Can the Operating Leaves of a Distillation Column Really Be Expanded?

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Residue curves and pinch point curves are used to determine the operation leaves and hence the feasible region for distillation columns operating at a specific distillate and bottoms composition for all possible constant reflux and reboil ratios. In this paper we will experimentally show that we can expand the operating leaves of the rectifying section beyond the pinch point curve by varying the reflux ratio within the distillation column, and we will also show theoretically that this method can be used to cross the simple distillation boundaries.

1. Introduction

Batch distillation is becoming more important as a result of the recent increase in the production of high-value-added, low-volume specialty chemicals and biochemicals. The flexibility in operation and the lower cost for separating relatively pure components are the advantages offered by batch distillation over continuous distillation. In many cases, the objective of the batch distillation is to recover the most volatile component of a feed mixture at a high degree of purity, leaving the relatively heavy components in the still.

The behavior of azeotropic mixtures complicates the prediction of feasible separation processes. Wahnschafft[1] showed a relatively simple analysis to determine the feasibility of separation processes, which involves residue and pinch point trajectories for the special case of separating ternary mixtures using distillation columns that produce two products. On the basis of this analysis, Castillo[2] defined the operating leaves. Operation leaves define the region enclosed by the residue curve through a product composition and the respective pinch point curve for that product. This region comprises a whole range of possible column profiles for all constant reflux ratios with respect to the product composition. In a two-product column, leaves can be generated for the bottoms and the distillate composition. A distillation column is known to be feasible if these product leaves intersect.

In this paper, we will experimentally show that we can expand the operating leaves for the rectifying section of a distillation column beyond the pinch point curve by varying the reflux ratio within the distillation column. By expanding the operation leaves we can design columns to do separations that were not previously considered possible.

2. Theoretical Background

2.1. Operating Leaf for Constant Reflux Ratio. Doherty and Perkins[3] have shown that eq 1 can be used to approximate the rectifying section of a distillation column.

$$\frac{dx}{dn} = \frac{r+1}{r}(x - y^*) + \frac{1}{r}(x_d - x) \tag{1}$$

where x_d is the distillate composition, r is the reflux ratio, and y^* the vapor composition in equilibrium with the liquid composition x.

Different reflux ratios, for a specific value of x_d, result in different column profiles, as shown in Figure 1. The outermost profile being the residue curve as the reflux ratio tends to infinity.

All column profiles shown in this paper have been generated using the NRTL model at a system pressure of 0.83 bar. In general, column profiles start at distillate composition x_d and initially run along the residue curve. They then deviate from the residue curve, depending on the reflux ratio, and end at their respective pinch point. The locus of all pinch points from a specific distillate composition is called a pinch point curve; this is shown as the dashed−dotted line in Figure 1. The region that is enclosed by the residue curve through x_d and the pinch point curve is called the operating leaf.[2] This region represents the whole range of attainable profiles for all constant reflux ratios defined by the composition x_d. A pinch point curve can be determined mathematically by finding the solutions for eq 1 that are equal to zero.

$$\frac{dx}{dn} = 0 = \underset{\text{separation}}{(x - y^*)} = \underset{\text{mixing}}{-(x_d - x)} \tag{2}$$

Setting eq 1 equal to zero gives us the above eq 2, which is the equation defining the pinch point. This equation has two vectors, namely the separation and the mixing vector. At the pinch point these two vectors are collinear, as shown in Figure 2.

From eq 2 it can be seen that the pinch point curve is only a function of the distillate composition x_d and not of the reflux ratio r. In other words, only the different compositions of x_d result in different paths of the pinch point curve. The pinch curve can also be easily constructed graphically by finding the points on the residue curves with their tangents passing through the composition x_d. This makes it a quick and easy tool to find the attainable region for a certain x_d.

2.2. Operating Leaf for Nonconstant Reflux Ratio. The reflux ratio does not necessarily need to be constant throughout the column. It can be changed by

