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The design and optimisation of an ethanol-water pressure swing distillation train

by

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Abstract

The design and optimisation of a pressure swing distillation (PSD) train to separate a 10% ethanol-water mixture into 99% bottom products of water and ethanol is presented. The PSD was simulated on MATLAB to determine the optimal number of stages and operating reflux from the FUG method. The low-pressure column was operated at 1 bar while the high-pressure column at 5 bars. A global optimisation scheme was set on MATLAB® using the *Fmincon* function to determine the optimal distillate compositions for column 1 and column 2. The objective of the optimisation was to minimise the total number of stages in column 2. The optimal distillate compositions were obtained to be 88.87% and 87.50% ethanol in column 1 and 2, respectively. Results showed that 13 theoretical trays are required in the first column and 69 theoretical trays in the second column. The operating reflux in column 1 and 2 was obtained to be 1.68 and 2.56, respectively. The ratio of R/R_{min} was selected to 1.35 for both columns based on recommendations from the literature. The ratio of N/N_{min} was determined to be 2.17 and 1.88 for column 1 and 2, respectively.

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Introduction

Separation by distillation is by far the most adopted separation technique in chemical industries. Distillation exploits the difference in volatility of components to achieve separation, where at equilibrium, the vapour and liquid have different compositions. For (nearly) ideal binary systems, the liquid phase is rich in the heavy component (less volatile) while the vapour phase is rich in the more volatile component. However, in highly non-ideal systems such as the ethanol-water binary system, there exists an azeotropic point where the vapour and liquid at equilibrium have the same composition, making separation by conventional distillation difficult.

For systems forming azeotropes such as the ethanol-water system, pressure swing distillation (PSD) technique is usually adopted. Two columns in series operated at different pressures are used to effect separation. PSD harness the sensitivity of the azeotropic composition to pressure. Varying the pressure has the effect of shifting the azeotropic composition, and the distillation boundary is evaded by sending the azeotropic mixture from the low-pressure column to a second column operated at a higher pressure.

The current work presents the design and optimisation of a PSD set up for the separation of a 10% ethanol-water mixture fed at 100 kmol/hr; with the intent of achieving two 99% water and ethanol bottom products from column 1 and 2, respectively. The FUG ([Fenske, 1932](#), [Gilliland, 1940](#), [Underwood, 1932](#)) method will be implemented on MATLAB® to estimate the optimal reflux ratio and the total number of stages for the two columns in series. The first column is operated at 1 bar and the second column at 5 bars. The Kirkbride empirical correlation ([Kirkbride, 1944](#)) will also be adopted to estimate the optimal feed stage. Vapour-liquid-equilibrium data predicted from the NRTL + ideal gas law model on Aspen plus will be treated as experimental data and used for interpolation using a smoothing spline function.

Results and Discussions

Designing and optimising the PSD train in the present work required the selection of the distillate compositions in both columns. From a bevy of possible compositions, selecting the optimal compositions was essential to ensure minimum operating and capital costs.

As shown in Table 1, varying the distillate compositions in both columns while ensuring that ($x_{Eth_D1} > x_{Eth_D2}$) had a modest effect on the total number of stages in column 1. However, the total number of stages in column 2 changed significantly with a change in the distillate compositions. It was concluded that the total number of stages in column 1 is not a strong function of the distillate compositions (x_{Eth_D1} & x_{Eth_D2}). This conclusion corroborates well with the VLE data of the ethanol-water binary system at 1 bar, where before the azeotropic composition of 0.8955 ethanol, the system behaves (nearly) ideal with a broader phase envelope. Therefore, during optimisation for the distillate compositions, the total number of stages in column 1 was excluded as a variable in the objective (cost) function.

Obtaining the optimal number of stages and reflux ratio in column 2 was tantamount to answering the question: *For what values of the distillate compositions x_{Eth_D1} and x_{Eth_D2} will yield the smallest number of stages and reflux ratio for column 2?* A global optimisation scheme was set in MATLAB® using the *Fmincon* function where the distillate compositions for both columns were used as optimisation variables, and the minimum number of stages in column 2 as the objective (cost) function.

