Analysis of Closed Multivessel Batch Distillation of Ternary Azeotropic Mixtures using Elementary VLE Cells

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Abstract - Introducing the concept of elementary topological cells, we illustrate how vapor-liquid equilibrium (VLE) diagrams like distillation lines and isotherms maps may be used in analysis of the closed (total reflux) multivessel batch distillation column. An indirect level control strategy is implemented that eliminates the need for pre-calculated vessel holdups and makes the closed operating policy flexible and simple to implement in practice.

Keywords: Closed multieffect batch distillation, operation and control, distillation lines

INTRODUCTION

By closed multivessel batch distillation we mean a "total reflux" operation where the products are accumulated in vessels along the column (including the reboiler and condenser). There are no input or output streams, but the internal liquid reflux flows may vary during the operation causing accumulation or depletion of mass in the vessels. Thus, *closed system* is a more correct term than "total reflux", since we generally only achieve total reflux as time approaches infinity (i.e. steady state). Treybal (1970) proposed a closed (total reflux) operation of the conventional batch distillation column with a condenser vessel for separation of (ideal) binary mixtures. Kiva *et al.* (1988) extended this idea to separation of ternary azeotropic mixtures. Robinson and Gilliland (1950) proposed a combined system of a batch rectifier and a batch stripper column, later called the middle vessel column. A further generalization is the multivessel column suggested by Hasebe *et al*. (1995). Skogestad *et al.* (1997) proposed a simple feedback control strategy for operation of the closed multivessel batch distillation column where the reflux flow out of each vessel is manipulated to control the temperature at some location in the column section below. This indirectly adjust the vessel holdups and pure products can be collected from each vessel at the end of the operation. The feasibility of this strategy was demonstrated by simulations for an ideal four component mixture, and later experimental verification was given for a system of methanol, ethanol, n-propanol and n-butanol (Wittgens and Skogestad 1997). In this paper we study separation of ternary azeotropic mixtures in the closed three vessel or *middle vessel* column shown in Figure 1 where all three components (or azeotropes) are separated simultaneously during one closed operation.

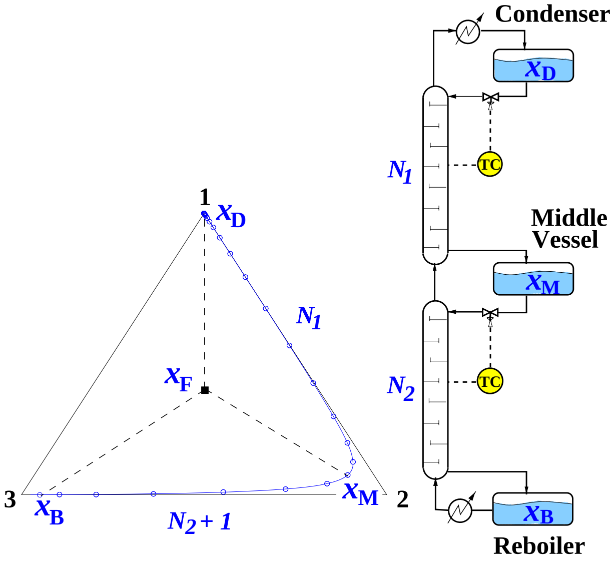

Figure 1: *Steady state composition profile in closed middle vessel batch distillation column (solid line with open circles) and mass balance lines (dashed) for a ternary ideal mixture of components 1, 2 and 3.*

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ELEMENTARY VLE CELLS

Distillation lines are defined as connection lines of chains of conjugated vapor-liquid equilibrium mapping vectors (Zharov 1968). Total reflux distillation column profiles at steady state coincide exactly with distillation lines as defined by Zharov (1968) and Zharov (1969) and Stichlmair (1988) for equilibrium staged columns. Simple distillation residue curves coincide exactly with total reflux packed distillation column profiles when all resistance to mass transfer is in the vapor phase (Serafimov *et al.* 1973, Pöllmann and Blass 1994). This make distillation line and residue curve maps as representations of the mixture's VLE particularly suited to identify feasible products at the limiting operating condition of total reflux. Serafimov *et al.* (1971) give a complete classification of possible topological structures of VLE diagrams for ternary mixtures. Within the 26 classified VLE diagrams one can identify four *elementary cells* that may be further categorized according to the shape of the distillation lines, or, equivalently, the simple distillation residue curves (Kiva *et al.* 1999). The idea is that by knowing the elementary cells we also have information about any complex VLE diagram. The four elementary topological cells are (Kiva *et al.* 1999):

I. *Node-saddle-node cell* - "triangular" cell with two nodes and one saddle. The distillation lines are either C- or S-shaped depending on the existence of univolatility lines causing inflexion points.

