SEPARATION OF TERNARY HETEROAZEOTROPIC MIXTURES IN A CLOSED MULTIVESSEL BATCH DISTILLATION-DECANTER HYBRID

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The feasibility of a novel multivessel batch distillation-decanter hybrid for simultaneous separation of ternary heterogeneous azeotropic mixtures is addressed in this work both theoretically and by simulations. The multivessel column is operated 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 are applied on three common classes of azeotropic mixtures. This theoretical distillation line map analysis shows that classes 1.0-2, 1.0-1a and 2.0-2b can be separated in the proposed process. Simulated results verify the feasibility of the novel process in separating heterogeneous azeotropic mixtures of these three topological classes.

1. INTRODUCTION

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 multicomponent 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 modifications 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, one where both liquid and vapor streams from the top section enter the middle vessel and one with a vapor bypass from the bottom section to the top section of the column. In this work we use the vapor bypass modification, which is the most common in the literature and is shown in Figure 1.

Until recently most of the work on the MVC was for ideal or constant relative volatility systems. Hasebe et al. [4-6] studied some characteristics of the column and presented simulation results for binary and ternary mixtures. They also proposed the total reflux (closed) operation of such a column. Davidyan et al. [7] presented a rigorous mathematical analysis of the MVC and tried to describe the dynamic behavior of the column. Meski and Morari [8] provided a limiting analysis of a mathematical model for the MVC under the assumptions of negligible holdup on the trays and constant molar flows. Barolo et al. [9,10] performed experiments in a continuous column modified in order to resemble 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, a feedback control structure, based on temperature controllers, has been proposed by Skogestad et al. [11]. 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. The temperature setpoints are taken simple 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. [12]. 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.
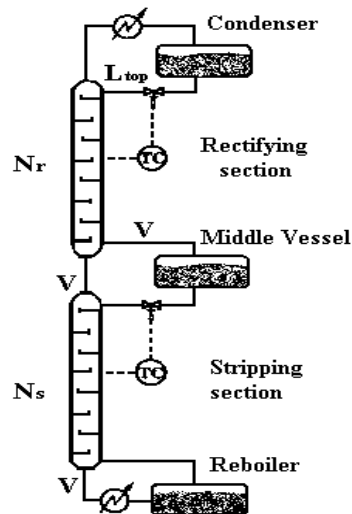

Figure 1: *The multivessel batch column with a vapor bypass.*

The first who studied the performance of the MVC in the separation of azeotropic mixtures was Safrit et al. [13,14]. The case of extractive batch distillation where a heavy entrainer is continuously added at the top of the multivessel column was investigated. Warter and Stichlmair [15] and Hilmen et al. [16] reported some advantages of this novel process over conventional extractive batch distillation. Recently, Warter et al. [17] 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 [18-20] developed a mathematical model in order to study the qualitative dynamics of the MVC when it is used to separate multicomponent azeotropic mixtures. The theoretical insights from the analytical tools developed, were also verified by simulations. Warter and Stichlmair [21] 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 can be recovered. Hilmen [22] 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. [23] provided simulated results when heterogeneous entrainers were used instead and the column operated with product withdrawal (open system). In this case a decanter was combined with the MVC for doing the liquid-liquid split (distillation-decanter hybrid process).

This work addresses heterogeneous azeotropic batch distillation in a distillation-decanter hybrid. The basic principle behind the novel process is that the heteroazeotrope achieved in the decanter vessel of the MVC is separated into its two liquid phases by condensation and decantation. One liquid phase is then recycled to the column, while the other is accumulated in the decanter vessel. In this way a part of the separation 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 the original ternary mixture is separated into its constituent components which are accumulated in the vessels.

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 they are 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, simulation results 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. It has been shown in the literature that a distillation line corresponds to the liquid composition profile of an equilibrium-staged column under total reflux. On the other hand 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.

In the closed multivessel column the correspondence between the distillation lines and the steady state column profile is simple and straightforward. Hilmen [22] notes that, '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:

$$\underline{\text{Overall:}} \qquad M_F = M_T + M_M + M_B \tag{1}$$

$$\underline{\text{Component:}} \qquad M_F\, \mathbf{x}_F = M_T\, \mathbf{x}_T + M_M\, \mathbf{x}_M + M_B\, \mathbf{x}_B \Rightarrow$$

