EXPERIMENTAL COLUMN PROFILE MAPS WITH VARYING DELTA POINTS IN A CONTINUOUS COLUMN FOR THE ACETONE METHANOL ETHANOL SYSTEM

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Traditionally, distillation column profiles have been divided into rectifying and stripping profiles, described by the liquid composition along the column. Recently, Tapp et al. (2003) defined a generalised column section and the composition profiles in these sections are described by the Difference Point Equation. Column sections can be sequenced by the designer (within certain constraints) and column profiles can be achieved that are neither stripping nor rectifying, allowing the designer much more flexibility.

An experimental investigation has been undertaken for the acetone, methanol and ethanol system. By controlling the vapour and liquid feed compositions, temperatures, and flowrates, a number of column profiles at finite reflux were obtained. The results were compared with column profile maps predicted by the Difference Point Equation and found to be in good agreement. An interesting and counterintuitive prediction was that certain column profiles follow an inverse temperature profile, in that temperature decreases monotonically down the column. This prediction was verified experimentally and is highlighted in this work.

KEYWORDS: distillation, experimental, column profile maps, residue curves

INTRODUCTION

Residue curves were one of the first graphical representations useful for understanding the volatility and compositional changes of three component batch evaporative systems. Hausen (1952) and Rische (1955) later extended their function and showed their equivalence to the compositional profile of a packed column at infinite reflux. Serafimov (1968) suggested predicting feasible separations from the use of structural information in VLE diagrams. In this way, Residue Curve Maps (RCM's) are useful for split feasibility and thermodynamic understanding of VLE behaviour.

Doherty and Perkins (1978) introduced the use of ordinary differential equations as a differential approximation to the liquid composition profiles in the rectifying and stripping sections of a distillation column. It was later shown that the differential model results were very similar to those for stage by stage calculations (Van Dongen & Doherty 1985). Feasible column profiles were indicated by an intersection of the approximated rectifying and stripping profiles but the differential equations were not valid near the feed stage.

Optimal placement of the feed stage was based on heuristics (Fenske 1932) or rigorous calculation methods (Yeomanns & Grossman 1998).

The limitation of simple distillation analysis was addressed by Tapp et al. (2003) with use of the Difference Point Equation adapted from Doherty and Perkins (1978) original rectifying and stripping differential equations. Use of the difference point in the design of non-reactive and extractive cascades had been made by Hoffman (1964) and later Hauan et al. (1998). The difference point was re-defined by Tapp et al. (2003) as a pseudo net molar flow composition within a column section.

A column section was redefined as a length of column between points of addition or removal of material or heat (Tapp et al. 2003). The use of a net flux allowed a degree of freedom within mass balance constraints of a column section whereby mass balances could be achieved by simple addition (or subtraction) of the net fluxes within the column section (Tapp et al. 2004).

The work by Tapp et al. (2004) is an extension of the work by Franklin (1986) where the idea of producing composition profiles with a difference point other than product composition point was proposed. If the initial condition is allowed to vary, the composition space can be populated with trajectories that represent feasible column profiles. This set of trajectories is defined as a Column Profile Map (CPM) by Tapp et al. (2004). The difference point equation is a linear transform of the RCM and thus CPM's are simply transformations of the RCM. *An important result of this linear relationship is the shifting of the topology of composition profiles that lie outside the mass balance triangle (MBT) in RCM's, into the MBT for the CPM's.*

This work aims to investigate and verify these transformations experimentally at finite reflux for a real system. The acetone, methanol and ethanol system was used and experimentally measured column profiles were compared to the theoretically predicted profiles. An important consequence is that the experimental method described in this paper is a relatively accurate way of measuring CPM's regardless of whether one has vapour-liquid equilibrium models or not. Furthermore the method may be extended to four or more component systems.

THE DIFFERENCE POINT EQUATION

Tapp et al. (2003) defined a column as a series of sections rather than just a rectifying and stripping section. Under the new definition, the column sections are defined as sections with no feed addition or side stream withdrawal.