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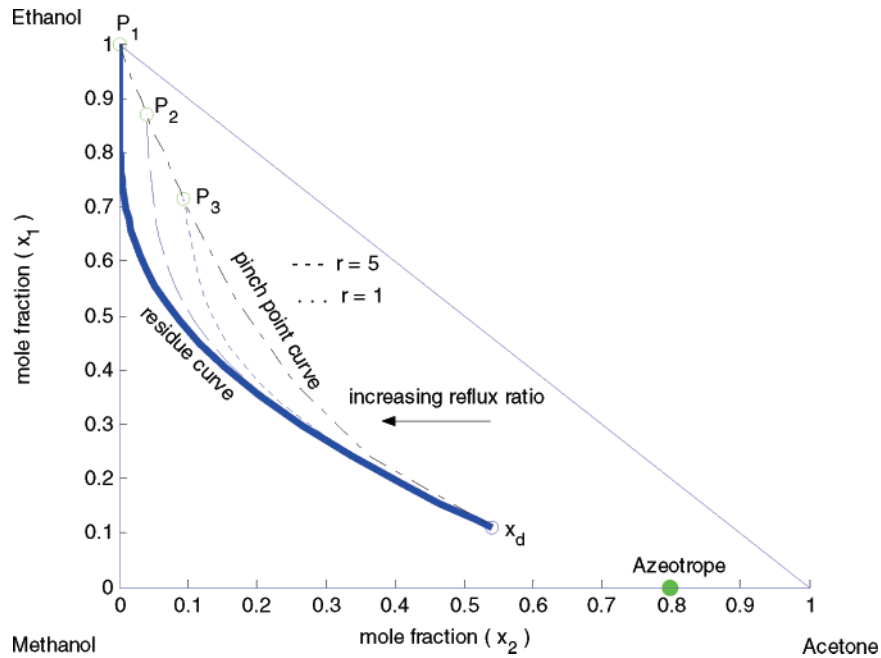
Figure 1. Column profiles for the ethanol/methanol/acetone system using eq 1 for different reflux ratios and x_d = [0.54, 0.11, 0.35] with the respective pinch point curve.
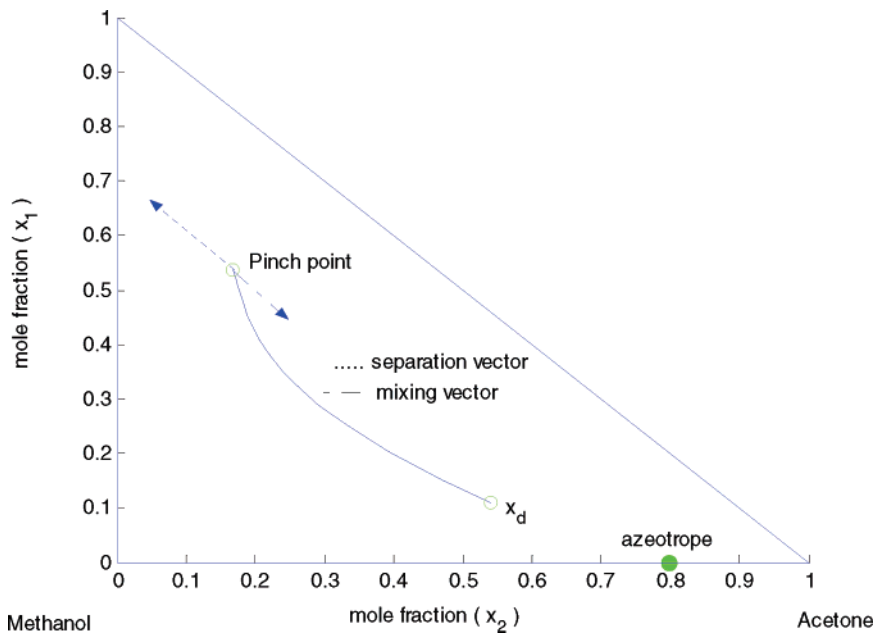

Figure 2. A column profile with its respective pinch point showing the collinearity of separation and mixing vector. x_d = [054, 0.11, 0.35].

using side condensers or reboilers or by adding or removing feed or side streams.

Increasing the reflux ratio along the column profile causes the column profile to run closer to the residue curve; this column profile pinches closer to the pinch point P_1 of the residue curve. This implies that the column profile will always be inside the operating leaf when the reflux ratio is increased along the column profile, as shown in Figure 3 (see ref 4).

Decreasing the reflux ratio along the column profile can cause the profile to turn back to its new pinch point, P_3, which is closer to x_d. The profile crosses the pinch point curve and expands the operating leaf, as illustrated in Figure 4. In other words, compositions outside the operating leaf can be achieved. This behavior can be explained by looking at the net flow within the

column. In a rectifying section $V - L = D > 0$ and all composition x_i are greater than zero. This means there is a net flow up the column. By varying the reflux ratio, all x_i are still greater than zero, but $V - L \neq D$, rather $V - L = \Delta$ (see ref 13), with Δ = net flow rate in a column section, which can be negative. A negative Δ would result in a net flow down the column; in other words, the profiles runs in the opposite direction. The greatest extension of the operating leaf can be achieved by following the residue curve until its respective pinch point and then reducing the reflux ratio to the lowest reflux ratio possible, as shown in Figure 5.

