THE EXPERIMENTAL SIMULATION OF THE SADDLE POINT REGION IN A DISTILLATION COLUMN PROFILE MAP BY USING A BATCH APPARATUS

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The experimental technique uses a semi-batch apparatus and measures all boiling liquid concentrations in the still as a function of time. This still is immersed in a bath and the feed is added at a controlled rate to the boiling liquid at regular intervals, and samples of the residue are taken periodically. The samples are analyzed using gas chromatography. The concentration profiles achieved in the semi-batch still are essentially the same as those of a continuous distillation column section, see Modise (2005). The experimental measurements are shown around the saddle point region to illustrate the shifting of a stationary point into the mass balance triangle and to show that column profiles with the same reflux ratio can have different pinch points.

KEYWORDS: distillation boundary, pinch point curve, column profiles, distillate, azeotropes

INTRODUCTION
The most important issue in designing a chemical process is feasibility. A design is usually performed by solving a mathematical model of the process which is normally subject to constraints such as nonnegative flow rates and mole fractions, bounds on temperature because of thermal degradation, pressure or on the cost of the design. The worst scenario is that after extensive and lengthy simulation one discovers that the desired specification cannot be met, and significant changes must be made to the flowsheet structure to achieve the process goals, Koehler (1995). In this paper we will show that experimental simulations of distillation column profile maps by using a semi-batch apparatus may also be desirable in the preliminary design of a distillation column.

OPERATION LEAVES
Every real distillation column operates between two ideal extremes; total reflux and minimum reflux (King 1980). The two operational conditions are equally impractical, but they are useful in setting bounds or limits on the separation. For a specific separation, operation at total reflux requires the least number of separation stages, but no overhead or bottom product is withdrawn from the column and no feed is introduced into the column as shown in Figure 1, see Castillo (1998).

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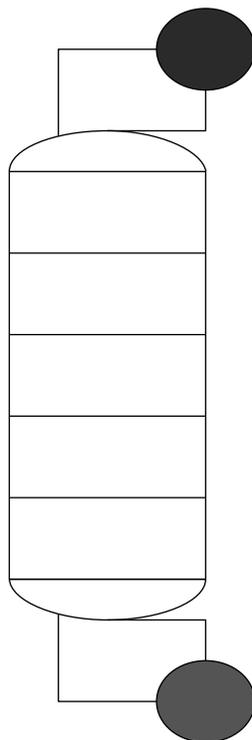
Figure 1. Distillation column with no bottoms or distillate withdrawn and no feed

At minimum reflux, the separation is performed using the minimum possible energy at the expense of the number of separation stages, which approaches infinity. Minimum reflux operation is characterized by the existence of a zone in the column of constant composition for all the components King (1980). This zone is known as the column pinch. A pinch occurs in a distillation column when, despite adding more stages to the column, the composition profile does not change. Wahnschafft (1992) showed graphically that the point where the line passing through the product composition is tangential to the residue curve at the pinch point, see Figure 2. The set of pinch points forms a curve that we call the pinch point curve. The region bounded by the pinch point curve and residue curve is called the operating leaf, see Figure 2, a closed leaf in this case Castillo (1998).

