

Application of the Rectification Body Method to Batch Rectification

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Abstract

This contribution focuses on the development of a dynamic conceptual model for a batch rectifier having an infinite number of stages without resorting to multistage calculations. For a given instantaneous still composition, the key feature of the method is the estimation of the instantaneous minimum reflux or the instantaneous distillate composition by using the **Rectification Body Method**. The usefulness of Bifurcation Analysis of pinch profiles is emphasized to model highly non-ideal behavior.

Keywords: Conceptual Design, Batch Distillation, Azeotropic Mixtures, Rectification Body Method (RBM), Bifurcation Analysis.

1. Introduction

Dynamic conceptual models are useful in the synthesis and design of batch distillation systems as shown by Espinosa et al. (2004). In the past several authors resorted to linearization of internal profiles in the neighborhood of pinch points to calculate the instantaneous performance of a batch rectifier (Offers et al., 1995; Espinosa and Salomone, 1999). In this contribution, we propose the use of the Rectification Body Method (RBM, Bausa et al., 1998) previously developed for continuously operated distillation columns. First, a simple method to calculate instantaneous column performance at different operating policies is developed using the rectification bodies based on the pinch points corresponding to limiting values of reflux ratio and distillate composition; i.e. R^* and x_D^* (see Figure 1). Thus, by integrating the differential equation system modelled under the assumption of quasi-stationary operation of a rectifier column having an infinite number of stages, the still path evolution and the trajectory of all other variables of interest such as component recoveries, compositions and temperatures in the still and at the top as well as the reflux ratio can be obtained for different operating policies. After that, some illustrative examples of separations involving highly non-ideal azeotropic mixtures are presented. It will be shown that the

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combination of RBM with bifurcation analysis can be used to deal with limitations caused by distillation boundaries or the appearance of tangent pinches.

2. Instantaneous Column Performance From RBM

Figure 1(a) shows the behavior of liquid composition profiles at different reflux ratios as calculated from simulations in Hysys. The respective balance envelope is shown in Figure 1(b). The profiles emphasize the invariance of pinch x_p^{II} for instantaneous reflux ratios above R^* . Therefore, the rectification triangle corresponding to R^* and x_D^* directly allows the calculation of the instantaneous column performance. The idea of pinch invariance, despite representing an approximation for non-ideal mixtures, is the basis of the proposed conceptual model.

2.1. Operation at constant reflux

For a given constant reflux ratio r the instantaneous distillate composition x_D can be determined using the following algorithm:

Step 1. Set values for the instantaneous still composition x_S and reflux ratio r .

Step 2. Calculate $y^*(x_S)$ (vapor in equilibrium with x_S) first and then x_D^* , which is located at the intersection of the equilibrium vector with the binary axis $x_{D,2-PrOH}=0$.

Step 3. Calculate the limiting reflux ratio R^* through the lever arm rule (equation 1):

$$R^* = \frac{x_D^* - y^*(x_S)}{y^*(x_S) - x_S} \quad (1)$$

Step 4: If $r \leq R^*$ there exists a pinch at the column end with the composition x_S . The instantaneous distillate composition is located on the line given by the equilibrium vector (also known as line of preferred separation; Offers et al., 1995). Use the lever arm rule to calculate the distillate composition (equation 2) and go to Step 8.

$$x_{i,D} = y^*(x_S) + r[y^*(x_S) - x_{i,S}] \quad (2)$$

Step 5: If $r > R^*$, a controlling saddle pinch located on the binary edge corresponding to the two more volatile components may control the separation. Calculate the pinch branches for x_D^* and select the solution corresponding to the limiting reflux ratio R^* (x_p^{II} and x_S) to build the rectification body.

Step 6: Calculate both x_D and x_N by solving the mass balance around the column.

Step 7: If $x_{D,MeOH} > 1$ set $x_{D,MeOH} = 1$. A pinch at column top controls the separation.

Step 8: Exit.