This method of expanding the operating leaf can be very useful, as it expands the region of operation in a distillation column, as well as crossing the distillation boundaries.
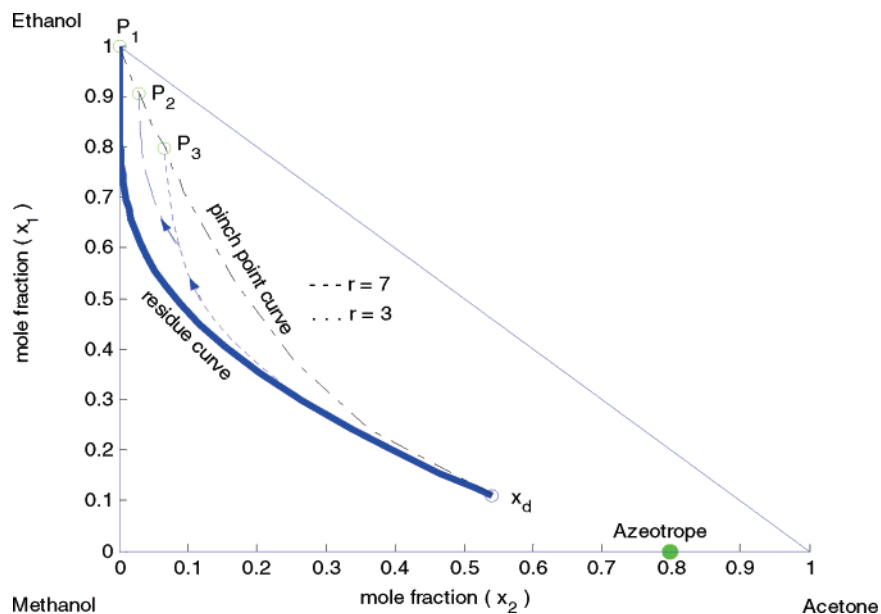
Figure 3. Increasing the reflux ratio along a column profile. $x_d = [0.54, 0.11, 0.35]$.
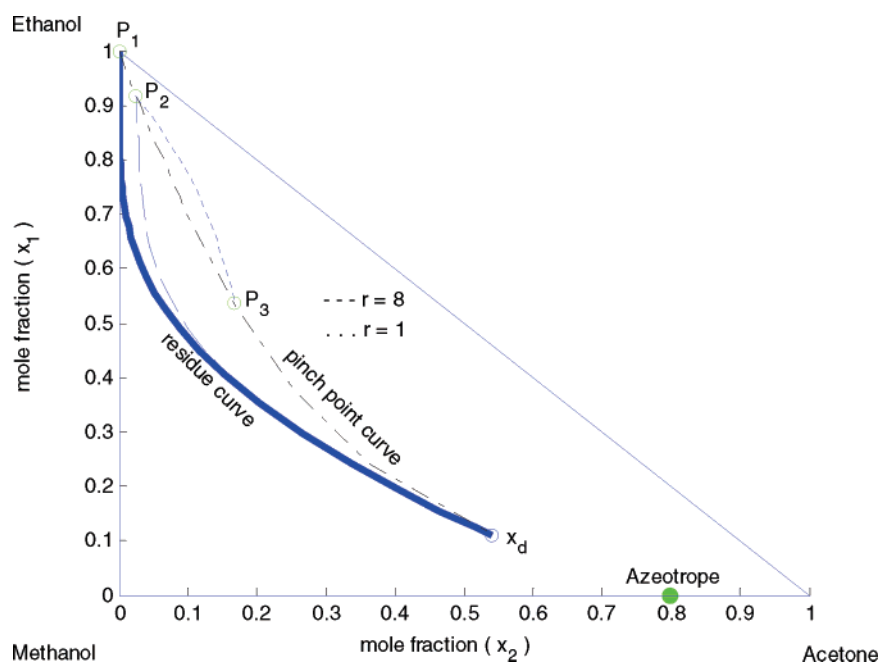

Figure 4. Decreasing the reflux ratio along the column profile with an $x_d = [0.54, 0.11, 0.35]$.

2.3. Crossing Simple Distillation Boundaries.

The chloroform, benzene, and acetone system is used as an example to illustrate the crossing of a simple distillation boundary by expanding the operating leaf, as illustrated in Figure 6. The acetone/benzene/chloroform system has one simple distillation boundary that divides the residue curve map into two distillation regions, as shown in Figure 6. Fixing the distillate composition $x_d = [0.132, 0.2, 0.668]$ results in a column profile. The greatest extension of the operating leaf can be achieved by following the residue curve until its respective pinch point and then reducing the reflux ratio to the lowest reflux ratio possible. Applying this technique, an operating leaf can be achieved that lies in both distillation regions. In other words, profiles can be generated that start in one distillation region (at x_d) and crossing over the simple distillation boundary to its respective pinch point.

3. Experimental Section

To measure a column profile that expands the rectifying leaf, an apparatus has been designed in such a way that the column profile composition could be measured during batch or simple boiling. The associated temperature and vapor curve in equilibrium with the liquid residue can also be obtained. This apparatus was first introduced by Chronis[6] to measure residue curves and has been further developed by Tapp[11] to measure column profiles. The design of the apparatus is based on the fact that material and component balance over a still pot is mathematically identical to the differential equation derived by Doherty (see eq 1). For further details see Appendix A.