Table 1: Local minimums resulting from global optimisation. ' x_{Eth_Di} ' = Ethanol liquid composition in the distillate of the i^{th} column. ' N_DCi ' = total number of stages in the i^{th} column. ' R_DCi ' = reflux ratio in the i^{th} column.

Local min	x_{Eth_D1}	x_{Eth_D2}	N_DC1	R_DC1	N_DC2	R_DC2	$N_DC1 + N_DC2$	$R_DC1 + R_DC2$
1	0.8887	0.8750	13	1.68	69	2.56	84	4.23
2	0.8809	0.8635	13	1.54	77	4.42	90	5.96
3	0.8704	0.8660	15	2.53	98	0.589	113	3.12
4	0.8881	0.8480	12	1.38	80	10.28	92	11.66
5	0.8859	0.8585	13	1.42	76	6.89	89	8.31

Table 1 shows the local minimums obtained from the optimisation, together with their corresponding column specifications. The first local minimum seemed to be the global minimum as it yielded the least number of stages for both column 1 and 2 summed

together. The reflux ratio in each column was also within tolerance. Therefore, the optimal distillate compositions in column 1 and 2 were selected to be 0.8887 and 0.8750 ethanol, respectively.

Table 2 and Table 3 list the stream properties of the feed, bottoms and distillate for column 1 and 2, respectively. VLE data predicted from the NRTL + ideal gas law model in Aspen Plus (Provided in the problem statement) was utilised to construct a smoothing spline function in MATLAB curve fitting toolbox. The constructed spline function was used to interpolate between compositions and temperatures in each column.

The feed to distillation column 2 was assumed to be pressurised across a valve to 5 bars before entering column 2. For this assumption, the feed properties to column 2 were evaluated at 5 bars. Moreover, the distillate from column 2 which is recycled back to column 1 was also assumed to be depressurised from 5 to 1 bar before being mixed with the fresh feed containing 10% ethanol. In both scenarios, a throttling process was assumed, where there is no change in enthalpy and the process being adiabatic. In mixing the distillate from column 2 with the fresh feed, the heat of mixing was also assumed to be negligible. The mass balance on both units was conducted assuming steady-state conditions. Both feeds to each column were assumed to be a saturated liquid ($q = 1$).

Table 2: Specifications of column 1 operated at 1 bar

Specification	Overall feed	Feed mixture	bottom	distillate
Ethanol mole frac	0.1	0.4416	0.01	0.8887
Flowrate [kmol/hr]	100	167.91	90.82	77.01
Relative volatility (α)	-	2.21	10.98	1.01
Temperature [°C]	85.94	79.8	96.9	77.81

The close saturation temperature of the feed, bottoms and distillate stream in column 2 shows that the ethanol-water system behaves like a close boiling binary system after the azeotropic composition. Moreover, the low relative volatilities which approach unity indicates a difficulty in separation; hence the large number of stages required to effect separation in column 2, shown in Table 4.

Table 3: Specifications of column 2 operated at 5 bars

Specification	Feed	Bottom	Distillate
Ethanol mole frac	0.8887	0.99	0.8750
Flowrate [kmol/hr]	77.1	9.18	67.91
Relative volatility (α)	1.05	1.15	1.03
Temperature [°C]	124.29	125.3	124.93

The Fenske equation (1) was utilised to estimate the minimum number of stages (N_{min}) for column 1 and 2 at total reflux ([Fenske, 1932](#)).

$$N_{min} = \frac{\log \left[\left(\frac{d_i}{d_j} \right) \left(\frac{b_j}{b_i} \right) \right]}{\log(\alpha_m)} \quad (1)$$

$$\text{where } \alpha_m = [(\alpha_{ij})_T (\alpha_{ij})_F (\alpha_{ij})_B]^{1/3}$$

In distillation column 1, ethanol was selected to be the light key because it had a higher K-value compared to that of water at the feed conditions. Good approximates of the compositions of each specie were obtained from interpolation using a spline function created in MATLAB. In column 2, the Fenske equation (1) was also adopted to estimate the minimum number of stages. However, ethanol was selected to be the heavy key due to its low K-value at the feed conditions. In both columns, the number of stages obtained from the Fenske equation were rounded up, to ensure that the reported values are above the minimum stages required for separation.