Figure 1(a) shows results for the mixture methanol/ethanol/2-propanol. The triangular rectification body is formed by the limiting distillate composition x_D^* , the binary pinch x_p^{II} and the instantaneous still composition x_S . The unknown distillate composition x_D in Step 6 can be iteratively calculated from the mass balance around the column by considering that whilst x_D belongs to the binary axis between MeOH and EtOH, the composition x_N at the column end pertains to the line defined by the two pinch points calculated from the RBM. The vapor $y^*(x_S)$ in equilibrium with the instantaneous still composition is the feed to the batch rectifier as shown in Figure 1(b).

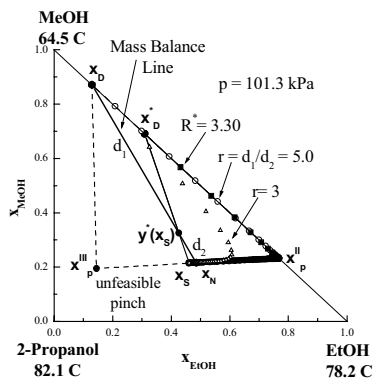


Figure 1(a). RBM and Hysys simulations for an instantaneous still composition x_S .

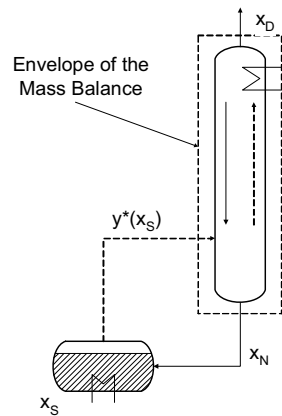


Figure 1(b). Mass Balance Envelope. Note that x_N is located in the line $x_S-x_P^{II}$.

Figure 1(a) also shows the triangular rectification body corresponding to the actual distillate composition x_D and reflux ratio r . The saddle pinch x_P^{II} is the same for both rectification bodies and hence, the rectification body corresponding to the limiting distillate composition and reflux ratio can be used to estimate the instantaneous distillate composition for a batch rectifier operating at reflux ratio r .

2.2. Operation at constant distillate composition

Analogously to the algorithm for a batch rectifier operating at constant reflux ratio, the rectification bodies are built by using limiting values of reflux ratio and distillate mole fraction (i.e., R^* and x_D^*). By selecting the pinch points corresponding to the limiting values, the composition of the liquid leaving the column bottom, x_N can be calculated from intersection of lines $(x_S-x_P^{II})$ and $(x_D-y^*(x_S))$. The remaining variables are calculated from the overall mass and energy balances.

3. Non-ideal Azeotropic Distillation

The design algorithm developed above for zeotropic mixtures can be extended to highly non-ideal systems with distillation boundaries. However, some limitations arising from thermodynamics of such mixtures must be taken into account. Figure 2 shows the triangular rectification body for an instantaneous still composition x_S for the limiting reflux ratio R^* and distillate composition x_D^* in the case of a mixture where x_D is limited by a distillation boundary. The rectification triangle is formed by the distillate composition x_D^* lying on the boundary, a saddle pinch x_P^{II} and a stable pinch with the composition x_S of the still pot. In order to place x_D^* on the boundary an additional equation is required for the evaluation of the pinch points in steps 2 and 5 of the algorithm presented in section 2.1 which replaces the assumption that x_D^* should lie on a binary edge of the composition space. The bifurcation-theoretic formulation of the pinch distillation boundary (PDB) presented by Brüggemann and Marquardt (2004) provides this additional equation and links the location of x_D^* to the appearance of a pitchfork bifurcation.

Figure 2 shows that for this limiting distillate composition a pitchfork bifurcation of the reversible (pinch) profiles occurs and, therefore, x_D^* can be obtained at the intersection of the equilibrium vector with the PDB in step 2 of the algorithm. In addition, x_D in step 6 is located (as an approximation) on a line connecting x_D^* and the unstable node acetone. This kind of behavior can be easily automated from the knowledge of azeotropes and pure components stabilities.