Analogous to the derivation of the differential equations by Doherty and Perkins (1978), a component mass balance for the general column section in Figure 1 leads to equation (1).

$$\frac{dx}{dn} = \left(\frac{1}{R_\Delta} + 1\right)(x - y) + \frac{1}{R_\Delta}(x_\Delta - x) \tag{1}$$
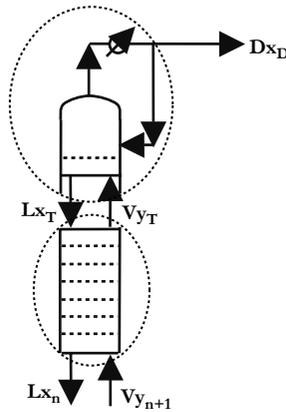
Figure 1. Column showing rectifying and general column sections

Whereby the difference point x_Δ and reflux ratio R_Δ (not to be confused with the traditional reflux ratio ($\dot{L}/\dot{D}$) may be defined as:

$$x_\Delta = \frac{(\dot{V} \cdot y_T - \dot{L} \cdot x_T)}{\Delta} \tag{2}$$

$$R_\Delta = \frac{\dot{L}}{\Delta} \tag{3}$$

Where Δ is the flow rate difference point defined as:

$$\Delta = (\dot{V} - \dot{L}) \neq 0 \tag{4}$$

The composition difference point and flow rate difference point were first defined by Hoffman (1964) and later adapted by Hauan et al. (1998). The above equation applies to all general column sections and is referred to as the Difference Point Equation.

The difference point equation may be solved by integrating from a starting composition for a specific reflux ratio (R_Δ) and difference point (x_Δ). Integrating in the positive and negative directions yields a complete profile in both directions depending on the number of stages specified. By choosing a number of different starting compositions for the same reflux and difference point, the entire composition space may be populated with column profiles. For a finite reflux and a fixed difference point at a set reflux, the result is a map of transformed composition trajectories, known as a CPM.

An example of a CPM is given in Figure 2. The RCM for the system is given as dashed lines and the solid lines are the CPM. The bold solid curve in Figure 2 corresponds to a specific column profile that we will use in this paper to compare with an
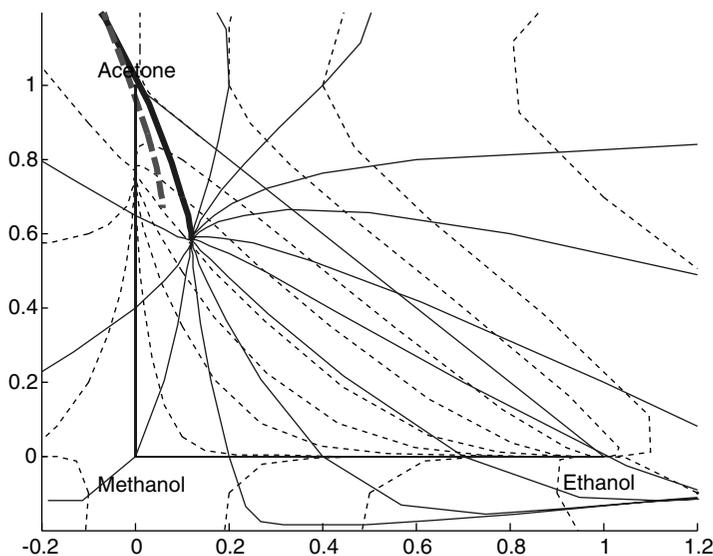
Figure 2. Comparison of shifted column profiles with residue curves. Intended liquid (bold) and vapour (dashed) profiles are highlighted. $x_\Delta = [0.492; 0.188]$, Reflux $= -2.3$

experimentally measure profile. The red, bold dashed line represents the predicted vapour profile corresponding to the column profile of interest. Notice that the CPM has a stationary point in the MBT and this stationary point is an unstable node. Thus the composition at the bottom of the column lies closer to the pure acetone vertex and the composition of at the top of the column lies closer to the stationary point. We can also see by comparing the RCM to the CPM that the unstable node in the CPM results from the topology around the acetone-methanol binary azeotrope in the RCM shifting into the MBT for the CPM.

Also worth noting is the fact that mathematics of the difference point and residue curve equations are not bound inside the MBT although only profiles inside the MBT may be realised. The topology of the RCM outside of the MBT is very useful however when manipulation of column profiles is to be performed in CPM synthesis. *The topology of the RCM that lies outside of the MBT in the RCM may be moved into the MBT for the CPM.*

EXPERIMENTAL APPARATUS AND PROCEDURE
The apparatus consisted of a 90 mm diameter aluminium tube with sampling ports and stainless steel intalox random packing. The column was 1.2 m high with liquid sample ports.

