

Separation of ternary heteroazeotropic mixtures in a closed multivessel batch distillation–decanter hybrid

S. Skouras, S. Skogestad*

Norwegian University of Science and Technology, Department of Chemical Engineering, Sem Saelandsvei 4, Trondheim 7491, Norway

Received 8 November 2002; received in revised form 6 June 2003; accepted 6 June 2003

Abstract

The feasibility of a novel multivessel batch distillation–decanter hybrid for simultaneous separation of ternary heterogeneous azeotropic mixtures is addressed both theoretically and by simulations. The multivessel column is operated as a closed system without product withdrawal and the three components are accumulated in the vessels during one closed operation. The closed mode (total reflux) operation of the column enables us to make direct use of the distillation line (or residue curve) map. Simple rules for predicting the products in the vessels and identifying feasible separation regions are developed and applied on three common classes of azeotropic mixtures. This theoretical distillation line map analysis shows that Serafimov's classes 1.0-2, 1.0-1a and 2.0-2b can be separated in the proposed process. Dynamic simulations verify the feasibility of the novel process in separating heterogeneous azeotropic mixtures of these three topological classes.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Heteroazeotropic batch distillation; Hybrid processes; Closed systems; Azeotropic mixtures; Serafimov's classification

1. Introduction

1.1. Previous work on the multivessel column

Much attention has been given lately to a special batch distillation column configuration called 'multivessel column' or 'multi-effect batch distillation system' or 'batch distillation column with a middle vessel' or 'middle vessel column'. The novel column configuration was first mentioned by Robinson and Gilliland [1] in 1950, but the use of such a column for the separation of binary and multi-component mixtures was not analyzed until 1970, independently by Bortolini and Guarise [2] and Treybal [3]. The interest into this column configuration was renewed after the work of Hasebe et al. [4] and since then it often appears in the related literature.

The multivessel column (MVC) is a combination of a batch rectifier and a batch stripper. The column has both a rectifying and a stripping section, so it is possible to obtain a light and a heavy fraction simultaneously from the top and the bottom of the column while an intermediate fraction may also be recovered in the middle vessel. Several con-

figurations of the MVC have been suggested in the literature. One with a liquid bypass, where the liquid stream from the rectifying section bypasses the middle vessel and enters the stripping section [5], one where both liquid and vapor streams from the top section enter the middle vessel [6–11] and one with a vapor bypass from the bottom section to the top section of the column [4,12–16]. The last one, usually called vapor bypass configuration, is the most common in the literature and it is the one studied here (Fig. 1).

Until recently, most of the work on the MVC was for ideal or constant relative volatility systems. Hasebe et al. [4,12,13] studied the characteristics of the column for the separation of binary and ternary ideal mixtures. They also proposed the closed (total reflux) operation of such a column, where no distillate or bottom streams are taken out from the column and the products are accumulated in the vessels during the process. Davidyan et al. [6] presented a rigorous mathematical model for the MVC and tried to describe the dynamic behavior of the column. Barolo et al. [17,18] performed experiments in a continuous column modified in order to resemble to the MVC. They implemented different control configurations and also discussed the effect of some operating parameters on column performance.

For the closed operation of the MVC, with product accumulation in the vessels, a simple feedback control structure,

* Corresponding author. Tel.: +47-73-59-41-54; fax: +47-73-59-40-80.

E-mail addresses: skouras@chemeng.ntnu.no,
skoge@chemeng.ntnu.no (S. Skogestad).

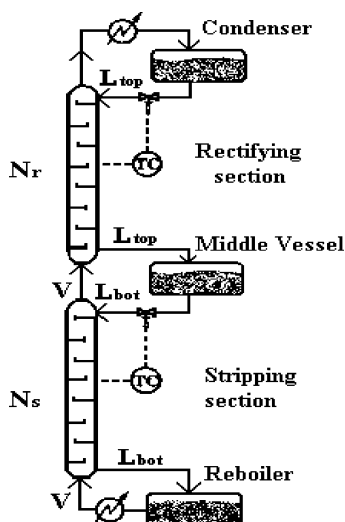


Fig. 1. The multivessel batch column with a vapor bypass.

based on temperature controllers, was proposed by Skogestad et al. [14]. The liquid flow rates out of each vessel are adjusted based on a temperature measurement in the middle of the column section below each vessel, as shown in Fig. 1. The temperature setpoints are simply taken as the average of the boiling points of the two components (or azeotropes) separated in this section. The feasibility of this simple control strategy was demonstrated both by simulations and experiments by Wittgens et al. [15]. A constant relative volatility quaternary system was studied and at the end of the process four pure products were accumulated at the vessels. This control strategy was also proved to be robust and achieved high purity products independent of uncertainties in the feed composition.

The first who studied the performance of the MVC in the separation of azeotropic mixtures was Safrin et al. [7] and Safrin and Westerberg [8]. The case of extractive batch distillation with a heavy entrainer continuously added from the top of the multivessel column was investigated. Warter and Stichlmair [5] and Hilmen et al. [16] reported some advantages of this novel process over conventional extractive batch distillation. Recently, Warter et al. [19] showed experimental results on extractive distillation in the multivessel column. A binary azeotropic mixture of water–ethanol was separated by using ethylene glycol as entrainer.

In a series of three papers, Cheong and Barton [9–11] developed a mathematical model in order to study the qualitative dynamics of the MVC for the separation of homogeneous azeotropic mixtures. The theoretical insights from the analytical tools developed, were also verified by simulations. Warter and Stichlmair [20] has also showed simulated results for the separation of binary azeotropic mixtures by using homogeneous entrainers, which are added batchwise in the original mixture. They showed ways to cross the distillation boundaries by placing the feed at the concave side of the boundary and by manipulating the vapor flows in the two

sections of the column. In this way, all three original components were recovered in pure form. Hilmen [21] provided also simulated results on the closed multivessel batch distillation of ternary homogeneous azeotropic mixtures when the control strategy proposed by Skogestad was implemented. In a recent work, Rodriguez-Donis et al. [22] showed results when heterogeneous entrainers were used instead. The column was operated as an open system with product withdrawal from the top and the bottom vessel and a decanter was combined with the MVC for doing the liquid–liquid split, in a distillation–decanter hybrid process.

1.2. Previous work on azeotropic systems

Throughout this work, ideas and results presented by Kiva et al. [23] and Hilmen et al. [24] are frequently cited and used. These two papers mainly comprise published results on azeotropic systems from the Russian literature, which are very little known in the West. Three important issues from these papers are frequently cited in this study. Thus, it is wise to briefly present them.

The first issue is Serafimov's classification for azeotropic systems. Most of the people in the West are familiar with the classification of azeotropic mixtures in 113 classes proposed by Matsuyama and Nishimura in 1977 [25]. This classification was recently included also in Perry's Chemical Engineering Handbook [26]. However, after the work of Kiva et al. [23] and Hilmen et al. [24], it became known that in the former Soviet Union a complete classification of feasible VLE structures for ternary systems was presented already in 1970. Serafimov showed that the feasible structures of VLE diagrams for azeotropic mixtures are limited by topological and thermodynamical constraints and classified them under 26 topological structures. The foundation of this work was represented again in 1996 by Serafimov [27], but even this recent book, as well as the original papers from the Soviet Union, are difficult to access. Kiva et al. [23] showed that among the 113 Matsuyama's classes there was still only the 26 topologically distinct structures of Serafimov. The correspondence between the two classifications was also provided in Kiva et al. (see Table 3 in [23]).

The second issue frequently mentioned here is Rehetov's statistics on the physical occurrence of different classes of azeotropic systems. All 26 Serafimov's classes are topologically and thermodynamically feasible but their occurrence is determined by the probability of certain combinations of molecular interactions. Kiva et al. [23] provided some statistics on the physical occurrence of these 26 classes. The statistics were given to Kiva et al. by Dr. S.A. Reshetov and the original source is not available [23]. The hereafter called 'Reshetov's statistics' are based on thermodynamic data for 1609 ternary systems from which 1365 are azeotropic. The database covers data published from 1965 to 1988. The results show that 16 out of the 26 Serafimov's classes were reported in the literature. Although Reshetov's statistics do not necessarily reflect the real occurrence in nature they can

be used (and are used in this study) as an indicator of common azeotropic classes that worth further investigation.