The simplest example of elementary cell I is Serafimov's zeotropic class 0.0-1. An example mixture that represent this class is the ideal system of methanol, ethanol and 1-propanol shown in Figure 2. Note that the distillation lines in Figure 2 are drawn as smooth curves (spline interpolation) through the chains of conjugated equilibrium vectors according to the definition by Stichlmair (1988). For the other example mixtures presented in this paper, the distillation lines are drawn with solid straight tie-lines between each point of conjugation. Liquid isotherms are contour plots of the bubble-point temperature surface and given as dotted lines in all the figures presented in this paper.

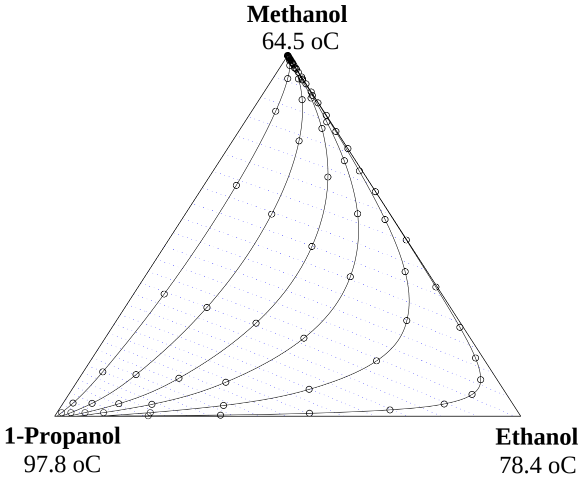


Figure 2: *Example mixture of elementary cell I: Distillation lines and liquid isotherms for the ternary zeotropic mixture of methanol, ethanol and 1-propanol at atmospheric pressure (Serafimov's class 0.0-1).*

II. *Node-saddle/saddle-node cell* - "rhombic" cell with opposite directed nodes and saddles. The distillation lines are either C- or S-shaped, or both.

The simplest example of elementary cell II is Serafimov's class 1.0-1a with one binary azeotrope and where the azeotrope-forming components are both saddle points. An example mixture that represent this class is acetone, methanol and water shown in Figure 3.

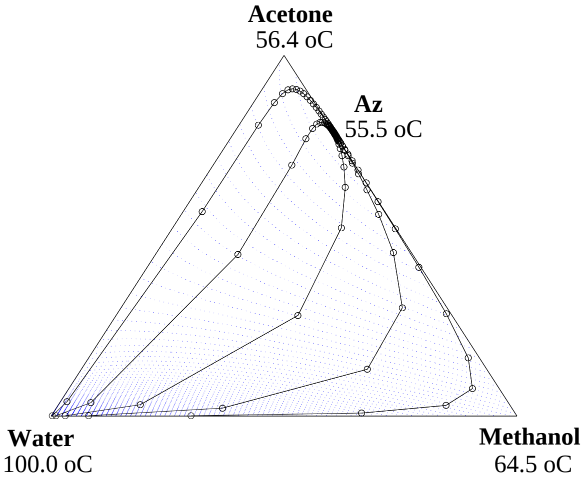


Figure 3: *Example mixture of elementary cell II: Distillation lines and liquid isotherms for the ternary azeotropic mixture of acetone, methanol and water at atmospheric pressure (Serafimov's class 1.0-1a).*

III. *Node-saddle-saddle-node cell* - "trapezoidal" cell with two saddles between unstable and stable nodes. The distillation lines are U-shaped.

The simplest example of elementary cell III is Serafimov's class 1.0-1b with one binary azeotrope and where the azeotrope-forming components are a saddle and a node.

IV. *Node-(saddle/saddle-saddle)-node cell* - "pentagonal" cell with two saddles between unstable and stable nodes and a saddle. The distillation lines are both C(S)- and U-shaped.

The simplest example of elementary cell IV is Serafimov's class 2.0-1 with two binary azeotropes and where the three azeotrope-forming components are all saddles.

Any mixture can be qualitatively represented by a combination of these elementary cells. A simple example is the mixture of acetone, chloroform and benzene shown in Figure 4 (Serafimov's class 1.0-2) where two "triangular" cells I with S-shaped distillation lines are combined.

In this paper, we present simulation results on closed middle vessel batch distillation for the example mixtures in Figure 2, 3, 4.