There was a single liquid and vapour feed at the top and bottom of the column section and the exit streams were not returned to the column. In other words the column was a single pass interaction between a controlled liquid and vapour feed simulating a general column section as shown in Figure 1. This was done purposefully to give greater manoeuvrability in achieving desired column profiles and various delta points.

The flowrate, composition and temperatures of the liquid and vapour feeds were controlled to ensure steady state operation. For the liquid, a rotameter provided flow control; the liquid was premixed for a constant composition; and pre-heated prior to entry to the column for temperature control. The vapour stream was a mixture of the product from three variable resistance heating mantles each containing a pure component. The relative heat settings indirectly controlled the vapour feed composition, flowrate and ultimately the temperature.

The column and its peripheries are insulated to ensure that all experimental runs are adiabatic in keeping with the definition of a column section. Liquid samples are taken along the length of the column and vapour sample ports were located at the vapour feed and exit. The samples were analysed in a TCD Gas Chromatograph to obtain the column composition profiles for particular experimental runs.

The reflux ratio can be set experimentally by controlling the vapour and liquid flowrates and the initial point of the column profile by controlling the feed liquid composition. The difference point however cannot be controlled experimentally as the column autonomously regulates this in response to the mass and energy balance constraints. The resulting composition difference point x_Δ thus has to be calculated from the experimental results as discussed below.

RESULTS
The data from the experiment was interpreted in three ways:

- The difference points for the top and bottom of the column were calculated from the experimental data and compared to check the consistency of the data.
- The experimental profiles of both the liquid and the vapour in the column were compared to the theoretical predictions.
- The predicted isotherms were superimposed in the MBT on the experimental temperature profile to validate the predicted temperature inversion.

DIFFERENCE POINTS
The difference points corresponding to the top and bottom of the column for each experiment may be calculated using equation (2) and the experimentally measured molar flowrates and compositions of the liquid and vapour streams at the top or bottom of the column.

Agreement between the top and bottom difference points is a consistency check for the experiments. Equivalent difference points for the top and bottom of the column imply constant molar overflow and adiabatic operation of the column.
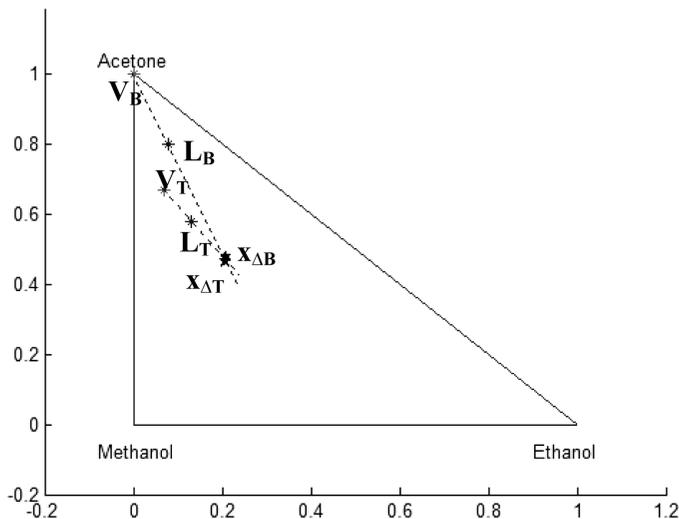
Figure 3. Difference points for top and bottom passing streams

The difference points were calculated for the top and bottom of the experiment and are shown in Figure 3 above. From this we can conclude that the difference points calculated for the top and bottom of the column, $x_{\Delta T}$ and $x_{\Delta B}$ respectively, closely coincide and hence that the column is closely approximating adiabatic, constant molar overflow operation.

COLUMN PROFILES

In Figure 4, the experimentally measured compositions of the vapour at the top and bottom of the column as well as the liquid compositions are plotted on the MBT for the acetone, methanol and ethanol system. The experimental liquid profile is shown as a series of points and the theoretically predicted vapour and liquid curves are included as solid lines and coincide with the bold lines in Figure 2. The RCM is marked in Figure 4 as dashed curves.

The highlighted proposed column profile in Figure 2 is rather extreme in that the top vapour and liquid compositions begin near the shifted azeotrope composition and end (in the MBT) at the pure acetone vertex. *In other words the column profile moves almost completely in the opposite direction to the residue curves.*

We can see from Figure 4 that the experimental data points closely approximated the predicted profile. Figure 4 is annotated and it can be seen that the liquid enters at the top (L_T) close to the composition of the unstable node and exits at the bottom (L_B) close to the acetone node as predicted. Similarly the vapour stream enters the column at the bottom (V_B) as nearly pure acetone and exits at the top (V_T) near the unstable node.