The third issue mentioned here is the idea of the elementary cells. Hilmen et al. [24] found that there are only four elementary topological cells (denoted I–IV) constituting all 16 Serafimov's classes reported in Reshetov's statistics. An elementary cell is defined as a residue curve region taken with its boundaries and it has one unstable and one stable node and a set of saddle points. The idea of elementary cells is a simplification made to reduce the number ternary VLE structures and is useful for preliminary qualitative analysis of azeotropic distillation, as it will become obvious later. The 26 Serafimov's topological classes, along with Reshetov's statistics on the physical occurrence and the elementary cells

within the 26 classes are shown in Fig. 2 (reprinted from Hilmen et al. [24]).

1.3. This study

This work addresses heteroazeotropic batch distillation in a closed multivessel distillation–decanter hybrid. The basic principle behind the novel process is that the heteroazeotrope accumulated in the decanter vessel of the MVC is separated into its two liquid phases by condensation and decantation. One of the phases is the entrainer-rich (organic) and the other is the entrainer-lean (aqueous) phase. The organic phase is then recycled to the column, while the aqueous phase is accumulated in the decanter vessel. Part of the separation

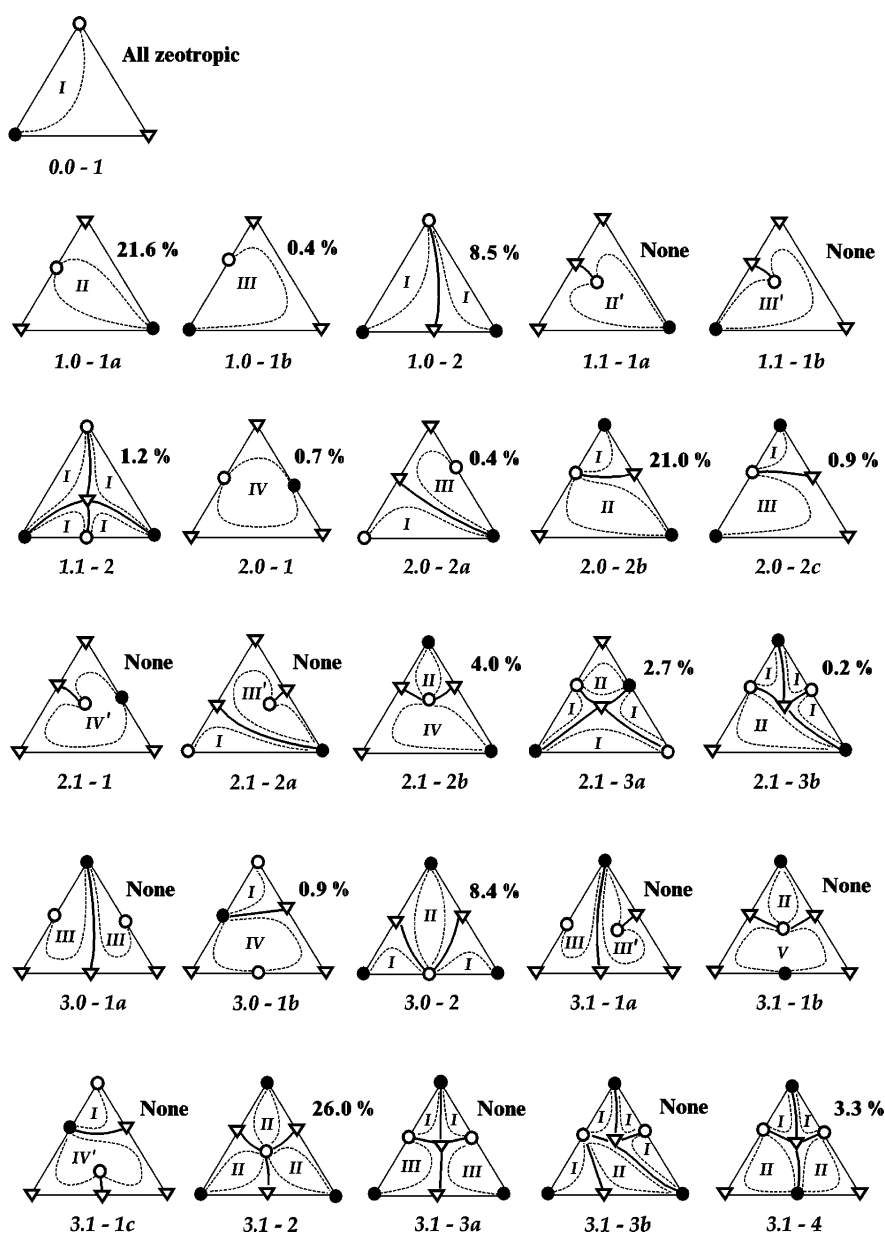


Fig. 2. Serafimov's 26 topological classes, elementary cells and Reshetov's statistics: (○) Unstable node; (△) saddle; (●) stable node. (Reprinted from [24].)

is performed by distillation while the liquid–liquid split in the decanter is used for crossing the distillation boundary. At the end of the process two pure components and an aqueous phase rich in the third component (water) are recovered from the vessels.

Three classes of azeotropic mixtures, namely Serafimov's classes 1.0-2, 1.0-1a and 2.0-2b are studied here. Each one of them represents a class of azeotropic systems frequently found in nature, according to Reshetov's statistics. Thus, the first system studied, class 1.0-2, corresponds to class 020 and 400 of Matsuyama and Nishimura [25] and represents 8.5% of the azeotropic systems reported in the literature. The second system of class 1.0-1a, corresponds to Matsuyama's and Nishimura's classes 100 and 030 and represents 21.6% of the azeotropic systems reported. Finally, the third system is that of class 2.0-2b or classes 102, 120 and 021 and represents 21% of the azeotropic systems. In total, the three classes represent more than half (51.1%) of all azeotropic systems reported, which simply indicates the practical importance of this study.

The rest of the paper is divided in two main parts. In the first one, the theoretical foundation of this work is presented. The relationship between the steady-state column profile and the distillation lines is established for the closed operation of the multivessel column. Moreover, simple rules for predicting the feasible products in the vessels based on the stability of the stationary points of the distillation line map are presented. Finally, the distillation line maps are used for identifying classes of azeotropic mixtures that could be separated in the novel column. Simple rules for identifying feasible separation regions are presented and applied on three common classes of azeotropic mixtures, namely classes 1.0-2, 1.0-1a and 2.0-2b. In the second part of the paper, results based on dynamic simulations of the proposed hybrid process are presented. First, the model used in our simulations is presented and, second, the feasibility of separating the above three classes of mixtures in the closed multivessel column is exhibited. The paper ends with some concluding remarks.

2. Theoretical foundation

2.1. Steady-state column profile and distillation lines

Distillation lines or residue curves are widely used as a graphical tool to qualitatively predict feasible separations in ternary and multicomponent azeotropic distillation. A distillation line named also tie-line curve, is a chain of conjugated vapor–liquid equilibrium vectors. The projection of this sequence of repeated equilibrium phase mappings onto the composition space is a discrete line that follows the direction of decreasing boiling temperature, that is opposite to that of a residue curve.

Stichlmair [28] has shown that a distillation line corresponds to the liquid composition profile of an equilibrium-staged column under total reflux. On the other hand,

Poellmann and Blass [29] have shown that a residue curve coincides exactly with the composition profile of a packed column under total reflux, when all resistance to mass transfer is in the vapor phase. Therefore, distillation line and residue curve maps are a useful tool for identifying feasible distillation products at the limiting operating condition of total reflux.

The multivessel column is operated under 'total reflux' or more precisely as a closed system since total reflux is only achieved as we approach steady state. This operating mode allows us to make direct use of the distillation lines or residue curves, thus extracting valuable information about the possible products in the vessels as we reach steady state. In this work, we use distillation line maps. However, using residue curve maps would not have been less useful or informative.

Hilmen [21] states that in the closed multivessel column the correspondence between the distillation lines and the steady-state column profile is simple and straightforward; "the steady-state vessel product compositions of a closed multivessel batch distillation column are connected by a distillation line with the given number of equilibrium trays. In addition, the material balances must be satisfied". At steady state the material balances, in the case of zero or negligible column holdup, can be written as:

Overall:

$$M_F = M_T + M_M + M_B \quad (1)$$

Component:

$$\begin{aligned} M_F x_F &= M_T x_T + M_M x_M + M_B x_B \Rightarrow M_M (x_F - x_M) \\ &= M_T (x_T - x_F) + M_B (x_B - x_F) \end{aligned} \quad (2)$$

The above material balances reveal that the feed composition (x_F) is a linear combination of the vessel compositions (x_T , x_M , x_B) and the vessel holdups must obey the so-called lever rule. In addition, the steady-state vessel compositions (x_T , x_M , x_B) must lie on the same distillation line because total reflux has reached at steady state.

