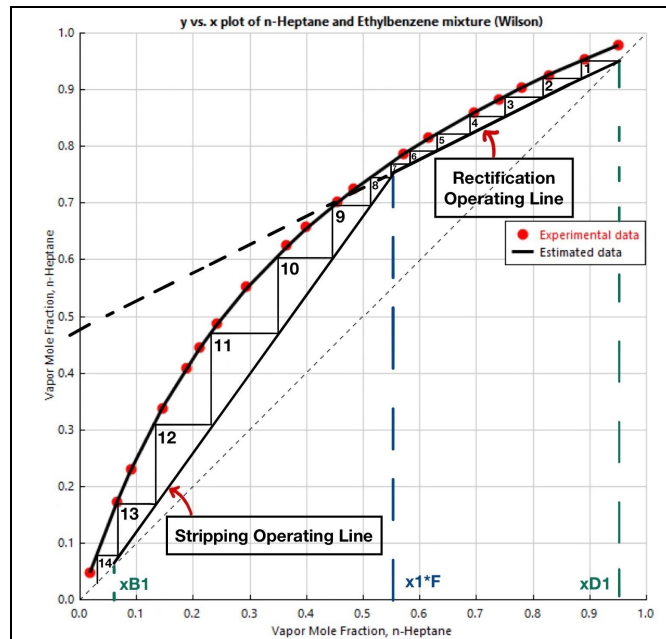


Figure 3: McCabe Thiele Analysis on The Mixture with $R = 1.2R_{\min}$

Table 1: Distillation Results of Three Distinct Column Analysis

Column Design	Number of Stages, N	Reflux Ratio, R	Feed Stage, F	x_{D1}	x_{B1}	Condenser Heat Duty ($\frac{kJ}{s}$)	Reboiler Heat Duty ($\frac{kJ}{s}$)
¹ Mc-Cabe Thiele	14	0.984	7	0.9500	0.0611		
² DSTWU	13	0.956	7	0.9501	0.0611	-9.599	9.329
RadFrac	13	1.053	7	0.9500	0.0611	-10.004	9.734

$$^1 N_{\min} = 6, R_{\min} = 0.8199, R = 1.2R_{\min}$$

$$^2 N_{\min} = 5.57, R_{\min} = 0.7970, R = 1.2R_{\min}$$

Table 1 shows the results obtained for three different distillation analysis as mentioned earlier. At the same feed stage, molar purity and recovery, it was found that the reflux ratio required for RadFrac design was greater than both DSTWU and Mc-Cabe, which are 1.053, 0.956 and 0.984 respectively. Mc-Cabe analysis was conducted graphically as shown in Figure 3. These differences are due to the assumptions made by each method. Mc-Cabe employs interpolation of data plots which creates large uncertainty in final values if poor interpolation was done. DSTWU meanwhile is just a simple distillation column, in which the data generated are frequently used as some initial values for other types of column, in this case, RadFrac design. RadFrac is suitable for a mixture that exhibits strong liquid phase nonideality ^[12]. The name itself suggests that it is a rigorous model where more energy is required to run the distillation column. By comparing the condenser and reboiler heat duty of RadFrac and DSTWU, it is always higher for RadFrac than that of DSTWU. Besides, RadFrac could handle the pumparounds that leave any stage and return to the same or different stage in its rigorous model ^[12]. It is better in dealing with solid phase mixture separation, as this might be the case for some mixture. Due to these reasons, it is more reliable to choose the RadFrac model than DSTWU and Mc-Cabe Thiele models.