The minimum reflux ratio (R_{min}) in each column was estimated from the Underwood equation ([Underwood, 1932](#)). Adopting the classification criterion by ([Shiras et al., 1950](#)), the ethanol-water binary system was classified as a class 1 pinch point system, since all the feed components distribute in the distillate and bottom products. Moreover, the point of infinitude was assumed to be at the feed stage in both columns. The assumption made about the points of infinitude was pragmatically incorrect in both columns as the binary system form an azeotrope away from the feed point.

The point of infinitudes in both columns occurs in the rectifying section. The shift in the point of infinitude in each column is a consequence of the typical azeotrope formed by the ethanol-water binary system. The incorrect assumption about the points of infinitude may affect the compositions obtained for the distillate and bottoms in each

column. Superior techniques, such as solving the MESH equations using the inside-out method, can be adapted to evade the use of the abovementioned assumption. For class 1 pinch point separation of a saturated liquid feed stream, the Underwood equation reads;

$$R_{min} = \frac{\left[\left(\frac{x_{i,D}}{x_{i,F}} \right) - (\alpha_{ij})_F \left(\frac{x_{i,D}}{x_{i,F}} \right) \right]}{(\alpha_{ij})_F - 1} \quad (2)$$

where the subscripts 'F' refers to properties at feed conditions.

As shown in eq. (2), the minimum reflux is a strong function of the distillate composition, which highlights the need for finding the optimal distillate compositions to reduce operating costs. Shown in Table 4 are the design specifications of column 1 and 2. The minimum reflux (R_{min}) was used to obtain the operating reflux (R) by weighting R_{min} by a constant factor $K_R = \frac{R}{R_{min}}$ such that: $R = K_R \times R_{min}$. The value of K_R was set to be 1.35 in both columns, which is a typical industrial value for the ethanol-water binary system ([Seader et al., 2011](#)).

The empirical Gilliland correlation was adopted to estimate the actual number of stages ([Gilliland, 1940](#)). The selected Gilliland correlation shows a strong functional dependence of the total number of stages (N) to the reflux ratio (R), signifying the dependence of capital costs on the operating costs through the reflux (R).

$$Y = \frac{N - N_{min}}{N + 1} = 1 - \exp \left[\left(\frac{1 + 54.4X}{11 + 117.2X} \right) \left(\frac{X - 1}{X^{0.5}} \right) \right] \quad (3)$$

where $X = \frac{R - R_{min}}{R + 1}$

The ideal number of stages reported by eq. (3) include the partial reboiler ([Seader et al., 2011](#)). The present work assumed a total condenser and a partial reboiler in both columns, and the number of stages obtained from eq. (3) were corrected accordingly by subtracting 1 in both columns to account for the partial reboiler.

The Gilliland correlation was tailored for systems where rectification is more important than stripping, since it is based on the reflux and not the boil-up ([Seader et al., 2011](#)). In PSD, stripping is more important since (nearly) pure products are collected at the bottom rather than the distillate. Therefore, the limitation of ignoring the boil-up in the

Gilliland correlation could yield an incorrect total number of stages for both columns, which may subsequently affect the purities of the end products.

The Gilliland correlation also assumes that trays are 100% efficient—vapour and liquid leaving each tray are at equilibrium. However, work from the literature ([Drickamer and Bradford, 1943](#), [Murphree, 1925](#)) have shown through empirical data that vapour and liquid leaving a tray are not always at equilibrium. The assumption of 100% efficient trays could result in a column with fewer stages, which subsequently yield lower purities of the desired products.

The correlation in eq. (3) is also reported to be more accurate for feeds with low values of q ([Seader et al., 2011](#)). However, ([Donnell and Cooper, 1950](#)) showed that the effect of q is more significant when the relative volatility $\alpha_{LK,HK}$ at the feed deviate significantly from unity. In column 2, where the feed is near the azeotropic composition $\alpha_{LK,HK} \approx 1$, the Gilliland correlation is likely to yield a more accurate number of total stages compared to column 1, where the feed has a larger relative volatility away from unity.