$$M_M\,(\mathbf{x}_F - \mathbf{x}_M) = M_T\,(\mathbf{x}_T - \mathbf{x}_F) + M_B\,(\mathbf{x}_B - \mathbf{x}_F) \tag{2}$$
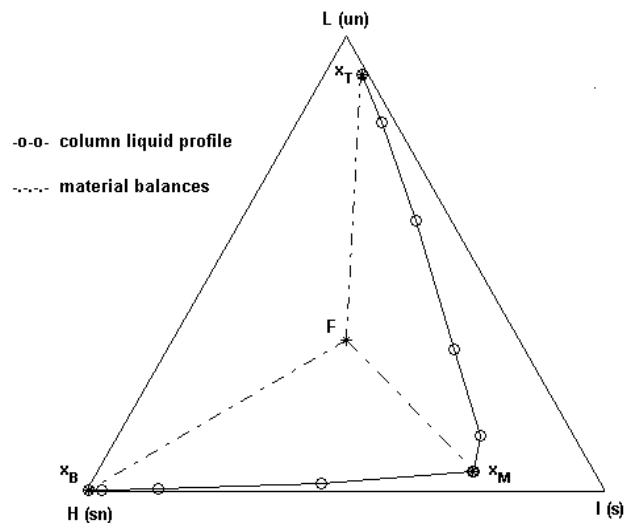

Figure 2: *Steady state column profile and material balance triangle*

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 is reached at steady state. All the above are visualized in Figure 2 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 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'.

2.2 Simple rules for predicting the products in the vessels

Suppose that a zeotropic mixture like the one shown in Figure 2 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 a little more complicated when an azeotropic mixture is to be separated. In this case the interior of the composition triangle can be separated in many distillation regions and the number of the stationary points is increasing. However, the following rules can be used for predicting the products in the vessels.

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 lines 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 all three original components in the three vessels, at the end of the process. 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.

Having in mind, in principle, how the mixture will be separated, the question to be replied is 'what kind of azeotropic mixtures can be separated in this way'. In order to reply to this question in a systematic way, we should know what classes of azeotropic mixtures are feasible.

Serafimov [24] was the first to propose a complete classification of feasible VLE structures for ternary systems. The structures of VLE diagrams for azeotropic mixtures are limited by topological and thermodynamical constraints and Serafimov has classified them under 26 topological structures. Although all 26 classes are topologically and thermodynamically feasible their physical occurrence is determined by the probability of certain combinations of molecular interactions. Reshetov has provided some statistics on the physical occurrence of these 26 classes. His statistics are based on thermodynamic data for 1609 ternary systems from which 1365 are azeotropic, published from 1965 to 1988. He concluded that 16 out of the 26 Serafimov's topological classes were reported in the literature. Although these statistics are not necessarily representative of the real occurrence in nature they are interesting and can be used for some deductions. These research developments from the former Soviet Union, very little known in the West, were presented recently by Hilmen et al. [25]. The reader is advised to read this last reference since the original references are not easily available. In the same paper the novel idea of elementary cells is also introduced. Serafimov's 26 topological classes, Reshetov's statistics and the elementary cells within the 26 classes are shown in Figure 3. A survey paper on azeotropic phase equilibrium diagrams and comparisons between the work done in the former Soviet Union and in the West is also soon to be published by Hilmen et al. [26].

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, 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 singular points [26]. 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-boiling 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.