3.1. Experimental Setup. There are various components to the experimental setup, as shown in Figure 7, the still being the main component. The still was
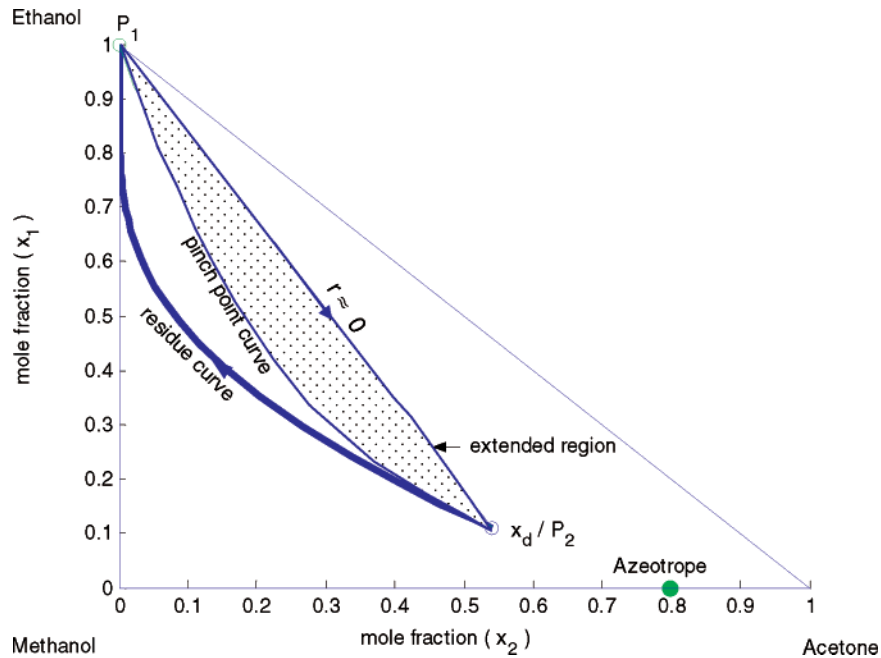
Figure 5. The greatest extension of the operating leaf with an $x_d = [0.54, 0.11, 0.35]$.
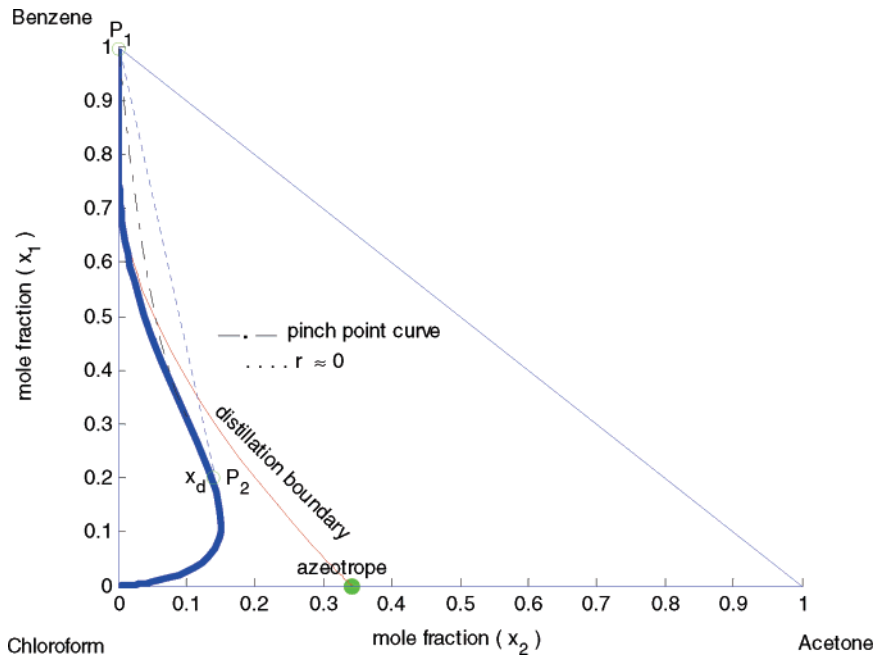

Figure 6. Acetone, benzene, and chloroform system showing the crossing of a simple distillation boundary with an $x_d = [0.132, 0.2, 0.668]$.

graduated in such a way that the level of the liquid inside the still can be measured and the volume calculated. There are four ports in the still. Two of the ports are used for the sampling and injection of material, respectively. The other two were for the thermocouple probe and for keeping the pressure constant by releasing vapor below the oil in a bubbler. The bubbler was also used to measure the rate of vaporization, in turn measuring the rate of boiling. A condenser was attached to the bubbler to capture the vapor from the system. A magnetic stirrer was used for the mixing of the liquid. Boiling stones were placed inside the still to assist nucleation. A HP6890 Hewlett-Packard gas chromatograph was used for the analysis. The still was immersed in a water bath. The purpose of the bath was to maintain an even heat distribution and also to ensure
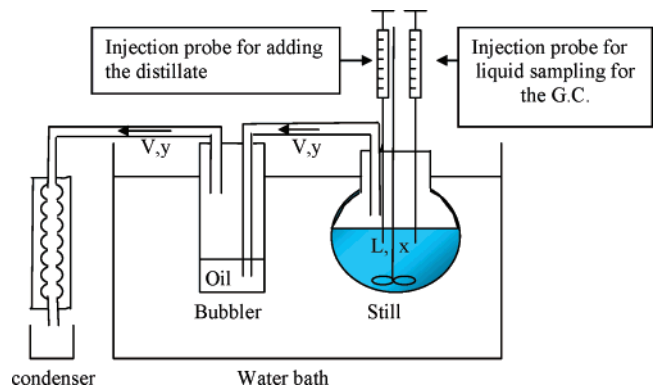

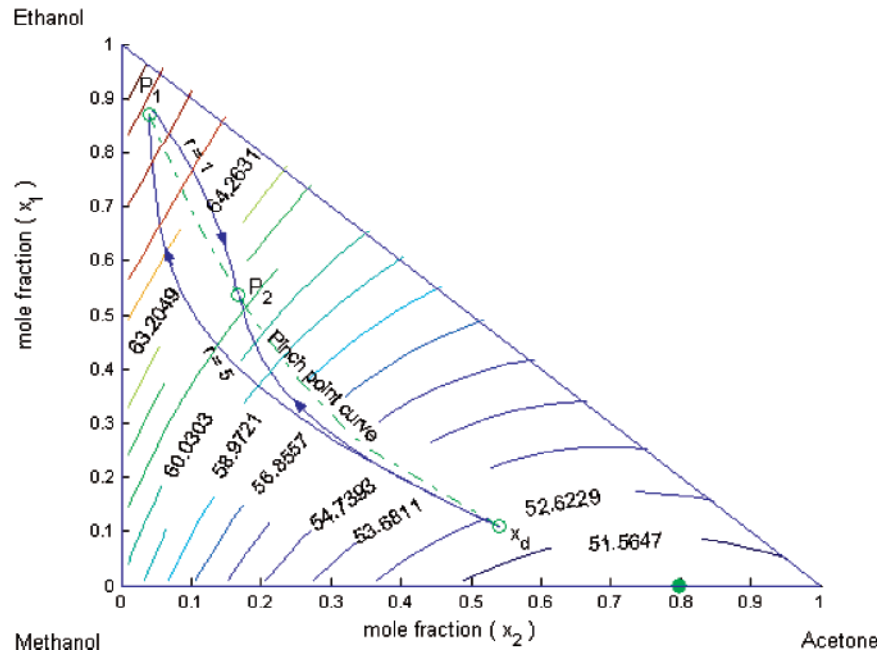**Figure 7.** Experimental setup with the still being the main component.