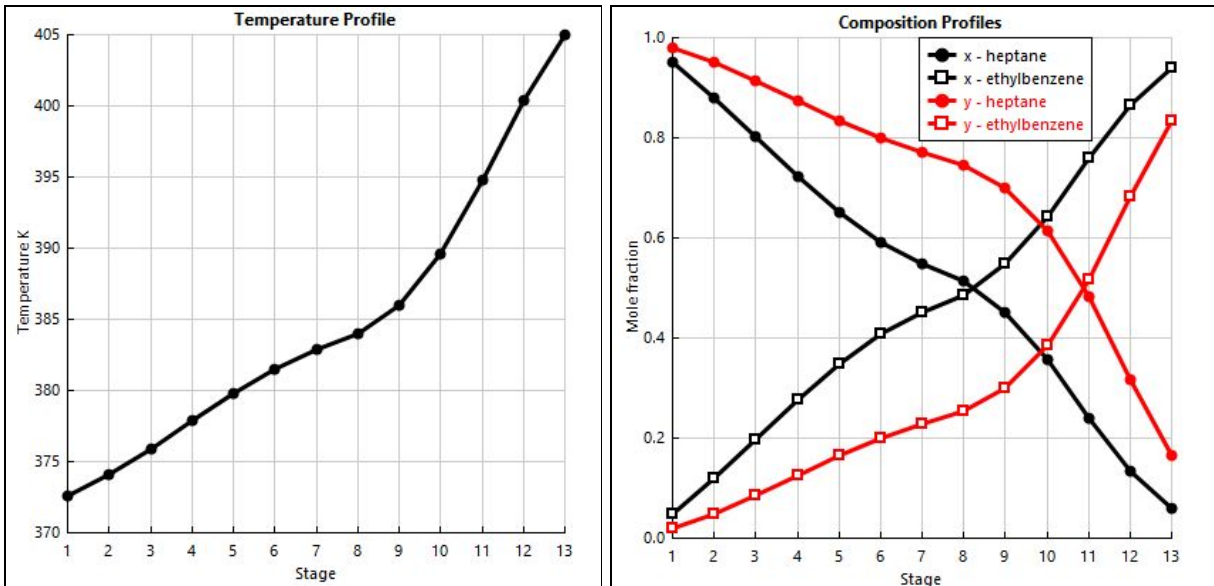


Figure 4: Temperature (left) and Composition (right) Profiles of RadFrac Design (N = 13, R = 1.053, F = 7)

Looking at the temperature profile at Figure 4, temperature increased when going down the distillation column. Since it was set at isobaric condition, the temperature was expected to vary from stages to stages. The temperature at the distillate and bottom were just above and below the n-heptane and ethylbenzene's boiling point (371.5 K and 409.3 K) ^{[3][13]} to remain as vapor and liquid respectively, which equally reflected in Figure 4 (left). Since it was desired to distillate n-heptane and remained ethylbenzene as liquid at the bottom, it is expected for n-heptane to have a higher and lower concentration in both phases at the first and last stage respectively; vice versa for ethylbenzene, which was clearly shown in Figure 4 (right).

Table 2: Comparison of Results between DSTWU and RadFrac Analysis

Number of Stages, N	Reflux Ratio, R		Feed Stage, F	* Condenser Heat Duty ($\frac{kJ}{s}$)	* Reboiler Heat Duty ($\frac{kJ}{s}$)
	DSTWU	RadFrac			
14	0.933	1.015	7	-9.819	9.549
15	0.915	0.998	7	-9.732	9.462
16	0.901	0.989	7	-9.690	9.419
17	0.891	0.985	7	-9.670	9.400
18	0.882	0.983	7	-9.659	9.389

* For RadFrac model only

From Table 2, it was observed that RadFrac always has a higher reflux ratio compared to that of DSTWU, provided everything else remains constant. This is due to the rigorous nature of the RadFrac model, where more energy and liquid/vapor content required for the distillation in order to operate as desired. Also, there's an inverse relationship between the reflux ratio and number of stages, where decreasing one of them will increase the other. From an economic perspective, cutting down the operational cost by reducing the reflux ratio will increase the capital cost, since more stages are required. However, a substantially reduced reflux ratio reduced the amount of product circulating in the column, where only a small diameter of column is needed ^[5]. Moreover, decreasing reflux ratio would decrease the condenser and reboiler heat duty at the same time, where less energy is needed to operate, which will as well decrease the operational cost. Due to this, there is only a slight increase in capital cost, and the greater decrease in operational cost causes an overall decrease in total cost.

To better illustrate the analysis with numbers, ASPEN estimates that the equipment cost would be \$76,900 and \$97,400, with operating cost of \$0.34/hr and \$0.32/hr, for RadFrac design with N = 13 and N = 18 at feed stage of 7 respectively. Although the equipment cost is greater for N = 18, one should consider the long-run cost (variable cost varied by hour), rather than one time investment of capital. In the long run, one might operate the column longer for smaller N than higher N, where the total operational cost will increase, overall increasing the total cost. As a rule of thumb, it is suggested to operate at 20 % or higher than R_{min} to optimize the equipment and operating costs ^[5].

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