In this work we use Serafimov's classification in our attempt to find a systematic way of identifying classes of heteroazeotropic mixtures that can be separated in the multivessel column. Reshetov's statistics are just 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 7 out of the 26 feasible Serafimov's classes. According to Reshetov's statistics these systems represent 7 out of the 16 classes reported in the literature and more than half (53.5%) of the reported azeotropic mixtures.
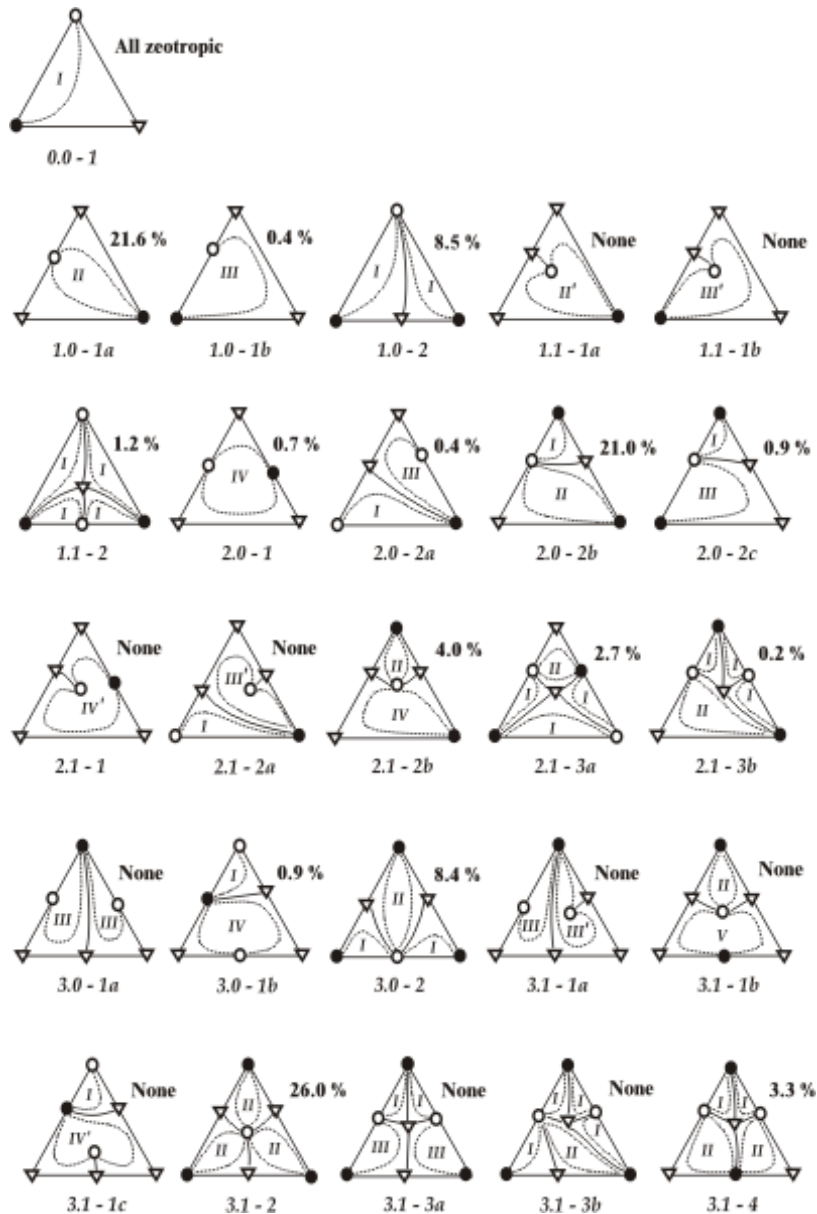

Figure 3: Serafimov's 26 topological classes, elementary cells and Reshetov's statistics. Reprinted from Hilmen et. al [25]

We explained before that the main idea is to recover one of the three original components in the decanter vessel by taking advantage of the liquid-liquid split, while the two other original components are recovered in the vessels by distillation. Given now a specific topological class the question to be replied is whether this class can be separated in the closed multivessel distillation-decanter hybrid or not. The necessary information in order to answer this question is the distillation line or residue curve map. When this information is available the following general 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 heteroazotrope should also be a stationary point of the operating region. The heteroazetrope 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. We will show now how these rules can be used in practice.

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. 3). 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.

A) Topological class 1.0-2
The system Methanol – Water – 1-Butanol is classified under class 1.0-2. Water and 1-butanol exhibit 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 4a. 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. 3 it is shown that class 1.0-2 consists of two Cells I [25].

Suppose a feed F placed at the left distillation region, as shown in Fig 4a. 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 is the stable node and the heteroazeotrope is 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. In this way the column can be operated in both distillation regions and all three original components can be recovered in the vessels in one closed operation. Thus, a distillation-decanter hybrid like the one showed in Figure 4b, where a decanter is placed in the middle vessel, seems like a promising alternative. Simulations showed 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 4a. Methanol is again the unstable node of the region, water is the stable node and the heteroazeotrope is 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. This means that the aqueous phase should be refluxed back in the column, while the organic phase should let accumulated in the middle vessel. A look at the binodal curve in Fig 4a reveals that the organic phase consists of almost 50% water, which means that it is not possible to obtain a pure component by the liquid-liquid split. 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.
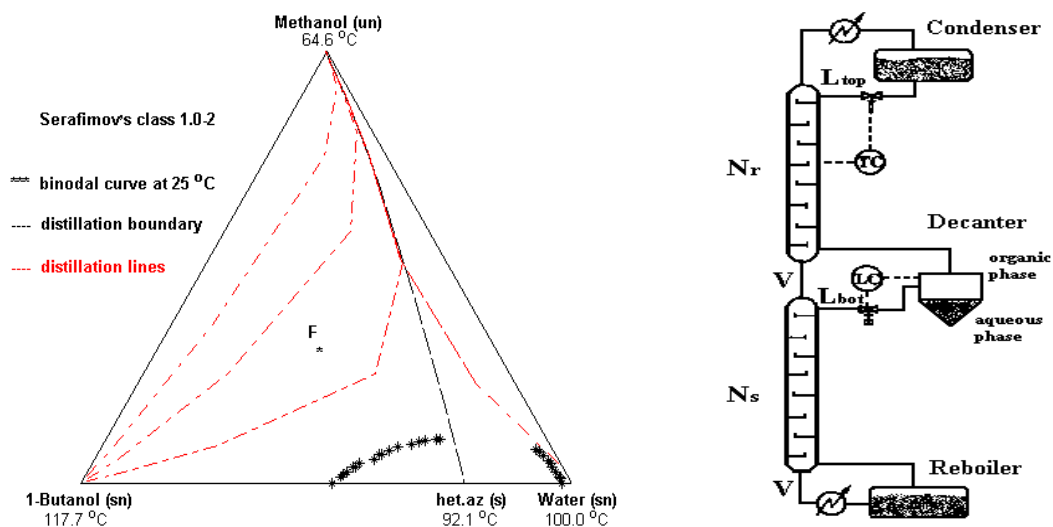