Figure 8. An isotherm plot showing column profile with a reflux of 5 and reflux of 1 and their respective pinch points P_1 and P_2. $x_d =$ [0.54, 0.11, 0.35].
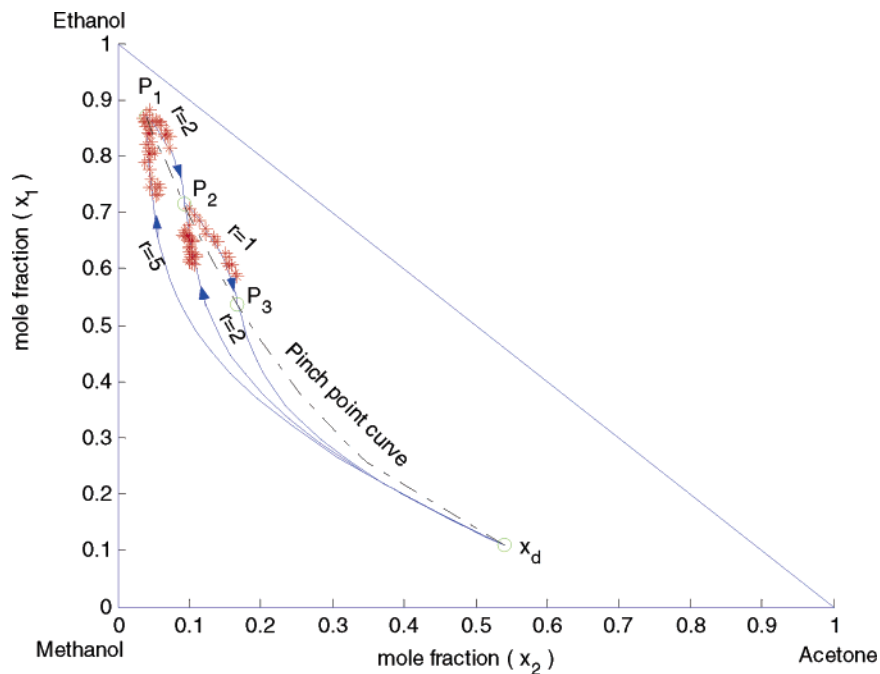

Figure 9. Experimental results of an extended region of an operating leaf with distillate composition $x_d =$ [0.54, 0.11, 0.35].

that the liquid residue would be at its bubble point. To maintain the bubble point temperature, the water bath temperature must be continuously increased to maintain the temperature driving force (ΔT of 6 °C) between contents of the still and the water bath.

3.2. Experimental Procedure. For this paper, experiments were first performed to simulate the rectifying section of a distillation column that would separate methanol, ethanol, and acetone. A bulk solution (about 200 mL) of known composition of methanol, ethanol, and acetone was prepared. A small quantity of this distillate was kept in a refridgerator to be used as a feed solution, while the rest of the distillate was placed in the still. The still was placed inside the hot water bath. The temperature of the bath was then adjusted to ensure that the liquid in the still was at its

bubble point at all times. The varying level of liquid in the still was continuously recorded during the experiment. It can be shown by material balance around the still that the reflux ratio r, the vapor flow rate v, and the distillate flow rate d can be related as follows (see Appendix A for the derivation):

$$d = \frac{v}{r+1} \tag{3}$$

The vapor flow rate was determined by the following mass balance equation
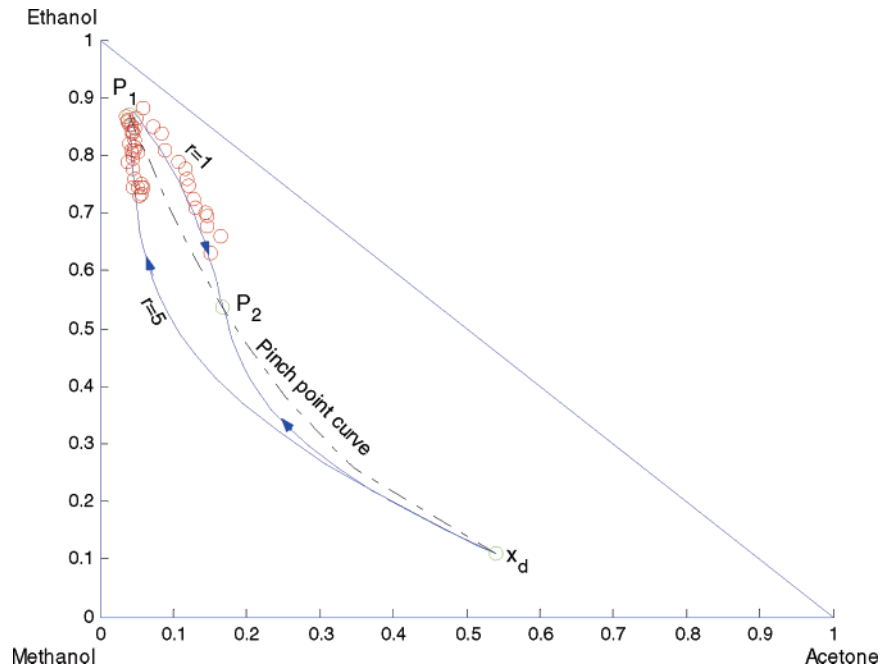
$$v = d - \frac{dl}{dt} \tag{4}$$

Figure 10. Experimental results showing the great extension of the operating leaf with the distillate composition $x_d = [0.54, 0.11, 0.35]$.