All the above are visualized in Fig. 3 for the case of a simple zeotropic mixture. The light component (L) is the unstable node (un), the intermediate component (I) is the saddle (s) and the heavy component (H) is the stable node (sn). Hilmen [21] concludes with the statement: "The feasible region of vessel compositions in the multivessel column are enclosed by the feed distillation line and the borders of the current feed distillation region and by the material balance triangle connecting the unstable node, the stable node and one of the saddles of the current feed distillation region".

Most of the people in the literature are using residue curves maps and others are using distillation line maps. Since distillation lines are running to the opposite direction of residue curves the characterization of a stationary point as a stable or unstable node is somewhat confusing. What is an unstable node in a residue curve map is a stable node in a distillation line map and vice versa. Luckily, this problem does not arise with saddles.

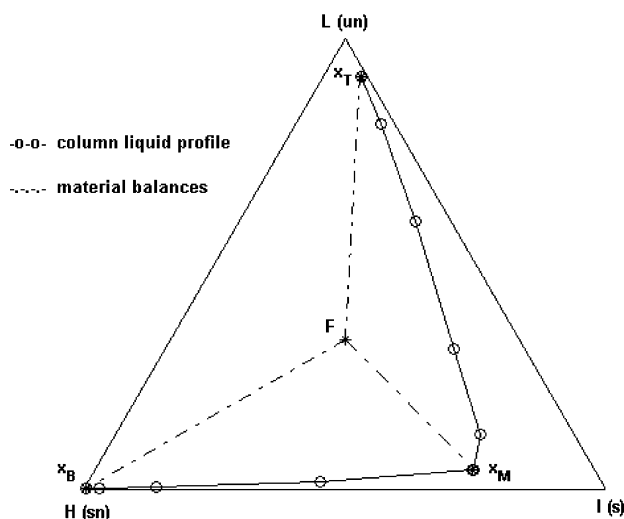


Fig. 3. Steady-state column profile and material balance triangle.

We believe that is less confusing to use a convention instead of a definition. The convention used here is that the light component is the unstable node and the heavy component is the stable node. Thus, an unstable (stable) node is a termini (origin) of distillation lines (residue curves), e.g. the light component (L) in Fig. 3. A saddle is both an origin and a termini of distillation lines (residue curves), e.g. the intermediate component (I). Finally, a stable (unstable) node is an origin (termini) of distillation lines (residue curves), e.g. the heavy component (H).

2.2. Simple rules for predicting the products in the vessels

Suppose that a zeotropic mixture, like the one shown in Fig. 3, is to be separated in the closed multivessel column. Predicting the possible products in the vessels is a simple task. The interior of the composition space is not divided in different distillation regions and the ternary system has three stationary points, which are the pure components. Not surprisingly, the light component is the unstable node and it will be accumulated in the top vessel, the intermediate is the saddle and it will be the middle vessel product and the heavy component is the stable node, thus accumulating in the bottom vessel.

The situation becomes more complicated when an azeotropic system is to be separated. In this case, the interior of the composition triangle can be separated in many distillation regions separated by distillation boundaries and the number of the stationary points is increasing. The distillation lines map will then have one of the 26 topologically different structures shown in Fig. 2. These maps carry all the necessary information for predicting the products in the vessels of a closed multivessel column. Note that the distillation line map is a simple phase transformation map and, therefore, depends solely on the VLE of the system and not on any operational or design characteristics

of the column configuration where the separation will be performed.

The question is and how we can use these distillation line maps (VLE maps) in order to predict the products in the vessels when the separation task will be performed in a closed multivessel column. The following simple rules can be used.

- (I) The feed F defines the distillation region where the column is operated. The column liquid profile is restricted in this region since the column is operated under total reflux.
- (II) The stability of the stationary points (pure components and azeotropes) of the operating region defines the products in the vessels. A distillation region has only one unstable node, only one stable node and may have more than one saddles. The top vessel product will be the unstable node of the region, the middle vessel product will be a saddle and the bottom product will be the stable node of the region.
- (III) When there are more than one saddles in the operating region then the shape of the individual distillation lines will point out which feeds ‘force’ to one saddle or the other.

It should be noted here that unless we have enough stages in the column, there would not be pure components in the vessels. Therefore, throughout this work we assume we have enough stages in the column sections so as to achieve pure products.

2.3. Distillation line maps and feasible separations in a distillation–decanter hybrid

We have discussed until now how the composition profile in the closed multivessel column is related to the distillation line maps and how we can predict the possible products in the vessels based on the stability of the stationary points of the distillation line maps. We have also mentioned that in this work we try to separate ternary heteroazeotropic mixtures by combining distillation and decantation in one unit operation. The objective is to recover each one of the three original components in each one of the vessels. The main idea behind the novel process is that one component can be recovered in the decanter vessel just by taking advantage of the liquid–liquid split, while the other two components are recovered by distillation. The component accumulated in the decanter is recovered in a composition determined solely by the liquid–liquid split (binodal curve), while the other two components can be recovered in pure form. If further purification is required for the component accumulated in the decanter this can be done in a subsequent distillation step.

Having in mind, in principle, how the mixture will be separated, the next question to be replied is “which classes of azeotropic mixtures can be separated in the closed multivessel column”. In order to reply to this question in a systematic way, we should know what classes of azeotropic

mixtures are feasible. Serafimov's classification is used for this reason.

It should be noted that the work of Serafimov is for homogeneous mixtures. To the best of our knowledge, a classification specifically for heterogeneous azeotropic mixtures has not been conducted yet. However, as noted by Kiva et al. [23], the topology of a residue curve map of a heterogeneous mixture does not differ from that of a homogeneous mixture with the same set of stationary points [23]. The main difference between heterogeneous and homogeneous mixtures is that a heteroazeotrope can only be a minimum-boiling azeotrope, while a homogeneous azeotrope can be either minimum- or maximum-boiling azeotrope. Thus, a heteroazeotrope can be either unstable node or saddle and can never be a stable node. Therefore, Serafimov's classification is in general valid also for heterogeneous mixtures but someone should always keep in mind that a maximum-boiling azeotrope could never be a heterogeneous one.

Given now a specific topological class, that is one of the 26 Serafimov's classes of Fig. 3, the question to be replied is whether this class can be separated in the closed multivessel distillation–decanter hybrid or not. The following rules can be used.

- (I) Choose an operating region. Two of the original components should be stationary points of this region. One of the components should necessarily be a stable node while the other can be either a saddle or an unstable node.
- (II) The heteroazeotrope should also be a stationary point of the operating region. The heteroazeotrope can be either unstable node or saddle.
- (III) Check all the operating regions in each class.

Rule I assures that two pure components are accumulated in the vessels by distillation. Rule II makes sure that the third component is recovered in the decanter after decanting and refluxing one of the phases back in column. Rule III just makes sure that the whole composition space is checked.

2.4. Applying the rules

We will show now how these rules can be applied in practice for different classes of azeotropic systems. Reshetov's statistics are used as indicators of the practical importance of each class. Systems with one binary heteroazeotrope and systems with two binary azeotropes, one of which heterogeneous, are investigated. These systems are classified under seven out of the 26 feasible Serafimov's classes, as we see in Fig. 2. The classes considered are 1.0-1a, 1.0-1b, 1.0-2 (systems with one binary azeotrope) and 2.0-1, 2.0-2a, 2.0-2b and 2.0-2c (systems with two binary azeotropes). According to Reshetov's statistics, all of these classes have been reported in the literature and they represent 53.5% of the azeotropic mixtures.

2.4.1. Systems with one azeotrope

According to Serafimov's classification there are three feasible topological classes for systems with one binary heteroazeotrope. Those are classes 1.0-2, 1.0-1a and 1.0-1b. Reshetov's statistics show that all three classes have been reported in the literature but classes 1.0-2 and 1.0-1a are by far the most common with a physical occurrence of 8.5 and 21.6%, respectively (see Fig. 2). Thus, classes 1.0-2 and 1.0-1a will be further studied and we will show that they can be separated in the closed multivessel column.

Topological class 1.0-2

The system methanol–water–1-butanol is classified under class 1.0-2. Water and 1-butanol form a heterogeneous azeotrope and an immiscibility gap over a limited region of ternary compositions exists. The distillation line map and the stability of the stationary points of the system are shown in Fig 4(a). One distillation boundary, running from methanol (unstable node) to the binary heteroazeotrope (saddle), divides the composition space in two distillation regions, thus limiting the feasible products under distillation. In Fig. 2, it is shown that class 1.0-2 consists of two elementary Cells I.