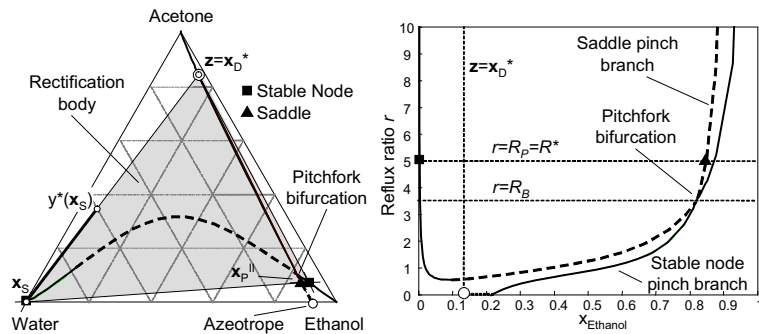


Figure 2. Rectification Body corresponding to the limiting distillate composition x_D^* and reflux ratio R^* .

Another characteristic that can appear in highly non-ideal mixtures is highlighted by an analysis of the pinch map of the system acetone-chloroform-benzene shown in Figure 3. Figure 3(a) shows the preferred separation for the still pot composition x_S and the pinch points corresponding to x_D^* and R^* (or Q_D^*/D). In addition, all pinch branches are depicted. The binary pinch x_P^{II} is a stable node whilst the still composition behaves like a saddle pinch point. This pinch topology suggests that the liquid profile departing from the instantaneous still composition cannot reach x_D^* at the binary axis due to the appearance of a tangent pinch point. This behavior was confirmed by simulations in *Hysys*. Figure 3(b) indicates that although the stable binary pinch x_P^{II} and hence x_D^* cannot be reached for any internal profile it controls the geometry of internal profiles. Therefore, the characteristic line departing from the instantaneous still composition and ending at the stable binary pinch as calculated from the RBM can be used to estimate the composition of the liquid x_N leaving the column.

Figure 4(a) shows the pinch map corresponding to a distillate composition very close to the binary edge in order to show how the pinch points x_P^{II} and x_S approach each other when x_D^* is moved into the ternary region. At the feasible distillate composition closest to the binary edge, a saddle-node bifurcation of the pinch branch occurs. Hence, bifurcation theory (Brüggemann and Marquardt, 2004) can be used to determine the true limiting distillate composition x_D^* when the separation is controlled by a tangent pinch point. Therefore, feasible distillate compositions can be found in the line of preferred separation until x_D^* (now having small amounts of benzene) and in the line from x_D^* to the unstable node acetone.

As saddle-node bifurcation represents a local maximum in the curve of cumulative condenser energy versus light component mole fraction x_{lk} (another way to represent a pinch point curve), this fact can also be used to determine the maximum feasible

distillate composition on the line of preferred separation. The key of the algorithm is the calculation of the condenser duties on the pinch map for three compositions (x_S^- , x_S , x_S^+) in order to calculate the derivatives $\Delta Q_D^-/\Delta x_{ik}^-$ and $\Delta Q_D^+/\Delta x_{ik}^+$ on both sides of the still composition. If the sign of the derivatives differ from one another, a saddle-node bifurcation at instantaneous still composition is found. Otherwise, another distillate composition must be picked up until convergence. A region elimination method was implemented beginning with two candidate distillate compositions. A very easy way to calculate the sensitivity on a pinch branch on both sides of x_S from the derivative of the pinch branch with respect to the temperature T developed by Pöllmann et al. (1994) is employed.

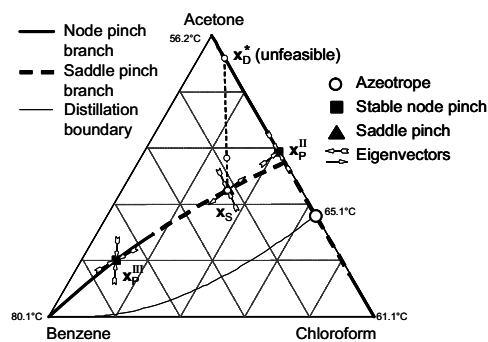


Figure 3(a). Pinch points corresponding to x_D^* .