Table 1. Results Using a Reflux Ratio of $r = 2$, with the Initial Composition of 22% Methanol, 67% Ethanol, and 10.5% Acetone and the Distillate Composition of 34% Methanol, 11.1% Ethanol, and 54% Acetone

temp, °C					mol fraction		
still pot	H$_2$O bath	time (dt), min	dl, mL	distillate Δd, mL	methanol	ethanol	acetone
63/64	67.8	8	6.3	3.2	0.195 604 45	0.712 762 511	0.091 633 04
64	67.8	7	6.3	3.2	0.208 446 567	0.698 771 508	0.092 781 924
64	67.8	6.3	6.3	3.2	0.206 977 523	0.703 101 383	0.089 921 094
64	67.8	6.3	6.3	3.2	0.210 548 048	0.696 291 172	0.093 160 78
64	67.8	6.2	6.3	3.2	0.225 089 067	0.681 855 058	0.093 055 875
64	67.8	6.3	6.3	3.2	0.210 925 488	0.695 119 81	0.093 954 702
64	67.8	6.2	6.3	3.2	0.205 640 854	0.699 895 647	0.094 463 499
64	67.8	6.2	6.3	3.2	0.207 147 298	0.695 006 297	0.097 846 405
64	67.8	7	6.3	3.2	0.194 378 264	0.710 893 395	0.094 728 341
64	67.8	7.3	6.3	3.2	0.209 264 437	0.693 525 735	0.097 209 828
64	67.8	6.3	6.3	3.2	0.206 579 077	0.695 812 442	0.097 608 481
64	67.8	7	6.3	3.2	0.210 004 666	0.687 179 269	0.102 816 065
64	67.8	8.3	6.3	3.2	0.206 598 446	0.697 012 038	0.096 389 516
64	68.9	6.3	6.3	3.2	0.206 909 608	0.697 277 989	0.095 812 404
64	68.9	5	6.3	3.2	0.216 151 354	0.690 889 354	0.092 959 292
64	68.9	5.1	6.3	3.2	0.211 363 197	0.685 919 059	0.102 717 744
64	68.9	5	6.3	3.2	0.205 980 511	0.702 969 555	0.091 049 934

where dl/dt is the change of liquid level in the still per change in time. Combining eqs 3 and 4 allows the determination of the distillate flow rate d.

$$d = -\frac{\dfrac{dl}{dt}}{r} \qquad (5)$$

In these experiments d was added in discrete amounts rather than continuously. This was done in the following way: The liquid level was observed to change by an amount dl in a time interval dt. Using eq 5, one can say, provided the value of dl is not too large, that

$$\Delta d = d \ dt = -\frac{dl}{r} \qquad (6)$$

where Δd is the amount to be added at the end of the time interval dt when the level has fallen by an amount dl. For our experiments, we used a value of dl of 6.3 mL, which happened in a time interval (dt) of 5 min.

For the initial experiments, a reflux ratio was chosen for each run and kept constant throughout the run; this made it possible to calculate the amount of Δd that must be added after each time interval. Liquid samples were drawn at regular intervals and analyzed using the gas chromatograph. The runs were aborted when the liquid level in the still was below the 20 mL mark in the still, since it was discovered that after this inaccurate results were obtained. For the experimental runs to produce the extended part of the operating leaf, the procedure was exactly the same as that described above, except that as we approach the pinch point the reflux ratio was changed to a lower reflux. According to the addition rate eq 6, as we change the reflux ratio to a lower value, the distillate addition flow rate will become higher. This implies that more distillate was added when working with a lower reflux ratio as compared to working at a higher reflux, which made it possible for the profile to move in the opposite direction from that of the residue curve. The bubble point temperature, after changing the reflux ratio, also changes to a lower

Table 2. Results after Changing the Reflux Ratio from $r = 2$ to $r = 1$

temp, °C		time (dt), min	dl, mL	distillate Δd, mL	mol fraction		
still pot	H_2O bath				methanol	ethanol	acetone
63	68	6.2	6.3	6.3	0.194 369 184	0.705 425 284	0.100 205 532
63	68	6.4	6.3	6.3	0.197 440 685	0.695 863 127	0.106 696 188
63	68	6.3	6.3	6.3	0.200 660 543	0.685 903 109	0.113 436 348
62/63	68	7.3	6.3	6.3	0.206 668 406	0.670 187 234	0.123 144 36
62	67	6	6.3	6.3	0.215 310 069	0.661 076 83	0.123 613 101
61/62	67	5.3	6.3	6.3	0.209 609 954	0.656 417 265	0.133 972 781
61/62	67	5.3	6.3	6.3	0.214 415 383	0.647 374 255	0.138 210 362
61	66	5.3	6.3	6.3	0.212 724 457	0.647 484 977	0.139 790 566
60/61	66	5.2	6.3	6.3	0.222 386 044	0.626 286 412	0.151 327 544
60/61	66	6	6.3	6.3	0.224 524 847	0.620 294 796	0.155 180 357
60	66	6	6.3	6.3	0.239 199 108	0.608 210 94	0.152 589 952
60	65	5.3	6.3	6.3	0.234 486 829	0.605 383 826	0.160 129 345
59/60	65	5.4	6.3	6.3	0.240 375 082	0.605 168 895	0.154 456 022
59/60	65	5.3	6.3	6.3	0.246 772 217	0.586 067 624	0.167 160 159
59/60	65	6	6.3	6.3	0.243 012 819	0.591 858 876	0.165 128 305