The optimal feed stage location in each column was estimated with the Kirkbride correlation ([Kirkbride, 1944](#)). The Gilliland correlation assumes that stages are evenly distributed between the rectification and stripping section—an assumption valid only for highly symmetrical systems. Below is the Kirkbride empirical equation.

$$\frac{N_{rectifying}}{N_{stripping}} = \left[\left(\frac{z_{HK,F}}{z_{LK,F}} \right) \left(\frac{x_{LK,B}}{z_{HK,D}} \right)^2 \left(\frac{B}{D} \right) \right]^{0.206} \quad (4)$$

Table 4: Design specifications of column 1 and 2

Specification	Distillation column 1	Distillation column 2
Minimum reflux ratio (R_{min})	1.24	1.91
Operating reflux (R)	1.68	2.56
Minimum stages (N_{min})	6	33
Total number of stages (N)	13	69
Feed stage location	9	59
R/R_{min} ratio	1.35	1.35
N/N_{min} ratio	2.17	1.88
Reboiler duty (kJ/hr)	6699	17164
Operating pressure (bars)	1	5

Reboiler and condenser duties were calculated from eq. (5), assuming that both columns satisfy the McCabe-Thiele assumptions such as constant molar overflow (CMO) and negligible heat loss to the surroundings.

$$Q_R = Q_C = D(R + 1)\Delta H^{vap} \quad (5)$$

The choice of the operating pressure for column 1 and 2 have a significant effect on the economics of PSD and the purity of products obtained. A recommended design heuristic from the literature is that the change in the azeotropic composition should be greater than 5% when the pressure is altered¹. Data obtained from Aspen Plus (provided in the problem statement) showed that at 1 bar, the azeotrope is at 0.8955 ethanol and 0.8464 ethanol at 5 bars. The change in composition with pressure is 4.91%, which is less than 5%. A percentage difference less than 5% signifies that the combination of operating pressures used in this work is suboptimal. Operating column 2 at a slightly higher pressure of 7 bars or greater and fixing column 1 at 1 bar can achieve a percentage difference greater than 5, thus making the process optimal and less costly.