There are however cases where the pinch point curve becomes more complex as shown in Figure 3. In this case the pinch point curve consists of two branches. The dark dashed line is tangential to two different residue curves, unlike other lines which are tangential to only one residue curve.
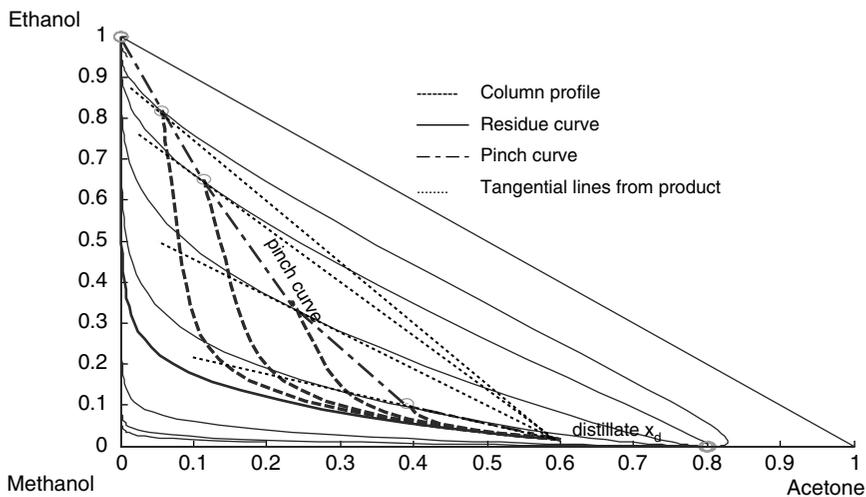
Figure 2. Residue curve map with tangential lines from product showing pinch points
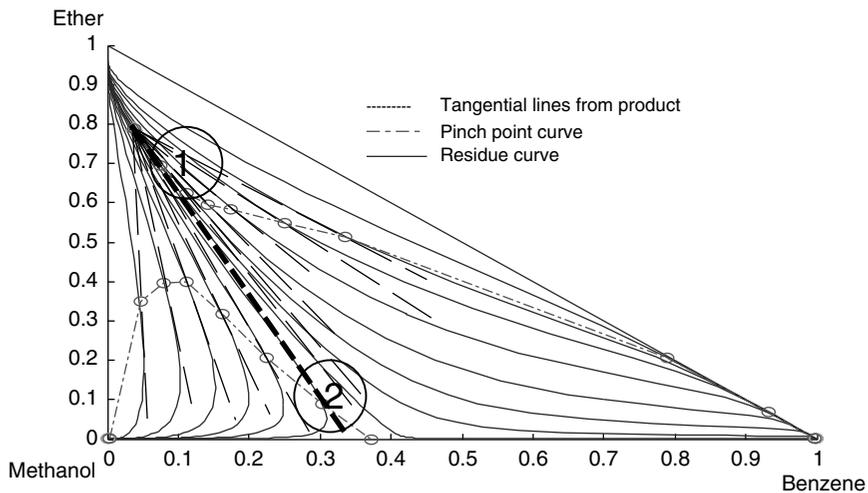
Figure 3. A branched pinch point curve
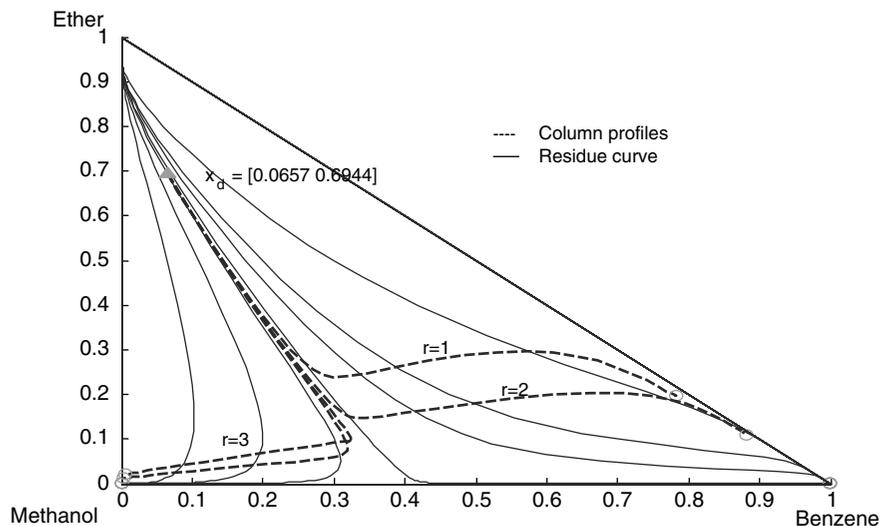
Figure 4. An open leaf