Table 3. Results Using a Reflux Ratio of $r = 5$, with the Initial Composition of 17.39% Methanol, 78.29% Ethanol, and 4.32% Acetone and the Distillate Composition of 34.12% Methanol, 11.2% Ethanol, and 53.7% Acetone

temp, °C		time (dt), min	dl, mL	distillate Δd, mL	mol fraction		
still pot	H_2O bath				methanol	ethanol	acetone
67/68	73	5	6.3	1.3	0.149 985 958	0.807 473 028	0.042 541 014
67/68	73	5	6.3	1.3	0.142 506 096	0.806 179 938	0.051 313 966
67/68	73	6.3	6.3	1.3	0.152 915 786	0.802 005 328	0.045 078 886
68	73	7	6.3	1.3	0.144 147 904	0.809 473 32	0.046 378 776
68	73.5	6	6.3	1.3	0.137 282 15	0.814 344 988	0.048 372 862
69	73.5	7	6.3	1.3	0.140 432 324	0.818 782 053	0.040 785 623
69	73.5	6.3	6.3	1.3	0.127 008 222	0.826 514 656	0.046 477 121
69	73.5	7	6.3	1.3	0.106 872 955	0.852 767 755	0.040 359 29
69	74.5	6	6.3	1.3	0.116 859 271	0.840 387 627	0.042 753 102
69	74.5	5.3	6.3	1.3	0.103 723 138	0.858 123 996	0.038 152 866
69	74.5	5.3	6.3	1.3	0.108 000 022	0.845 310 364	0.046 689 614
69	74.5	6	6.3	1.3	0.113 693 16	0.841 479 793	0.044 827 047
69	74.5	5.3	6.3	1.3	0.103 075 183	0.853 240 067	0.043 684 75
70	75	6	6.3	1.3	0.116 305 681	0.838 933 698	0.044 760 621
70	75	6.3	6.3	1.3	0.099 919 587	0.860 991 318	0.039 089 094
70	75	7	6.3	1.3	0.095 726 283	0.867 762 466	0.036 511 25
71	75	6	6.3	1.3	0.084 900 898	0.865 334 52	0.049 764 582

Table 4. Results after Changing the Ratio from $r = 5$ to $r = 1$

temp, °C		time (dt), min	dl, mL	distillate Δd, mL	mol fraction		
still pot	H_2O bath				methanol	ethanol	acetone
69	73	7	6.3	6.3	0.058 093 295	0.882 928 985	0.058 977 72
68	73	3	6.3	6.3	0.077 005 637	0.849 317 682	0.073 676 681
67	72	3	6.3	6.3	0.077 954 39	0.837 633 531	0.084 412 08
66	71	3.3	6.3	6.3	0.102 499 575	0.808 158 772	0.089 341 653
66/65	71	3	6.3	6.3	0.106 555 302	0.787 038 69	0.106 406 008
65	69.5	3	6.3	6.3	0.107 614 905	0.777 078 197	0.115 306 897
64	69	3.3	6.3	6.3	0.121 939 978	0.759 246 593	0.118 813 429
64	68	3	6.3	6.3	0.132 475 7	0.746 648 049	0.120 876 251
64/63	68	4.2	6.3	6.3	0.148 254 637	0.724 116 741	0.127 628 622
63	68	4	6.3	6.3	0.162 380 663	0.707 910 405	0.129 708 932
63	67.5	3	6.3	6.3	0.155 889 584	0.699 485 87	0.144 624 546
63	67	3.3	6.3	6.3	0.158 173 426	0.695 475 152	0.146 351 421
62	66	4	6.3	6.3	0.175 812 806	0.676 955 826	0.147 231 368
62	66	5	6.3	6.3	0.177 187 486	0.658 246 847	0.164 565 667
62/61	66	3.3	6.3	6.3	0.217 084 058	0.631 439 213	0.151 476 729
61	65	4.2	6.3	6.3	0.186 179 683	0.636 806 273	0.177 014 044
61	65	5	6.3	6.3	0.193 335 358	0.642 952 273	0.163 712 369
61	65	4.3	6.3	6.3	0.202 188 157	0.620 186 366	0.177 625 476
60	64	5.3	6.3	6.3	0.201 998 504	0.619 635 533	0.178 365 963

temperature, as shown in Figure 8. The liquid inside the still continued boiling; this is because the distillate composition x_d was richer in acetone, which is the most volatile component.

Figure 8 shows a plot of the isotherms in the ethanol/methanol/acetone system. The isotherms depend only on the thermodynamic data. Isotherms are not affected by the reflux ratio or the distillate composition x_d. That makes the isotherm plot a nice visual tool to understand the temperature change inside the distillation column.