Suppose a feed F placed at the left distillation region, as shown in Fig 4(a). Rules I and II are satisfied for this operating region since two of the original components are stationary points of this region and the same is valid for the heteroazeotrope. Methanol is the unstable node, 1-butanol the stable node and the heteroazeotrope a saddle. Thus, the left distillation region is a feasible operating region and topological class 1.0-2 is a possible candidate for separation in the closed multivessel column.

In more details, a feed F in the left distillation region will provide the unstable node (methanol) as a top product, the saddle (binary heteroazeotrope) as a middle vessel product and the stable node (1-butanol) as a bottom product. Water seems impossible to be taken as a product in a column operated in this feed region since it belongs to a different distillation region and the distillation boundary cannot be crossed under total reflux. However, the fact that the azeotrope accumulated in the middle vessel is heterogeneous provides a straightforward way of overcoming the azeotropic composition and cross the distillation boundary, namely by decantation. The heteroazeotrope consists of two liquid phases, one rich in water (aqueous phase) and one rich in 1-butanol (organic phase). A decanter is performing the liquid–liquid split and the organic phase is refluxed back in the column. The aqueous phase is gradually accumulating in the middle vessel. Most of the water is then recovered in the middle vessel with a purity determined by the binodal curve, while the other two components are recovered pure in the top and bottom vessels. In this way, the column can be operated in both distillation regions and all three components can be recovered in the vessels in one closed operation. Thus, a distillation–decanter hybrid like the one shown in Fig. 4(b), where a decanter is placed in the middle

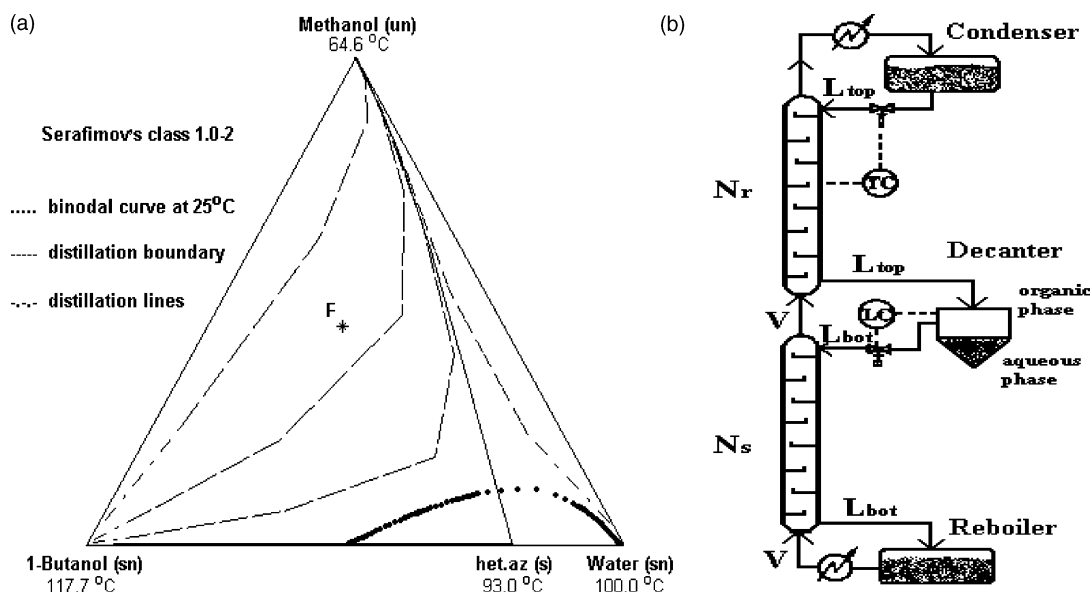


Fig. 4. (a) Azeotropic mixture of Serafimov's topological class 1.0-2. (b) Multivessel batch distillation–decanter hybrid (decanter in the middle).

vessel, seems like a promising alternative. Simulations shown in the third part of the paper will prove the feasibility of this process.

Suppose now that the column is operated in the right distillation region of Fig. 4(a). Methanol is again the unstable node of the region, water the stable node and the heteroazeotrope the saddle. Rules I and II are satisfied which means that this region is also a feasible region for the closed multivessel column. However, this would not be practical for this specific mixture. Operating the column in the right distillation region will provide water as the bottom product, since water is the stable node in this region. The aqueous phase should be refluxed back in the column, while the organic phase should be accumulated in the middle vessel. A look at the binodal curve in Fig. 4(a) reveals that the organic phase contains only 50% butanol, so the butanol cannot be recovered with acceptable purity in this way. However, this is a special characteristic of this mixture and operating the column in the right distillation region could be feasible and practical for another mixture with a different shape in the binodal curve.

Topological class 1.0-1a

The system ethyl acetate–water–acetic acid is a system classified under Serafimov's class 1.0-1a. Acetic acid and water is a close-boiling (low relative volatility) system and high purity acetic acid is difficult to be recovered from its aqueous solutions. The addition of a light heterogeneous entrainer eases the separation. One such entrainer can be ethyl acetate. The corresponding distillation lines map modeled by NRTL along with the stability of the stationary points is shown in Fig. 5(a).

The heteroazeotrope is the only unstable node and acetic acid is the only stable node of the system. The system has two saddles (ethyl acetate and water). Since there are no

repeated nodes of the same type, stable or unstable, the necessary condition for the existence of a boundary is not fulfilled [23] and no distillation boundary exists. Thus, no matter where the feed is placed, the heteroazeotrope will appear in the top and acetic acid in the bottom vessel. However, the product in the middle vessel can be either ethyl acetate or water (saddles) depending on the feed. This is obvious from the shape of the individual distillation lines. Imagine a straight line connecting the acetic acid vertex with the heteroazeotropic point vertex in Fig. 5(a). Feeds in the upper part of this imaginary line will provide ethyl acetate in the middle vessel, while feeds in the lower part of this imaginary line will provide water in the middle vessel. Note that this imaginary line is not a distillation boundary of the distillation line map (simple phase transformation map) since the definition for a distillation boundary is not fulfilled. From the distillation line map (Fig. 5(a)) is obvious that it is not possible to separate all original components in one closed operation of the multivessel column unless we take advantage of the heteroazeotrope accumulating in the top vessel. Class 1.0-1a is an example of elementary Cell II, as can be seen in Fig. 2.

Imagine now a feed F placed at the upper feed region, as shown in Fig. 5(a). That is the region over the imaginary line mentioned before. Rules I and II are satisfied in this operating region. Two of the pure components are stationary points in this region and the same is valid for the heteroazeotrope. Thus, the upper feed region is a feasible operating region and topological class 1.0-2 is a possible candidate for the closed multivessel column. Acetic acid (stable node) will be the product in the bottom vessel, while ethyl acetate (saddle) will be the product in the middle vessel. The heteroazeotrope accumulating in the top vessel is decanted and the organic phase, rich in ethyl acetate, is refluxed back in the column. Thus, the top vessel is steadily enriched in water (until the

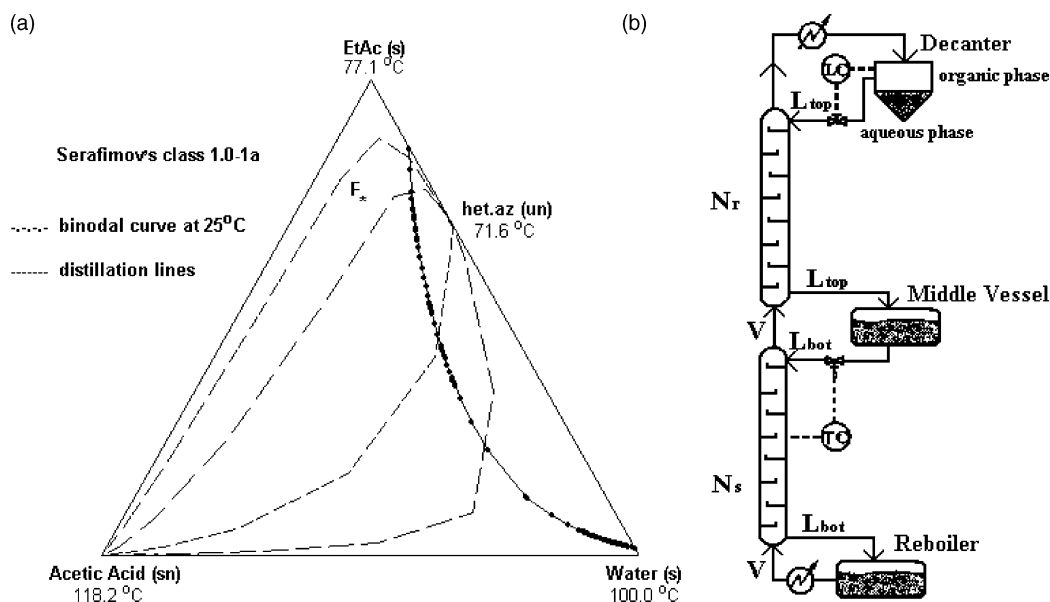


Fig. 5. (a) Azeotropic mixture of Serafimov's topological class 1.0-1a. (b) Multivessel batch distillation-decanter hybrid (decanter in the top).

point determined by the liquid–liquid equilibrium), while the middle vessel is enriched in ethyl acetate. Acetic acid remains in the bottom of the column because of low volatility. In this way, all components can be recovered in the vessels at the end of the process in a distillation–decanter hybrid, where the decanter is placed at the top of the column, as shown in Fig. 5(b). Simulations in the next part of the paper will exhibit the feasibility of the proposed process.