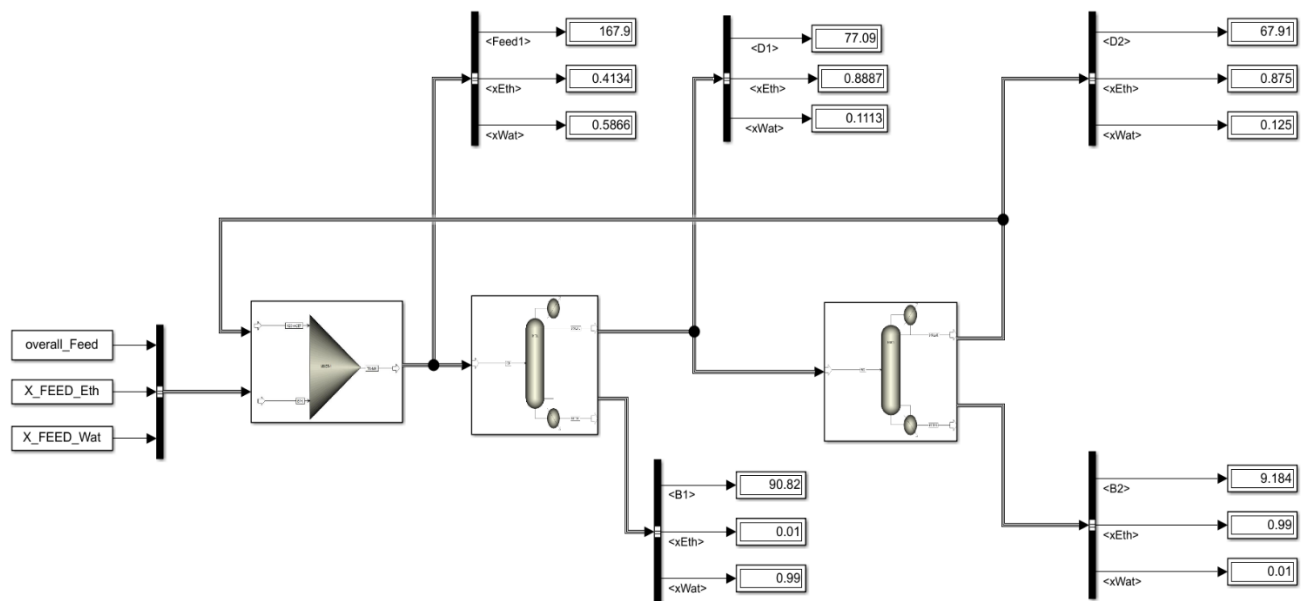


Fig. 1: A Simulink simulation depicting stream properties

¹ WAYNE, N. 2020. University of KwaZulu-Natal Moodle. Available: https://moodle.ukzn.ac.za/pluginfile.php/645520/mod_resource/content/1/ED%20V1.0.pdf [Accessed 08 02]

Other enhanced distillation techniques

Other separation techniques such as extractive distillation have been studied to separate the ethanol-water binary system. Extractive distillation uses an entrainer or solvent to alter the relative volatilities of components, thus removing the separation boundary. Benzene or cyclohexane are reported to be effective entrainers for the ethanol-water binary system ([Lee et al., 2011](#)). The use of entrainers such as benzene which is notorious for being carcinogenic and flammable increases the cost of maintaining safety in the workplace.

From an environmental point of view, the use of hydrocarbons is not environmentally benign since they cannot be easily disposed after their life span. Even though nearly pure components can be obtained from using extractive distillation, such technique poses a hazard in the workplace and not eco-friendly. A comparative study on PSD and extractive distillation showed that PSD is superior both from an economic and product purity perspective ([Wang et al., 2015](#)).

([Lee et al., 2011](#)) averred that below the pressure of 11.5 kPa, the azeotrope of the ethanol-water system disappears, and conventional distillation can be adopted to effect separation. However, operating at low pressures calls for vacuum distillation, which requires larger column diameters due to reduced vapour densities ([Lee et al., 2011](#)). Lower vapour densities translate to high vapour velocities inside the column resulting in entrainment between stages. Larger column diameters will mean higher capital costs.

Furthermore, a refrigerant is required as a coolant in the condenser due to lower temperatures of the vapour leaving the top stage. The use of refrigerants certainly increases the operating costs of the process and subsequently, the overall total cost (TAC). Therefore, from grounds of higher TAC, vacuum distillation is not considered an optimal technique for separating the ethanol-water binary system.

A less energy-intensive and eco-friendly separation technique is the use of membrane technology. Distillation coupled with membrane separation (Distillation + pervaporation) is typically adopted, with pervaporation treated as a polishing step to separate the azeotropic mixture emanating as the distillate. Ethanol rich mixture is usually collected as the retentate while water can pass through the membrane and collected as the permeate. Even though such technique is less energy-intensive, the

throughput is significantly lower (low recovery) compared to other methods reviewed above. Such a technique is, therefore, not suitable where the consumer demand for ethanol is very high.

Conclusions

Optimisation results showed that the number of stages of the first column is a weak function of the distillate compositions ($x_{\text{Eth_D1}}$, $x_{\text{Eth_D2}}$), and cannot be used as part of the variables making up the objective function. However, the number of stages in column 2 showed a strong functional dependence on both distillate compositions, and it was used as the objective function during optimisation.

The total number of theoretical stages in column 2 was significantly higher than that of column 1 due to the binary mixture behaving as a close boiling point system after the azeotropic composition. A salient observation in column 2 was that the relative volatility did not vary significantly and was closer to unity, which translated to a significantly large number of stages when compared to column 1. A comparison of pressure swing distillation (PSD) with other enhanced distillation techniques showed that PSD is a pragmatically expedient technique, both economically and environmentally.

Recommendations

The minimisation of a total cost function (TAC) during global optimisation is recommended in future works. A combined property method such as NRTL + Peng Robinson could be used to estimate the VLE data for the second column as the ideal gas assumption may not be valid at the high operating pressure of 5 bars.