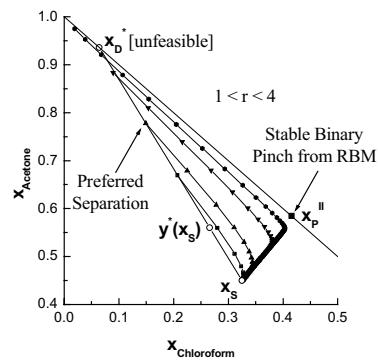


Figure 3(b). Results of simulations in Hysys.

As a final example, Figure 4(b) shows the distillate mole fraction versus the operation time for a column operating at constant distillate composition ($0 \leq t \leq 1.5$ h) and then at constant reflux ratio (until end of operation). The still is charged with a mixture of composition $x_S = (0.45, 0.325, 0.225)$ of acetone, chloroform and benzene, respectively. The second cut of variable distillate composition reveals the typical behaviour of systems showing stable distillation boundaries limiting the still path. In order to reproduce this behaviour, the code performs two equilibrium calculations for each instantaneous still composition. The equilibrium vector $y^*(x_S) - x_S$ is intersected with the acetone-chloroform axis to obtain the limiting distillate composition x_D^* . By performing an additional equilibrium calculation at x_D^* it can be detected if either acetone or chloroform can be achieved from the instantaneous still composition. Once the unstable node changes (from acetone to chloroform or vice versa) only preferred separation is allowed in order to describe batch operation. Therefore, a controlling pinch with the composition of the still controls the separation.

4. Conclusions

A very simple method to deal with the performance calculation of a batch rectifier processing near-ideal mixtures is presented. Key ingredients for the application of the method to highly nonideal mixtures are developed and highlighted with examples.

By studying the behavior of highly non-ideal mixtures several lessons were learned: i) the rectification triangle corresponding to the limiting distillate and reflux ratio gives a good approximation of the manifold of all potential profiles departing from the instantaneous still composition; ii) the method can be extended to deal with systems limited by controlling tangent pinch points and unstable boundaries (limiting distillate compositions) by including bifurcation analysis of the pinch map; iii) stable distillation boundaries limiting the still path can be detected through simple equilibrium calculations at each step of the integration of the conceptual model.

The main conclusion of this work is that the RBM together with bifurcation analysis has a great potential to model the behavior of highly non-ideal mixtures. Hence, it deserves additional research efforts.

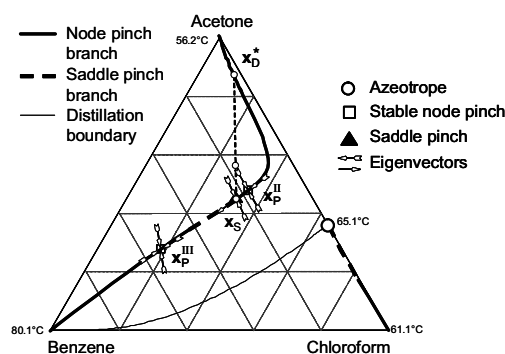


Figure 4(a). x_D^* near saddle-node bifurcation.

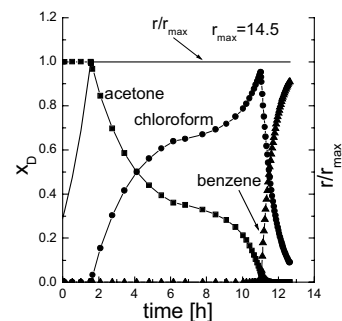


Figure 4(b). Distillate composition and reflux ratio evolution.

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Acknowledgements

The authors would like to acknowledge the financial support provided by the “Deutscher Akademischer Austauschdienst” of Germany, and ANPCyT-CONICET of Argentina.