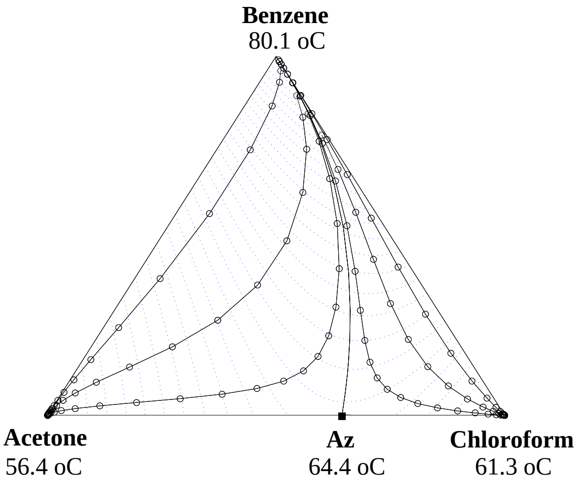


Figure 4: *Example mixture with distillation line boundary: Distillation lines and liquid isotherms for the ternary azeotropic mixture of acetone, chloroform and benzene at atmospheric pressure (Serafimov's class 1.0-2).*

MATHEMATICAL MODEL

The mathematical model of the closed multivessel batch distillation column used in the simulations presented in this paper are based on the following assumptions: equilibrium stages, negligible vapor holdup, constant molar liquid holdups on all trays (i.e. neglecting liquid dynamics), constant molar vapor flows (i.e. simplified energy balance), constant pressure, total condenser and ideal behavior in the vapor phase. The time and energy required to heat the feed charge to its boiling point is neglected ("hot" startup). We use the indirect level control strategy proposed by Skogestad *et al.* (1997) where the liquid reflux flowrates out of each vessel are adjusted based on temperature feedback control from the column section below.

SIMULATION RESULTS

In addition to some dynamic simulation results, we present the steady state values and composition profiles which would be achieved if we were to let the batch time approach infinity ($t \to \infty$). The column specifications and initial conditions for the simulations are given in Table 1.

Table 1: Column Data and Initial Conditions

Total no. of trays	30 (excl. reboiler)
No. of trays per section	$N_1 = 15$, $N_2 = 15$
Total initial charge	$H_{F_o} = 5.385$ kmol
Initial condenser holdup	$H_{D_o} = 0.035$ kmol
Initial middle vessel holdup	$H_{M_o} = 5.000$ kmol
Initial reboiler holdup	$H_{B_o} = 0.250$ kmol
Tray holdups (constant)	$H_j = 1/300$ kmol
Vapor flow (constant)	$V = 5$ kmol/h
Initial feed composition	$x_{F_o} = [0.33, 0.33, 0.33]$

In all the figures, the column composition profiles are given by solid lines with open circles for each tray. The temperature set-points are set to the mean value of pair of the desired products boiling points and are visualized by the corresponding liquid isotherms as dotted lines. The temperature measurements for the feedback controllers are on tray 8 in both sections of the middle vessel column (trays numbered from the top and down), see Figure 1.

Results on mixture of elementary cell I

The dynamic development of the composition profile for a mixture of methanol, ethanol and 1-propanol is illustrated in Figure 5. The steady state values of the purities and vessel holdups are given in Table 2 and are independent of the initial location or distribution of the feed charge. But, if the initial feed was charged to the reboiler instead of the middle vessel, as in Figure 5, we would have another dynamic development of the column composition profile.

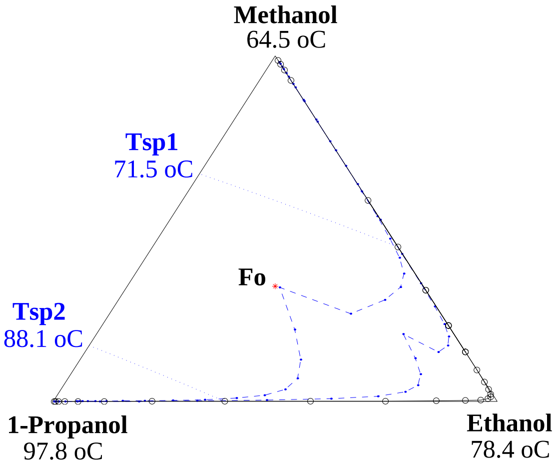


Figure 5: *Composition profiles in closed middle vessel batch distillation column for an equimolar feed of methanol, ethanol and 1-propanol: Instantaneous profiles at 6 minutes and 2 hours (dashed lines) and steady state profile (solid line with open circles).*