Operating the column in the lower feed region of Fig. 5(a) would not be practical, even if the process is feasible according to Rules I and II. The first reason is again the shape of the binodal curve. In this operating region, water is recovered in the middle vessel and the aqueous phase should be refluxed back in the rectifying section of the column. However, the binodal curve shows that the organic phase, that would be accumulated in the top vessel in this case, still contains a lot of water. The second reason is that in this operating region the stripping section of the column performs a water–acetic acid separation with a low driving force because of the low relative volatility between water and acetic acid. But recall that it was exactly this difficult separation that we tried to enhance by adding the entrainer (ethyl acetate). So, operating the multivessel column in the lower feed region does not sound wise from the practical point of view. However, theoretically, the separation would be feasible no matter where the feed was placed, if water and acetic acid were not a close-boiling system and if the binodal curve had a different shape.

2.4.2. Systems with two azeotropes

Until now we have studied systems with only one azeotrope. In the following we will show that even more complicated systems with two binary azeotropes can be

separated in the closed multivessel column. One of the two azeotropes will be heterogeneous while the other will be homogeneous. In Serafimov's classification there are four feasible topological classes with two binary azeotropes, namely classes 2.0-1, 2.0-2a, 2.0-2b and 2.0-2c. Topological class 2.0-2b is by far the most common and represents 21% of all azeotropic mixtures reported in Reshetov's database (Fig. 2). Thus, this class will be further studied and we will show that it can be separated in the closed multivessel column.

Topological class 2.0-2b

The system benzene–water–1,4 dioxane is an example of topological class 2.0-2b. Water and 1,4-dioxane cannot be separated by simple distillation because they form a minimum homoazeotrope. However, their separation is possible in the presence of a light entrainer that forms an azeotrope and is partially immiscible with water. Benzene was chosen as such a light entrainer. The distillation line map of the ternary system formed is shown in Fig. 6 and is an example of class 2.0-2b.

The heteroazeotrope is the unstable node while the homoazeotrope is one of the two saddles. There is one distillation boundary running from the heteroazeotrope to the homoazeotrope, thus dividing the composition space in two distillation regions. Therefore, not all three components can be separated in one column since they belong to different distillation regions. However, we will show that if we take advantage of the heteroazeotrope, this system can be separated in the closed multivessel column. Class 2.0-2b is a combination of elementary Cells I and II, as shown in Fig. 2. The left distillation region is an example of Cell II, while the right region is of Cell I type.

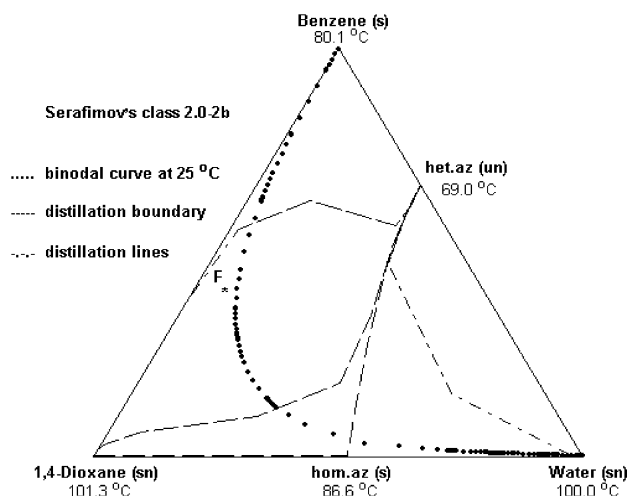


Fig. 6. Azeotropic mixture of Serafimov's topological class 2.0-2b.

Let us assume a feed F placed in the upper part of the left distillation region (Fig. 6). That is the region over the imaginary straight line connecting the stable node of the region with the unstable node. Dioxane is the stable node and benzene is the saddle of the region. Moreover, the heteroazeotrope is the unstable node of the region. Rules I and II are satisfied and, therefore, this region is a feasible one for the closed multivessel–decanter hybrid. Dioxane will be the bottom product, while benzene will be the product in the middle vessel. The heteroazeotrope is accumulated at the top of the column and after decantation the organic (benzene rich) phase is refluxed back in the column. In this way, the top vessel is steadily enriched in water, while the middle vessel is enriched in benzene. Dioxane is remaining in the bottom section of the column. At the end of the process, all three original components can be recovered in the vessels. The decanter should be placed in the top of the column, as shown in Fig. 5(b). Simulations in the next part of the paper will prove the feasibility of this process.

Class 2.0-2b exhibits some similarities with class 1.0-1a presented earlier. The left distillation region of class 2.0-2b is of elementary Cell II type. The separation of class 2.0-2b is feasible in the upper part of Cell II. The same was true for class 1.0-1a. So, the feasible region is common for both classes and it is the upper part of Cell II. Actually, it was class 1.0-1a and the characteristics of the upper part of Cell II that led us in class 2.0-2b as a possible candidate for separation in the hybrid process. This example illustrates the potential of the idea of elementary cells in reducing the complexity of the VLE diagrams and how the elementary cells can be used for preliminary qualitatively analysis of azeotropic distillation. However, a lot more work has still to be done in this area before general more sophisticated rules can be formulated.

If we try to operate the column in the lower left distillation region (lower part of Cell II) the separation would be infeasible. In this case, the homoazeotrope would be the product

in the middle vessel and the separation would stop. Both Rules I and II are violated in this region and the operating region is infeasible. The same is true for a feed in the right distillation region (Cell I). Rules I and II are not satisfied and the region is infeasible.

3. Simulations

3.1. The model

The model used in our simulations consists of overall and component material balances; vapor–liquid equilibrium and liquid–liquid modeled by NRTL equation [30–32]; indirect level control in the vessels with P temperature controllers; direct level control in the decanter with a PI level controller and temperature estimations in the stages by a bubble point calculation under atmospheric pressure.

The model is based on the following assumptions:

Staged distillation column sections; constant vapor flows (boilup) in the column; constant molar liquid holdup on all stages and negligible vapor holdup; perfect mixing and equilibrium in all stages; ideal vapor phase, except in the case of acetic acid where vapor phase association (dimerisation) is considered.

The resulting mathematical model takes the form of a set of differential and algebraic equations (DAE system) with a total of $(N_c + 1)(N_T + 3)$ state variables, where N_c is the number of components and N_T is the total number of stages inside the column plus the three vessels. The resulting DAE system is solved in Matlab with the DAE solver ODE15s [33].

Most of the initial feed is placed in the reboiler. This is the most practical and it is also optimal in most cases, in terms of batch time requirements. Initial stage compositions equal that of the feed and initial temperature is that of the feed in its boiling point. The liquid holdup in the column is negligible compared to the initial charge (almost 2% of the feed). The ratio of the vapor flow relative to the feed (V/F) is a measure of how many times the feed is reboiled and it is about once per hour. Column, controller and thermodynamic data for all simulations are given in Appendix B (Tables B.1–B.3).

3.2. Procedure

The separation is performed in two steps.

Step 1: The composition profile in the column is built up. The heteroazeotrope is accumulated in a vessel and no decantation is performed yet. The feedback control strategy proposed by Skogestad et al. [14] is applied. Two P temperature controllers are used for indirect level control in the top and middle vessel, as shown in Fig. 1. Simulations are stopped when all of the heteroazeotrope is accumulated in the corresponding vessel.

Step 2: Decantation starting. The two immiscible phases are separated and the organic phase is refluxed back in the column. Final products are accumulated in the vessels at the end of this step. The control strategy is partially changed. A PI level controller is used for direct level control in the decanter vessel, as shown in Figs. 4(b) and 5(b). The controller assures that all of the organic phase formed in the decanter is refluxed back in the column. A P temperature controller controls the level in the other vessel as before. Simulations are stopped when there is no more organic phase formed in the decanter and all of the aqueous phase has been accumulated.