This line is tangential to a residue curve (at point 1) which is a branch that ends at the pure benzene node and also tangential to a residue curve (at point 2) which is on a branch that ends at pure methanol node as shown in Figure 3. This type of behavior was discovered by Castillo (1998), who said there exists operating leaves with pinch curves on different sides of a distillation boundary. This type of operation leaf is called an open leaf. The area in which the distillate x_d product is positioned is also very important, a very small slight change in the composition might change the direction of the profile. In the case of the open leaf one can get situations where small changes in parameters can have dramatic effects on the column profile. Thus in Figure 4 we can see that for a given distillate value x_d a small change in the reflux ratio can have a dramatic effect on the column profile. The area which is close to the distillation boundary is very sensitive to this because the tangential lines from the product might be tangential to one or two residue curves. Figure 5 show profiles with small changes in the initial compositions which result in profiles moving in different directions.

This could be very important because one may end up with unstable column behavior. The two profiles with the same reflux ratio, same distillate but slightly different initial composition clearly shows this. However it is not very easy to see this unstable behavior directly using the residue curve maps (R.C.M). Nor is it very easy to understand why this should happen from these pictures. A much more instructive way to view this is using the column profile map (C.P.M) Tapp (2003). Suppose we draw the C.P.M for this system using a reflux ratio of 3, as is shown in Figure 6. We can immediately see that the
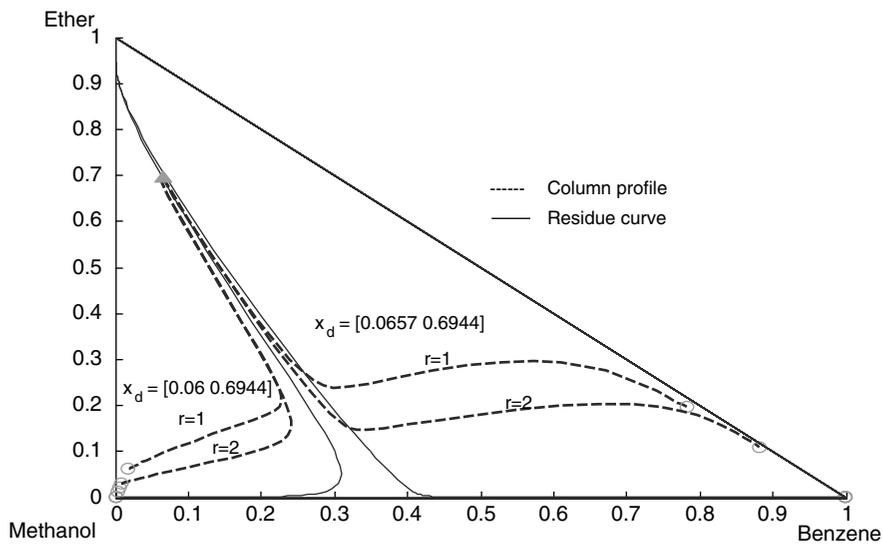
Figure 5. A slight change in the composition changes the direction of the column profile
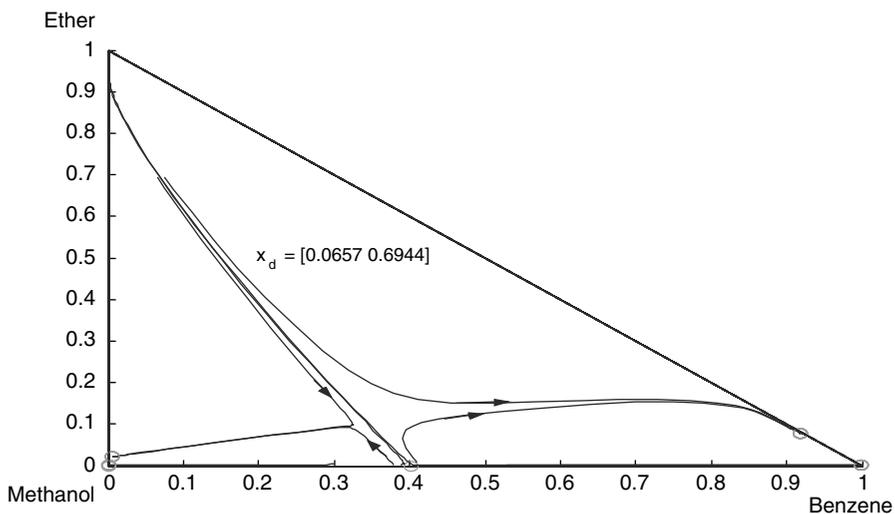
Figure 6. Column profile map of methanol, diethyl ether and benzene using a reflux ratio of three (r = 3) for a rectifying section of distillation column