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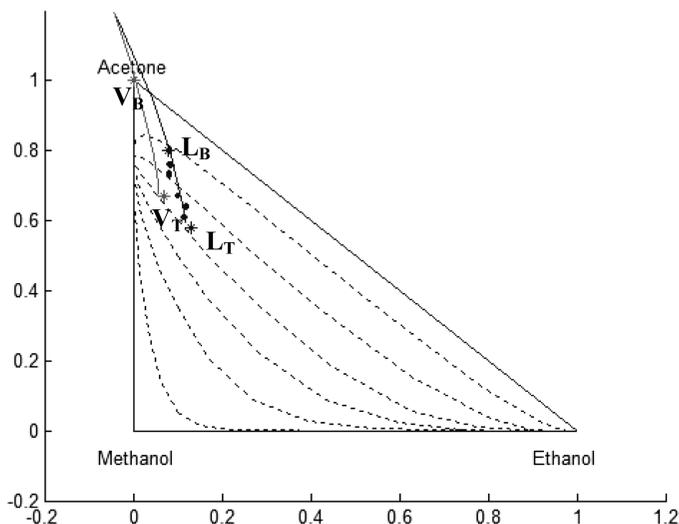
Figure 4. Composition profile points and corresponding theoretical liquid and vapour profile. $x_\Delta = [0.492; 0.188]$, Reflux $= -2.3$

The negative reflux ratio and positive x_Δ corresponds to a net flux down the column of all components as might occur in a stripping section. However this profile would not be found in a stripping section of a normal distillation column and would correspond more to one found in an absorption column.

INVERSE TEMPERATURE PROFILES

Isotherms are only dependent on composition. However transformed singular points do not retain their original temperature assignment, but take on the temperature at the composition that they occur at. Usually the distillate of a column has a lower boiling point than the bottoms. *In this case the experimental profiles have an inverse temperature profile as the distillate is warmer than the bottoms.* Inverse temperature profiles have been reported by Lee and Westerberg (2000).

The isotherms for the acetone, methanol and ethanol system are plotted along with the experimental profiles in Figure 5. As can be seen in Figure 5 the top temperatures for the vapour and liquid streams are at higher boiling isotherms than their corresponding bottom stream isotherms.

Note that the theoretical profiles are shown for clarity. This is sufficient as their equivalence to the experimental profiles was already verified in Figure 4.

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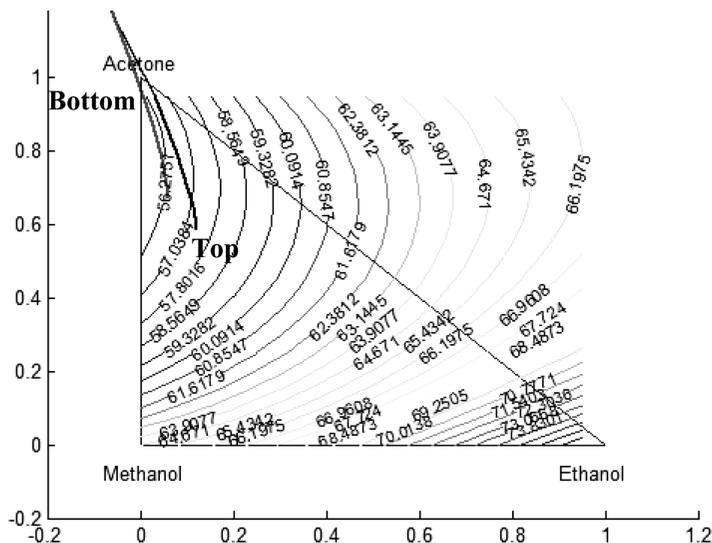
Figure 5. Theoretical profiles with isotherms to show a temperature profile inversion in the column

OTHER EXPERIMENTAL PROFILES
Other column profiles were measured and the measured and predicted profiles are shown in Figure 6 for two examples. It can be seen that in both cases there is a close correspondence between the measured and predicted profiles. In the profiles labelled 1 and 2 a distillation boundary is evident from the shifting of the methanol pure component node into the CPM space to form a possible binary azeotrope, causing the two divergent column profiles.