3.3. Results

Topological class 1.0-2

Step 1: The feed F is placed at the left distillation region, the composition profile in the column is built up and the products are accumulated in the vessels. Methanol is the unstable node of the region and starts accumulating in the top vessel. The saddle heteroazeotrope is accumulated in the middle vessel, while the bottom vessel is getting enriched in 1-butanol, which is the stable node of the feed region. Fig. 7(a) illustrates Step 1 of the process and shows the evolution of the compositions in the three vessels. The steady-state column liquid profile and the final products in the vessels (x_T , x_M , x_B) are also depicted in the figure.

Step 2: The heteroazeotrope accumulated in the middle (decanter) vessel consists of two immiscible liquid phases. The two phases are decanted and the organic phase (rich in 1-butanol) is refluxed back in the column. The 1-butanol previously ‘trapped’ in the azeotrope is now stripped down in the column and enters the bottom vessel. The aqueous phase

Table 1

Steady-state results for the three azeotropic systems

Class 1.0-2: Methanol–water–1-butanol			
Holdup (kmol)	1.771	1.809	1.704
X_{methanol}	1.000	0.000	0.000
X_{water}	0.000	0.981	0.000
$X_{1\text{-butanol}}$	0.000	0.019	1.000
Recovery (%)	98.7	98.9	94.9
Class 1.0-1a: Ethyl acetate–water–acetic acid			
Holdup (kmol)	0.821	3.680	0.784
X_{EtAc}	0.016	1.000	0.000
X_{water}	0.984	0.000	0.000
X_{acAc}	0.000	0.000	1.000
Recovery (%)	100	97.6	97.0
Class 2.0-2b: Benzene–water–1,4-dioxane			
Holdup (kmol)	0.269	2.351	2.665
X_{benzene}	0.001	0.999	0.000
X_{water}	0.999	0.000	0.000
X_{dioxane}	0.000	0.000	1.000
Recovery (%)	99.8	96.9	99.0

is accumulated in the middle vessel while the methanol stays at the top of the column. Fig. 7(b) shows how the middle vessel is getting enriched in water. The water composition in the middle vessel starts at the heteroazeotropic point ($x_{M0} = 0.792$) and ends up at the composition of the aqueous phase determined by the liquid–liquid experimental data ($x_M = 0.981$). At the end of the process, methanol and 1-butanol are recovered in pure form in the top and bottom vessel, respectively. The third component (water) is accumulated in the aqueous phase in the middle vessel. The steady-state vessel results are presented in Table 1.

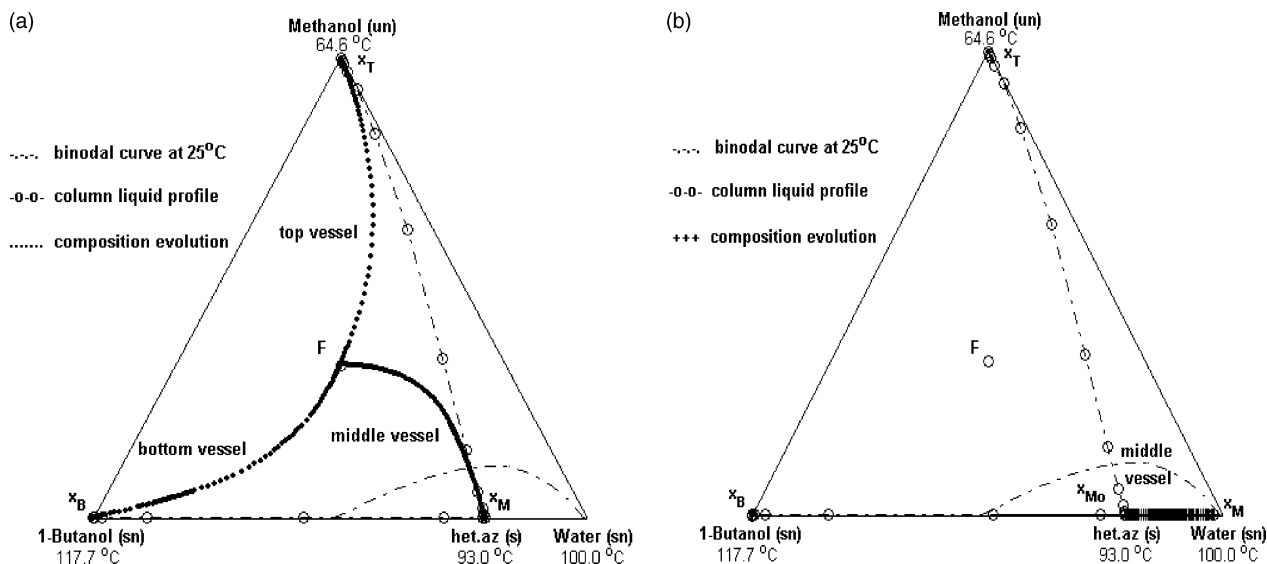


Fig. 7. Separation of the system methanol–water–1-butanol: (a) Step 1; (b) Step 2.

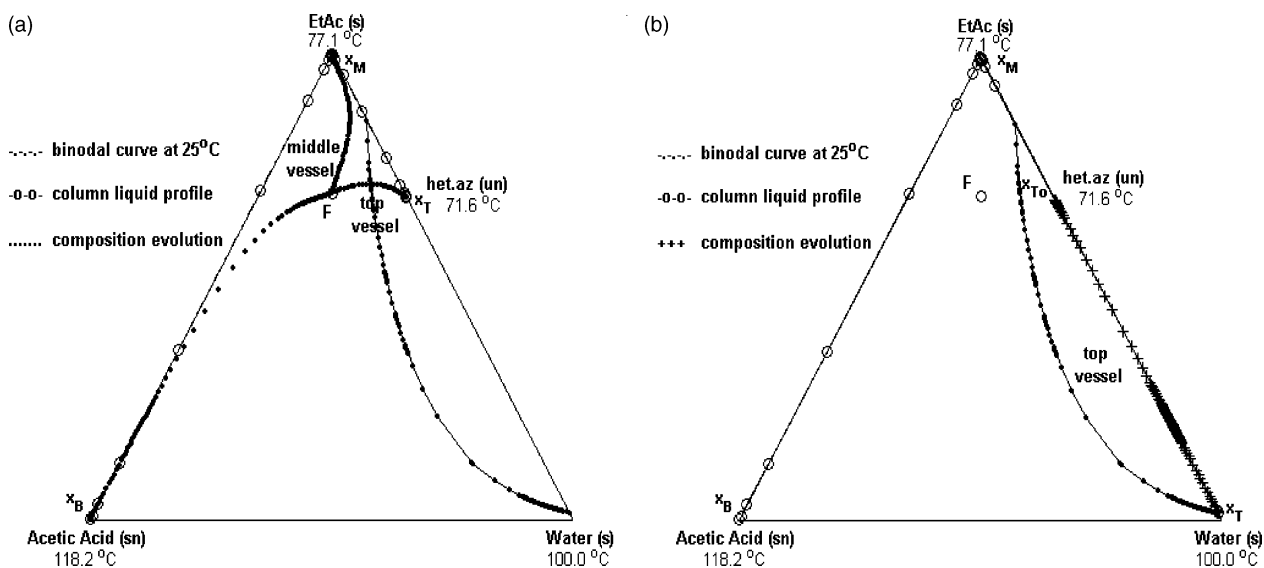


Fig. 8. Separation of the system ethyl acetate–water–acetic acid: (a) Step 1; (b) Step 2.

Topological class 1.0-1a

Step 1: The feed F is placed in the upper feed region (upper Cell II) and the composition profile is built up. The heteroazeotrope starts accumulating in the top vessel, while ethyl acetate and acetic acid are accumulated in the middle and bottom vessel, respectively, as predicted from the theoretical analysis. The composition evolution in the vessels is shown in Fig. 8(a).

Step 2: The heteroazeotrope in the top vessel is decanted and the organic phase (rich in ethyl acetate) is refluxed back in the column. The aqueous phase is gradually accumulated in the decanter vessel, as shown in Fig. 8(b). Ethyl acetate is running down the rectifying section of the column, thus entering the middle vessel. Acetic acid is staying in the bottom of the column, since it is the stable node of the system. At the end of the process, pure ethyl acetate and butanol

are accumulated in the vessels. Water in a composition of ($x_{\text{water}} = 0.981$) is recovered with the aqueous phase in the decanter (see Table 1).