problem is that we appear to have introduced a saddle point into the space or alternatively we can topologically regard the C.P.M as being a transformed R.C.M in which the stationary point (azeotrope) that was on the mass balance triangle (M.B.T) boundary has been moved into the space.

This topological interpretation is a very useful way of viewing the C.P.M namely as a movement of the stationary points as the parameters of the system change (in this case the reflux ratio). To do this we need to draw the R.C.M's in the negative space as well. However one might then reasonably ask the question; how good were the thermodynamic models in the negative space? We of course have no direct method of checking this but if in the system of interest our predictions of how in the C.P.M's, the stationary point move related to the R.C.M's, are borne out in practice, we will be reasonably happy that we are on the right track. Let us therefore see if we can reproduce the saddle point behavior in Figure 6.

EXPERIMENTAL PROCEDURE
In order to measure a column profile map of the rectifying section of the distillation column, an apparatus has been designed in such a way that the column profile composition could be measured during batch or simple boiling. An apparatus has been introduced by Chronis (1997) to measure residue curves and has been further been developed by Tapp (2003). There are various components to the experimental set-up but the main component is the still as shown in Figure 7. There are four ports in the still, two for sampling and injection of the feed respectively. The other two were for the thermocouple probe and for keeping the pressure constant by releasing vapour below the oil in a bubbler. The bubbler was also used to measure the rate of vaporization hence measuring the rate of boiling. A bulk solution (about 200 ml) of known composition of methanol, benzene and diethyl ether was prepared. A small quantity of this distillate was kept in a fridge to be used as a feed solution while the rest of the distillate was placed in the still. The still was placed inside a hot water bath. The level of liquid in the still was continuously recorded during the experiment. It can be shown by material balance around the still that equivalent reflux ratio r and the equivalent distillate flow rate d can be related as follows Modise (2005).