The profile with a reflux ratio of 5 in Figure 8 has an increasing temperature until its respective pinch point P_1. At the pinch point P_1, the reflux ratio is the changed to 1. The profile with a reflux ratio of 1 has a decreasing temperature profile as shown in the above Figure 8. Figure 8 shows the changes in temperature profiles for column profiles. This is an important result, as profiles can be made to run from high to low temperature; hence, the temperature along a profile does not need to be monotonically increasing.

4. Results

The stars and circles in Figures 9 and 10 represent experimental results. Figure 9 shows two experimental runs with different distillate adding policies, because of the different reflux ratios used, but the same distillate composition $x_d = [0.54, 0.11, 0.35]$. The first run started with the reflux ratio of 5; after approaching the pinch point P_1, the reflux ratio was changed to a reflux of 2. The second set of experimental data point was obtained by starting with a reflux ratio of 2 approaching pinch point P_2, and then the reflux ratio was the changed to 1. It is also interesting to note that the two profiles with a reflux ratio of 2 approaches the pinch point P_2 from different directions (along the direction of the eigenvector of the pinch point); see Figure 9. The experimental points follow the predicted path well. They cross the pinch point curve and expand the operating leaf.

The experimental results with a reflux ratio of 5 follow the theoretically simulated results and then reduced to a reflux ratio of 1 as shown in Figure 10. The experimental results with a reflux ratio of 1 clearly show that the pinch point curve can be crossed and in turn extend the operating leaf. Some of the experimental results of Figures 9 and 10 are shown in Tables 1−4.

5. Discussion

It has previously been shown that column profile curves approach pinch curves along the direction of the eigenvector with the smallest eigenvalues. When one operates a column from a fixed feed with different but constant reflux values, this will always approach the pinch point from the same side. However, if one effectively goes past the pinch for a low reflux ratio, using a higher reflux ratio and then reducing the reflux ratio, one must approach the pinch value along the same eigenvector. The only way to achieve this is to approach the pinch point in this direction from the outside. This means approaching the pinch point from outside the operating leaf. It has been shown experimentally using a batch analogue of a column profile that this effect is real and that one can extend the operating leaf in this way. The crossing of the so-called simple distillation boundaries has been shown theoretically. The respective experimental results will be shown in an upcoming paper.

6. Conclusion

We have shown that by having a variable reflux ratio in a column (in particularly going from a high value to a lower value) one can extend the operating leaf. The experimental results revealed that the pinch point curve could be crossed, hence expanding the operating leaf. The greatest extension will result by reducing the reflux ratio from a very large reflux to the smallest possible reflux ratio. This would result in the greatest extension of the operating leaf. It was shown theoretically that the extended region could be used to cross the simple distillation boundary. It is also important to mention that column profiles show a different behavior as residue curves. Residue curves move always from low to high temperatures, whereas column profiles can be made to run from high to low temperature as well. This might change synthesis distillation column sections, as it adds more degrees of freedom for the design of distillation columns.

7. Appendix A
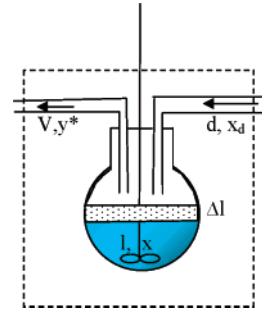
$$l_t = l_{\Delta t + t} + v\Delta t - d\Delta t \quad \text{material balance on the still} \tag{1}$$

$$l_t = l_t + l_{\Delta t} + v\Delta t - d\Delta t \tag{2}$$

$$l_{\Delta t} = d\Delta t - v\Delta t \tag{3}$$

$$\frac{dl}{dt} = d - v \tag{4}$$

Component Balance

$$\frac{d(lx)}{dt} = dx_d - vy \tag{5}$$

$$\frac{l\ dx}{dt} + \frac{x\ dl}{dt} = dx_d - vy \tag{6}$$

but $dl/dt = d - v$ from eq 4

$$\frac{l\ dx}{dt} + x(d - v) = dx_d - vy \tag{7}$$

$$\frac{l\ dx}{dt} = d(x_d - x) + v(x - y) \tag{8}$$

$$\frac{dx}{dt} = \frac{d}{l}(x_d - x) + \frac{v}{l}(x - y) \tag{9}$$

design equation for a rectifying section of a distillation column

$$\frac{d}{l} \div \frac{v}{l} = \frac{r}{r+1} \div r \tag{10}$$

$$\frac{d}{v} = \frac{1}{r+1} \tag{11}$$

$$d = \frac{v}{r+1} \tag{12}$$

but $dl/dt = d - v$ from eq 4

$$d = \frac{d - \dfrac{dl}{dt}}{r+1} \tag{13}$$

$$d(r + 1) = d - \frac{dl}{dt} \tag{14}$$

$$d = -\frac{\dfrac{dl}{dt}}{r} \tag{15}$$

$$\Delta d = d\ dt = -\frac{dl}{r} \tag{16}$$

8. Nomenclature

d = feed addition flow rate (mol/time)

D = feed addition flow rate in a continuous distillation column (mol/time)

l = amount of residue in the still (mol/time)

L = amount of liquid flow rate in a continuous distillation column (mol/time)

r = reflux ratio

t = time variable

v = amount of vapor formed in the still (mol/time)

V = amount of vapor formed in a continuous distillation column (mol/time)

x = liquid mole fraction

x_d = distillate mole fraction

y^* = vapor mole fraction

dl = change in liquid level

dt = change in time

dn = change in number of stages

dx = change in liquid composition

P_i = pinch point

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