Topological class 2.0-2b

Step 1: The feed F is placed in the upper left distillation region (upper Cell II) outside the immiscibility region and the composition profile in the column is built up. The heteroazeotrope is accumulated in the top vessel, while benzene and dioxane are accumulated in the middle and bottom vessel, respectively, as shown in Fig. 9(a).

Step 2: A decanter in the top of the column is performing the liquid–liquid split and the organic phase (rich in benzene) is refluxed back in the column. The aqueous phase is gradually accumulated in the decanter, while the benzene is running down the rectifying section and enters the mid-

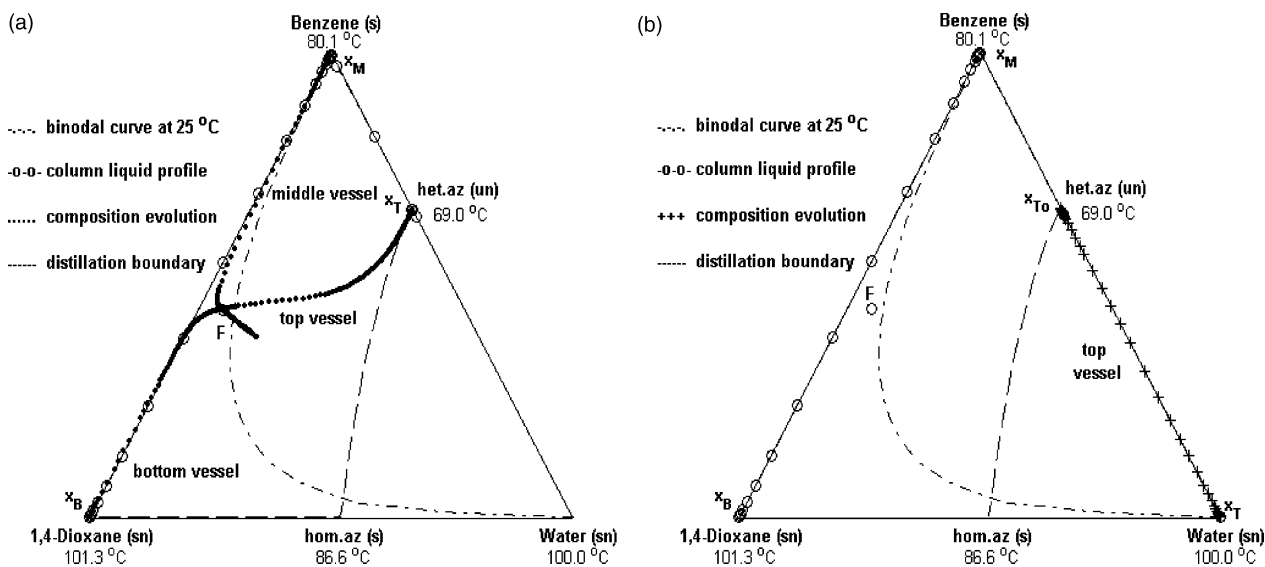


Fig. 9. Separation of the system benzene–water–1,4-dioxane: (a) Step 1; (b) Step 2.

dle vessel. Dioxane is staying in the bottom of the column. Fig. 9(b) shows how the top decanter-vessel is getting enriched in water. In this case, the aqueous phase accumulated in the top decanter vessel is almost pure water ($x_{\text{water}} = 0.999$). Benzene and water are quite immiscible and the binodal curve leads to a better separation of these two components in the immiscible liquid phases.

4. Conclusions

The feasibility of separating ternary heterogeneous azeotropic systems in a closed multivessel-decanter hybrid was investigated in this work.

In the first part of the paper, the theoretical foundation of this work is presented. The closed operation mode of the multivessel column without product withdrawal enables us to make direct use of distillation line or residue curve maps. Simple rules were given for predicting the products in the vessels and identifying feasible operating regions, before any simulations were run. The necessary information for applying these rules is the distillation line or residue curves map, depending solely on the VLE of the system.

Serafimov's classification for ternary azeotropic systems was used and systems with one and with two binary azeotropes were studied. The theoretical tools developed were applied on three common azeotropic classes and it was shown that Serafimov's classes 1.0-2, 1.0-1a and 2.0-2b could be separated in the proposed process.

In the second part of the paper, dynamic simulations verified the theoretical findings and proved the feasibility of separating classes 1.0-2, 1.0-1a and 2.0-2b in the novel column. Part of the separation is performed by distillation, while the liquid-liquid split in the decanter is used for crossing the distillation boundaries. The decanter is placed either in the middle or in the top of the column depending on the class of the mixture to be separated.

The novel process is simple and practical. The closed mode of operation requires minimum operator intervention and monitoring. The column runs by itself and the products are accumulated in the vessels during the process. Two pure components are always recovered in the vessels and an aqueous phase rich in the third component (water) is recovered in the decanter.

Appendix A. Nomenclature

K_c	controller gains (kmol/h °C)
M	liquid holdup (kmol)
N	number of stages
R	recoveries (%)
s	saddle
sn	stable node
T_{sp}	temperature setpoints (°C)
un	unstable node

x liquid compositions (x_{light} , $x_{\text{intermediate}}$, x_{heavy})
1, 2 process steps

Greek symbol

τ_1 integration time (h)

Subscripts

B bottom vessel
F feed
M middle vessel
o initial values
r rectifying section
s stripping section
T top vessel

Appendix B

Table B.1
Multivessel column data

No. of trays per section	$N_r = 25$, $N_s = 25$
Initial feed	$M_F = 5.385$ kmol
Initial condenser holdup	$M_{T0} = 0.035$ kmol
Initial middle vessel holdup	$M_{M0} = 0.250$ kmol
Initial reboiler holdup	$M_{B0} = 5.000$ kmol
Trays holdup (constant)	$M_i = 1/500$ kmol
Vapor flow (constant)	$V = 5$ kmol/h

Table B.2
Initial feed and controller data

Class 1.0-2: Methanol–water–1-butanol

$$x_{F0} = [1/3, 1/3, 1/3]$$

Step 1: Two P temperature controllers

$$K_{c,r} = 0.176 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,r} = 78.80 \text{ } ^\circ\text{C}$$

$$K_{c,s} = 0.202 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,s} = 105.35 \text{ } ^\circ\text{C}$$

Step 2: One P temperature controller and one PI level controller

$$K_{c,r} = 0.176 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,r} = 78.80 \text{ } ^\circ\text{C}$$

$$K_{c,s} = 10 \text{ kmol/h } ^\circ\text{C} \quad \tau_1 = 0.5 \text{ h, } M_{sp,s} = 0.001 \text{ kmol}$$

Class 1.0-1a: Ethyl acetate–water–acetic acid

$$x_{F0} = [0.7, 0.15, 0.15]$$

Step 1: Two P temperature controllers

$$K_{c,r} = 0.909 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,r} = 74.35 \text{ } ^\circ\text{C}$$

$$K_{c,s} = 0.122 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,s} = 97.65 \text{ } ^\circ\text{C}$$

Step 2: One PI level controller and one P temperature controller

$$K_{c,r} = 10 \text{ kmol/h } ^\circ\text{C} \quad \tau_1 = 0.5 \text{ h, } M_{sp,s} = 0.001 \text{ kmol}$$

$$K_{c,s} = 0.122 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,s} = 97.65 \text{ } ^\circ\text{C}$$

Class 2.0-2b: Benzene–water–1,4-dioxane

$$x_{F0} = [0.45, 0.05, 0.5]$$

Step 1: Two P temperature controllers

$$K_{c,r} = 0.451 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,r} = 74.55 \text{ } ^\circ\text{C}$$

$$K_{c,s} = 0.236 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,s} = 90.7 \text{ } ^\circ\text{C}$$

Step 2: One PI level controller and one P temperature controller

$$K_{c,r} = 10 \text{ kmol/h } ^\circ\text{C} \quad \tau_1 = 0.5 \text{ h, } M_{sp,s} = 0.0001 \text{ kmol}$$

$$K_{c,s} = 0.236 \text{ kmol/h } ^\circ\text{C} \quad T_{sp,s} = 90.7 \text{ } ^\circ\text{C}$$

Table B.3
Thermodynamic data [30–32]