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Appendices

Appendix 1: Sample calculations for column 1

Overall balance & Overall ethanol balance

a = ethanol, b = water

$$F = B_1 + B_2$$

$$X_{a,F} F = X_{a,b_1} B_1 + X_{a,b_2} B_2$$

$$\Rightarrow 100 = B_1 + B_2$$

$$0.1(100) = 0.01 \times B_1 + 0.99 \times B_2$$

Solving for B_1 and B_2 we obtain, $B_1 = 90.82$ and $B_2 = 9.18$

Balance over column 2

Overall balance and ethanol balance

$$D_1 = D_2 + B_2 ;$$

$$X_{a,D_1} D_1 = X_{a,D_2} D_2 + X_{a,b_2} B_2$$

$$D_1 = D_2 + 9.18$$

$$0.8887 \times D_1 = 0.8750 \times D_2 + 0.99 \times (9.18)$$

Solving for D_1 and D_2 we obtain: $D_1 = 77.09$ and $D_2 = 67.91$

The feed to column 1 is obtained as follows: $F + D_2 = F_1$

$$F_1 = 100 + 67.91 = 167.91$$

A smoothing spline function was used to interpolate for compositions in each of the streams (D_1 , F_1 and B_1).

Table 5: Specie compositions in column obtained from a spline function

Specie	F_1	D_1	B_1
X_a	0.4134	0.8887	0.01
Y_a	0.6257	0.8895	0.0999
X_b	0.5866	0.1113	0.99
Y_a	0.3743	0.1105	0.901

Taking ethanol as the light key and calculating K-values from the equation, $K_i = \frac{y_i}{x_i}$; the following relative volatility values are obtained, where $\alpha_{i,j} = \frac{K_i}{K_j}$.

$$\alpha_{F_1} = 2.37$$

$$\alpha_{D_1} = 1.008$$

$$\alpha_{B_1} = 10.98$$

The mean relative volatility α_m is obtained as follows: $\alpha_m = [\alpha_{F_1} \alpha_{D_1} \alpha_{B_1}]^{1/3}$

$$\Rightarrow \alpha_m = [2.37 \times 1.008 \times 10.98]^{1/3} = 2.972$$

To estimate the minimum number of stages, eq. (1) is adopted

$$N_{min} = \frac{\log\left[\left(\frac{0.8887 \times D_1}{0.1113 \times D_1}\right) \left(\frac{0.99 \times B_1}{0.01 \times B_1}\right)\right]}{\log(\alpha_m)} = \frac{\log\left[\left(\frac{0.8887 \times 77.09}{0.1113 \times 77.09}\right) \left(\frac{0.99 \times 90.82}{0.01 \times 90.82}\right)\right]}{\log(2.972)} = 6.13$$

Rounding up the value of N_{min} , we obtain $N_{min} = 7$, which corresponds to 6 theoretical trays and one partial reboiler

Equation (2) can be adapted to estimate the minimum reflux ratio R_{min} .

$$R_{min} = \frac{\left[\left(\frac{0.8887}{0.4134}\right) - 2.37 \left(\frac{0.1113}{0.5866}\right)\right]}{2.37 - 1} = 1.24$$

To translate R_{min} to R , the ratio $\frac{R}{R_{min}} = 1.35$ was assumed as recommended in the literature ([Seader et al., 2011](#)). From this ratio, $R = 1.68$.

The actual number of stages were estimated from the Gilliland correlation presented in eq. (3).

$$X = \frac{R - R_{min}}{R + 1} = \frac{1.68 - 1.24}{1.68 + 1} = 0.164$$

$$\frac{N-7}{N+1} = 1 - \exp\left[\left(\frac{1+54.4 \times 0.164}{11+117.2 \times 0.164}\right) \left(\frac{0.164-1}{0.164^{0.5}}\right)\right]$$

Solving the above equation for N , we obtain $N = 13.61$. The value obtained here includes the partial reboiler. Rounding up, we obtain: $N = 14$ stages made of 13 theoretical trays and one partial reboiler.

The feed stage location can be estimated from the Kirkbride correlation shown in eq. (4).

$$\frac{N_{rectifying}}{N_{stripping}} = \left[\left(\frac{0.5866}{0.4134}\right) \left(\frac{0.01}{0.1113}\right)^2 \left(\frac{90.82}{77.09}\right)\right]^{0.206} = 0.412$$

Solving for the rectifying section stages from $\frac{N_{rectifying}}{N - N_{rectifying}} = 0.412$ we obtain the feed stage to be 9.