$$\Delta d = d^*\Delta t = -\frac{\Delta l}{r}$$

where Δd is the amount to be added at the end of the time interval Δt when the level has fallen by an amount Δl. For our experiments we used a value of Δl of 6.3 ml which happened in a time interval (Δt) of 5 min, the reflux ratio was chosen to be three throughout the run and was kept constant; this made it possible to calculate the amount of distillate that must be added after each time interval. The level of liquid in the still was continuously recorded during the experiment. Liquid samples were drawn at regular intervals and analysed using the gas chromatograph.
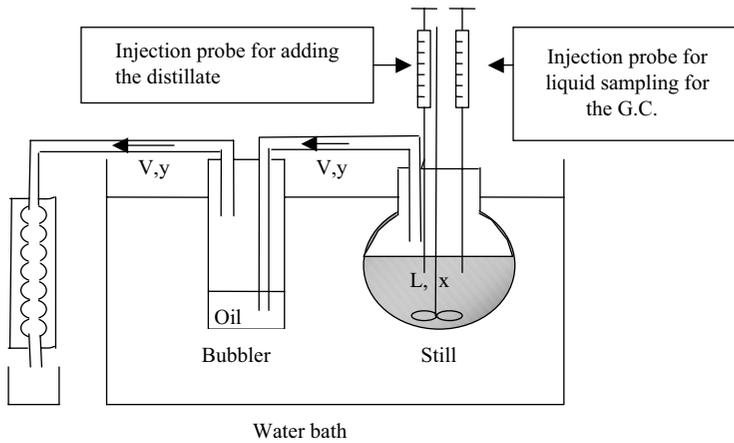
Figure 7. Experimental setup with still pot being the main component
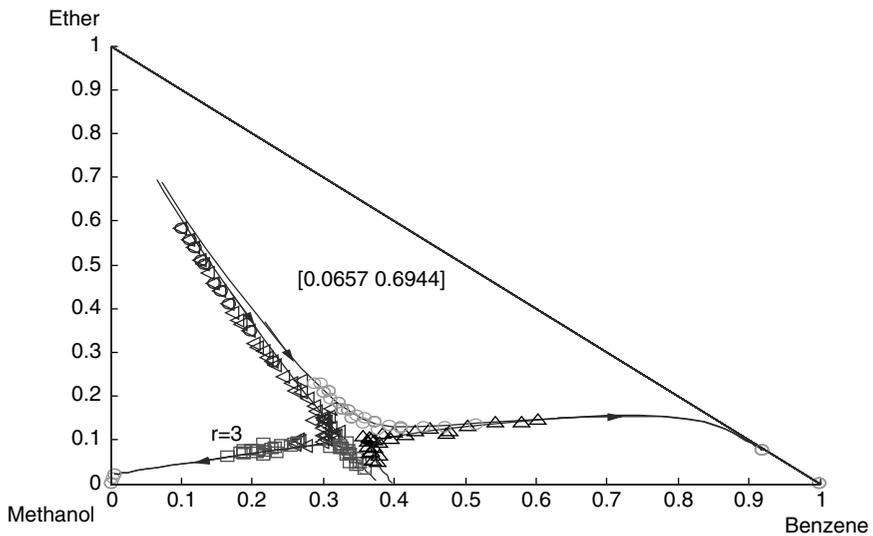
Figure 8. Column profile map with a reflux ratio of three, starting with different initial points with a fixed distillate composition $x_d = [0.0657\ 0.6944]$

Table 1. NRTL parameters for the ethyl ether, methanol and benzene system

Component i	Ether	Ether	Methanol
Component j	Methanol	Benzene	Benzene
Temperature units	K	K	K
Source	VLE-IG	VLE-IG	VLE-IG
aij	−5.2556	0.0576	−1.7086
aji	7.0779	−0.4759	11.5801
bij	1893.486	94.4718	892.2404
bji	−1999.4722	27.468	−3282.554
cij	0.3	0.3	0.4

RESULTS

Figure 8 represents experimental results obtained for a column profile map with a reflux ratio of three, but different initial points. The solid lines represent the theoretical results while the points represent the experimental results. The NRTL model was used to simulate the theoretical results. The parameters of the NRTL model were obtained from Aspen and are tabulated below, Table 1.

DISCUSSION & CONCLUSION

The experimental results in figure 8 clearly show that one can effectively map the saddle point in C.P.M space. Furthermore they also clearly show the sensitivity of the results to the initial value, as one would expect close to a saddle point. These results are also very interesting from a more fundamental point of view. Because the results are so sensitive to the position of the saddle point, these measurements are an extremely good test of the underlying thermodynamic close to the saddle point. In the batch apparatus as we can effectively change the position of the saddle point by changing the effective reflux ratio we are in a position to test the underlying thermodynamics at different points in the space. This could prove a useful tool to discriminate among different thermodynamic models and the parameters used in these models. This result shows the value of looking at the residue curve in negative space, in that one could then predict that the saddle point would be moved into the real space (positive mole fractions) and so we could predict the likely unstable behavior from the residue curve map alone.

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