Class 1.0-2: Methanol (1)–water (2)–1-butanol (3)			
VLE	A_{ij} (cal/mol)	A_{ji} (cal/mol)	$a_{ij} = na_{ji}$
1–2	–48.6725	610.4032	0.3001
1–3	746.0477	–529.6674	0.3038
2–3	2794.6704	570.1362	0.4700
Binodal (25 °C)	A_{ij} (K)	A_{ji} (K)	$a_{ij} = a_{ji}$
1–2	45.740	–147.43	0.2
1–3	–178.09	703.82	0.2
2–3	1756.8	–344.40	0.2
Antoine	A	B	C
1	8.08097	1582.271	239.726
2	8.07131	1730.630	233.426
3	7.92484	1617.520	203.296
Class 1.0-1a: Ethyl acetate (1)–water (2)–acetic acid (3)			
VLE	A_{ij} (cal/mol)	A_{ji} (cal/mol)	$a_{ij} = a_{ji}$
1–2	935.6880	2316.3631	0.4104
1–3	844.2996	–436.9443	0.3138
2–3	712.1791	320.1059	1.4032
Binodal (25 °C)	A_{ij} (K)	A_{ji} (K)	$a_{ij} = a_{ji}$
1–2	163.41	1159.1	0.2
1–3	685.59	–647.88	0.2
2–3	–249.0	198.55	0.2
Antoine	A	B	C
1	7.10179	1244.950	217.881
2	8.07131	1730.630	233.426
3	8.02100	1936.010	258.451
Dimerization constant	A	B	
3	–10.421	3166	
Class 2.0-2b: Benzene (1)–water (2)–1,4-dioxane (3)			
VLE	A_{ij} (cal/mol)	A_{ji} (cal/mol)	$a_{ij} = a_{ji}$
1–2	1522.2402	1821.8322	0.3547
1–3	–293.8487	434.1172	0.3022
2–3	1551.5163	1097.8251	0.5457
Binodal (25 °C)	A_{ij} (K)	A_{ji} (K)	$a_{ij} = a_{ji}$
1–2	1411.4	1320.6	0.2
1–3	129.49	11.834	0.2
2–3	525.41	49.551	0.2
Antoine	A	B	C
1	6.87987	1196.760	219.161
2	8.07131	1730.630	233.426
3	7.43155	1554.679	240.337

References

- [1] C.S. Robinson, E.R. Gilliland, Elements of Fractional Distillation, vol. 4, McGraw Hill, New York, 1950.
- [2] P. Bortolini, G.B. Guarise, A new method of batch distillation, Quad. Ing. Chim. Ital. 6 (1970) 1–9 (in Italian).
- [3] R.E. Treybal, A simple method of batch distillation, Chem. Eng. 77 (1970) 95–98.
- [4] S. Hasebe, B. Abdul Aziz, I. Hashimoto, T. Watanabe, Optimal design and operation of complex batch distillation column, in: Proceedings of the IFAC Workshop on Interactions between Process Design and Process Control, London, UK, 1992, Pergamon Press, Oxford, UK.
- [5] M. Warter, J. Stichlmair, Batchwise extractive distillation in a column with a middle vessel, Comput. Chem. Eng. (Suppl.) (1999) S915–S918.
- [6] A.G. Davidyan, V.N. Kiva, G.A. Meski, M. Morari, Batch distillation in a column with a middle vessel, Chem. Eng. Sci. 49 (18) (1994) 3033–3051.
- [7] B.T. Safrit, A.W. Westerberg, U. Diwekar, O.M. Wahnschafft, Extending continuous conventional and extractive distillation feasibility insights to batch distillation, Ind. Eng. Chem. Res. 34 (1995) 3257–3264.
- [8] B.T. Safrit, A.W. Westerberg, Improved operational policies for batch extractive distillation columns, Ind. Eng. Chem. Res. 36 (1997) 436–443.
- [9] W. Cheong, P.I. Barton, Azeotropic distillation in a middle vessel batch column. Part 1. Model formulation and linear separation boundaries, Ind. Eng. Chem. Res. 38 (1999) 1504–1530.
- [10] W. Cheong, P.I. Barton, Azeotropic distillation in a middle vessel batch column. Part 2. Non-linear separation boundaries, Ind. Eng. Chem. Res. 38 (1999) 1531–1548.
- [11] W. Cheong, P.I. Barton, Azeotropic distillation in a middle vessel batch column. Part 3. Model validation, Ind. Eng. Chem. Res. 38 (1999) 1549–1564.
- [12] S. Hasebe, T. Kurooka, I. Hashimoto, Comparison of the separation performances of a multi-effect batch distillation system and a continuous distillation system, in: Proceedings of the IFAC Symposium DYCORS+’95, Elsingore, Denmark, Pergamon Press, Oxford, 1995, pp. 249–254.
- [13] S. Hasebe, M. Noda, I. Hashimoto, Optimal operation policy for total reflux and multi-effect batch distillation systems, Comput. Chem. Eng. 23 (1999) 523–532.
- [14] S. Skogestad, B. Wittgens, R. Litto, E. Sorensen, Multivessel batch distillation, AIChE J. 43 (4) (1997) 971–978.
- [15] B. Wittgens, R. Litto, E. Sorensen, S. Skogestad, Total reflux operation of multivessel batch distillation, Comput. Chem. Eng. S20 (1996) S1041–S1046.
- [16] E.K. Hilmen, S. Skogestad, M.F. Doherty, M.F. Malone, Integrated design, operation and control of batch extractive distillation with a middle vessel, in: Proceedings of the Presentation at AIChE Annual Meeting, Los Angeles, USA, 1997.
- [17] M. Barolo, G.B. Guarise, N. Ribon, S.A. Rienzi, A. Trotta, S. Macchietto, Some issues in the design and operation of a batch distillation column with a middle vessel, Comput. Chem. Eng. 20 (Suppl.) (1996) 37–42.
- [18] M. Barolo, G.B. Guarise, N. Ribon, S.A. Rienzi, A. Trotta, S. Macchietto, Running batch distillation column with a middle vessel, Ind. Eng. Chem. Res. 35 (12) (1996) 4612–4618.
- [19] M. Warter, D. Demicoli, J. Stichlmair, Operation of a batch distillation column with a middle vessel: experimental results for the separation of zeotropic and azeotropic mixtures, in: Proceedings of the International Conference on Distillation and Absorption, Baden-Baden, Germany, 2002.
- [20] M. Warter, J. Stichlmair, Batch distillation of azeotropic mixtures in a column with a middle vessel, in: Proceedings of the ESCAPE-10, Elsevier, Amsterdam, 2000, pp. 691–696.
- [21] E.K. Hilmen, Separation of azeotropic mixtures: tools for analysis and studies on batch distillation operation, Ph.D. Thesis, Norwegian University of Science and Technology, Norway, 2000 (Chapter 7). (Available at: www.ntnu.no/users/skoge/publications/thesis/2000/hilmen).
- [22] I. Rodriguez-Donis, V. Gerbaud, X. Joulia, Middle vessel heterogeneous batch distillation of an azeotropic mixture, in: Proceedings of the Eleventh European Symposium on Computer Aided Process Engineering, Elsevier, Amsterdam, 2001, pp. 499–2001e.
- [23] V.N. Kiva, E.K. Hilmen, S. Skogestad, Azeotropic phase equilibrium diagrams: a survey, Chem. Eng. Sci. 58 (2003) 1903–1953.
- [24] E.K. Hilmen, V.N. Kiva, S. Skogestad, Topology of ternary VLE diagrams: elementary cells, AIChE J. 48 (4) (2002) 752–759.

- [25] H. Matsuyama, H. Nishimura, Topological and thermodynamic classification of ternary vapor–liquid equilibria, *J. Chem. Eng. Jpn.* 10 (3) (1977) 181–187.
- [26] R.H. Perry, D.W. Green, J.O. Maloney, *Perry's Chemical Engineering Handbook*, seventh ed., McGraw-Hill, New York, 1997.
- [27] L.A. Serafimov, Thermodynamic and topological analysis of liquid–vapor phase equilibrium diagram and problems of rectification of multi-component mixtures, in: S.I. Kuchanov (Ed.), *Mathematical Methods in Contemporary Chemistry*, Gordon and Breach Publishers, Amsterdam, 1996, pp. 557–605.
- [28] J. Stichlmair, Separation of ternary mixtures by rectification, *Int. Chem. Eng.* 31 (3) (1991) 423–433.
- [29] P. Poellmann, E. Blass, Best products of homogeneous azeotropic distillations, *Gas Sep. Purif.* 8 (4) (1994) 194–228.
- [30] J. Gmehling, J. Onken, Vapor–liquid equilibrium data collection, DECHEMA Chemistry Data Series, Frankfurt am Main, Germany, 1977.
- [31] J.M. Sørensen, W. Arlt, Liquid–liquid equilibrium data collection, DECHEMA Chemistry Data Series, Frankfurt am Main, Germany, 1980.
- [32] DDBST GmbH, Dortmund data bank software package, 2003, www.ddbst.de.
- [33] The Math Works Inc., MATLAB 6.0, 2000, www.mathworks.com.