The same exact procedure was carried out for column 2 with the exception that ethanol becomes the heavy key and water becomes the light key.

Appendix 2

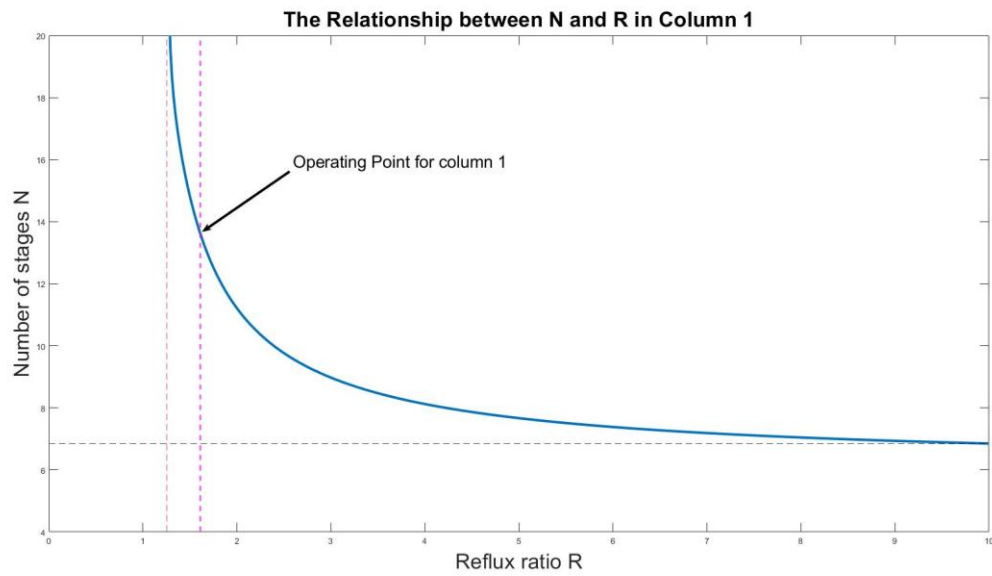


Fig. 2: Profile showing the relationship between N and R in column 1

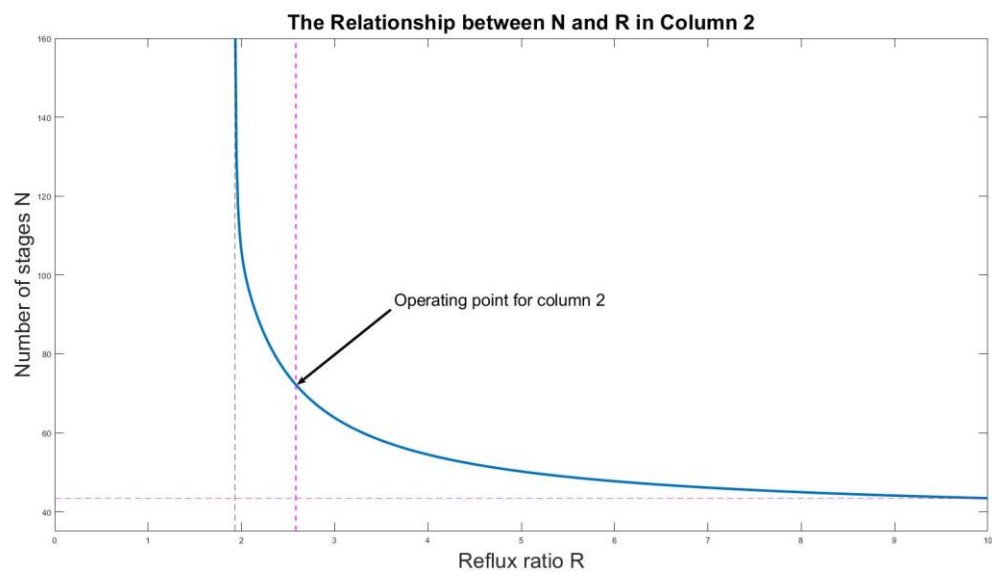


Fig. 3: Profile showing the relationship between N and R in column 2