DISCUSSION
The difference points for the top and bottom of the column are represented in Figure 3. The constant molar overflow assumption results in a constant net molar flow composition, x_Δ along the length of the column. Furthermore, the difference point composition must lie on the straight line joining passing stream compositions. The agreement of the difference points calculated for the top and bottom of the column indicates the degree to which thermal and mass steady state was achieved.

Figure 4 shows the equivalence of the theoretical predicted column profiles to those measured experimentally. Although theoretically the column profiles are not mathematically bounded to the MBT it should be clear that the experimental profiles are. It should also be noted that the entire space is not populated by a discreet number of profiles,
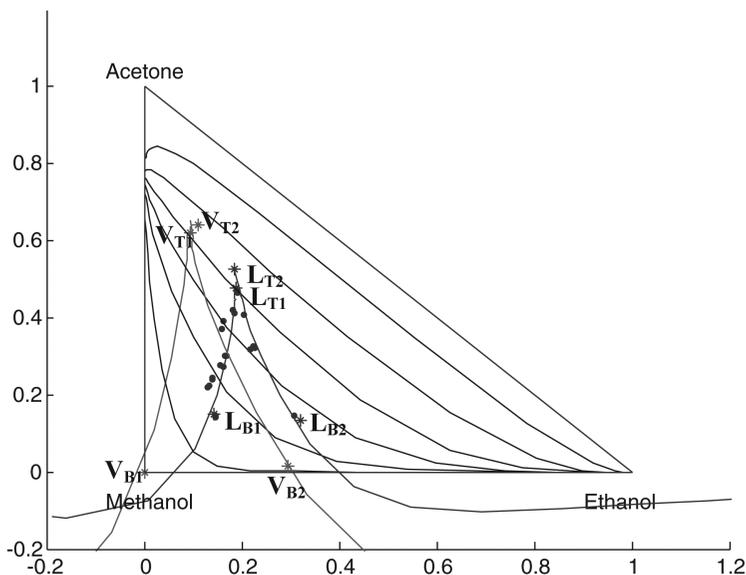
Figure 6. Composition profile points and corresponding theoretical liquid and vapour profiles for two different experiments shown on the same MBT. Note each experiment has a different reflux ratio and resulting difference composition point

but rather a surface of infinite ones. Each profile map is unique to a difference point and reflux, but the curves may be traversed by means of the initial composition from which integration takes place. In this way, the best fitting profile to the experimental data may be found. The column profile in Figure 4 moves diametrically opposite to the residue curves in that region of the MBT. Figure 5 also shows the measured temperature profile monotonically decreasing down the column.

In terms of CPM theory, this is the equivalent of modifying the orientation of the components within a column section. In this case acetone was made to strip instead of forming the distillate. In other words one could achieve pure acetone in the bottoms of the column! This phenomenon is an excellent example of how the difference point can be used to manipulate the system to achieve desired separations within mass balance constraints.

CONCLUSIONS
An apparatus has been built for an experimental verification of CPM theory. The acetone, methanol and ethanol system was investigated to demonstrate the deviation of maps from infinite reflux behaviour.

RCM's had previously been used to gain a qualitative understanding of finite reflux systems and batch experiments were done to investigate singular point complexities. The introduction of CPM's advanced the understanding of finite reflux systems by demonstrating the transformation of residue curves for deviations from total reflux. *This experiment has verified these transformations in a fairly simple continuous apparatus.*

The vapour flow rates were found to be limiting for the capacity of the column thus a larger liquid flow rate than vapour flow rate was used. This ensured sufficient wetting of the packing for consistent results and liquid sampling. *Careful pre-heating of the column and high quality insulation contributed to start-up times of less than 10 minutes for an experimental run.* Temperature control of the liquid feed ensured minimal temperature disturbances to the column temperature profiles.

Incorrect control of the input parameters of the experiment namely feed compositions, flow rates and temperatures manifest as discrepancies in the calculated difference points for the top and bottom of the column. Constant molar overflow was observed to within 5% for the liquid and vapour streams. *The difference point provides a useful internal check for constant molar overflow and adiabatic operation of the column.*

This experimental CPM investigation would be applicable in cases where discrepancies arise in the position of predicted singular points for different thermodynamic models. By doing a few simple carefully designed experiments, the best model for a particular system could be selected. Including potential mass transfer limitations could increase the accuracy of the method further.

An investigation at finite reflux for this system has given rise to an understanding of the column behaviour that would never have been realised with traditional qualitative techniques. The result has been obtained in a continuous apparatus where the equivalent results of batch experiments were slow to be accepted due to their batch nature.

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