Table 2: Steady State Data for Mixture of Methanol, Ethanol and 1-Propanol

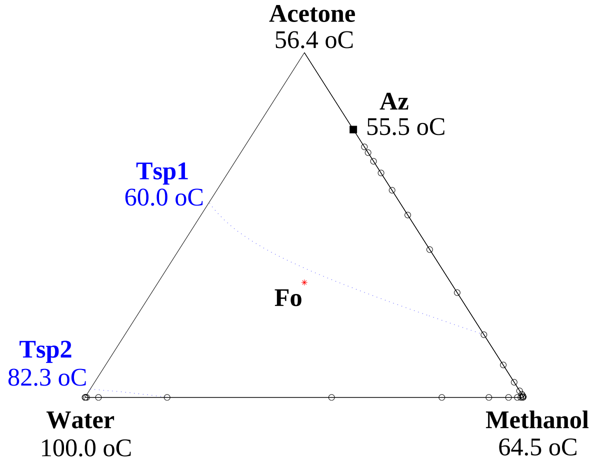
	Condenser	Middle	Reboiler
Holdup [kmol]	1.757	1.765	1.763
$x_{Methanol}$	**0.987**	0.021	0.000
$x_{Ethanol}$	0.013	**0.975**	0.001
$x_{1-Propanol}$	0.000	0.004	**0.999**
Recovery %	**96.6**	**95.9**	**98.1**

Results on mixture of elementary cell II

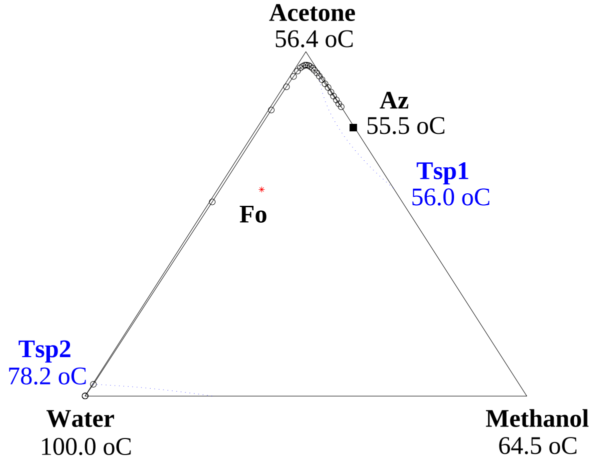
For the system of acetone, methanol and water given in Figure 3 we have a straight line from the azeotrope point to the zeotropic component vertex (pure water) that divides the composition space into two *feed regions* with different sets of possible steady state products in the closed middle vessel batch distillation column. In Figure 6 (a) and (b) the steady state composition profiles along the closed column are given for initial feed in the two feed regions. If the feed is shifted from the lower feed region to the upper feed region *without* changing the temperature set-points, we have no steady state.

Results on mixture with distillation line boundary

The steady state composition profile for an equimolar feed of acetone, chloroform and benzene is given in Figure 7.



(a) Lower feed region



(b) Upper feed region

Figure 6: *Steady state composition profiles in closed middle vessel batch distillation of acetone, methanol and water: (a) Lower feed* $x_{F_o} = [0.33, 0.33, 0.33]$*, (b) upper feed* $x_{F_o} = [0.6, 0.1, 0.3]$.

CYCLIC OPERATION

An alternative scheme of closed multivessel batch distillation for separation of ternary or multicomponent mixtures is the two vessel column operated in a sequence of closed operations, so-called cyclic operation. Sørensen and Skogestad (1994) found that the cyclic operating policy requires significantly less batch time for some ideal mixtures separations as compared to the conventional batch distillation operating strategies. While the achievable products in the closed middle vessel batch distillation column are limited by distillation line boundaries, the cyclic two vessel column is in some cases able to achieve products in two different distillation regions.

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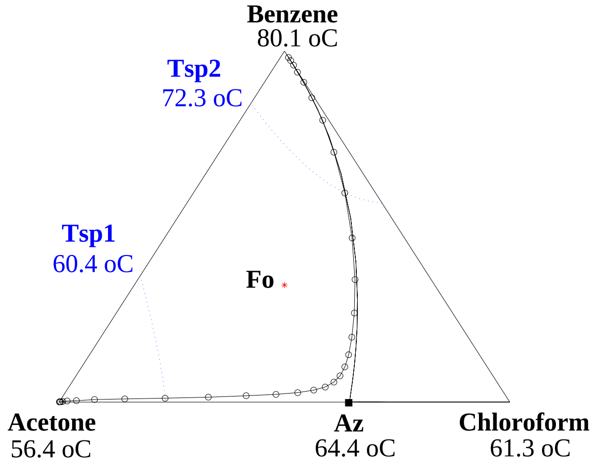

Figure 7: *Steady state composition profile in closed middle vessel batch distillation of acetone, chloroform and benzene.*

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