Figure 4: a) Azeotropic mixture of Serafimov's topological class 1.0-2.
b) Multivessel batch distillation – decanter hybrid (decanter in the middle)

B) 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 form a tangent pinch 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 UNIQUAC along with the stability of the stationary points is shown in figure 5a.

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, there exists no distillation boundary. 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 running from the stable node to the unstable node in fig 5a. 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. However, someone should be aware that this line is not a distillation boundary since the definition for a distillation boundary is not fulfilled. From the distillation line map (Fig 5a) is obvious that it is not possible to separate all three original components in one closed operation of the multivessel column unless we take advantage of the heteroazeotrope accumulating in the top vessel. Following the idea of elementary cells, Class 1.0-1a is an example of elementary cell II, as can be seen in Fig 3.

Imagine now a feed F placed at the upper feed region, as shown in fig 5a. 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 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 three original 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 Figure 5b. Simulations in the next part of the paper will exhibit the feasibility of the proposed process.

We should note here that operating the column in the lower feed region of Figure 5a 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 (same problem as in class 1.0-2). 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, accumulating in the top vessel 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 tangent pinch between water and acetic acid. This would result either in extremely long column sections with high number of stages or in a mixture of water-acetic acid in the tangent pinch composition recovered in the middle vessel in the case that the column does not have enough number of stages. However, theoretically the separation would be feasible no matter where the feed was placed, if water and acetic acid would not exhibit a tangent pinch and if the binodal curve had a different shape.
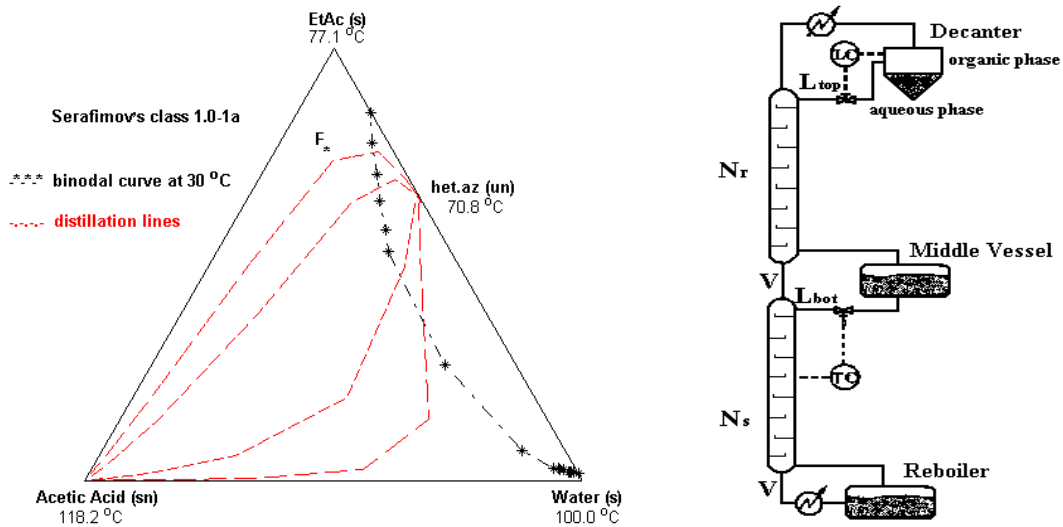

Figure 5: a) Azeotropic mixture of Serafimov's topological class 1.0-1a.
b) Multivessel batch distillation – decanter hybrid (decanter in the top)

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 4 feasible topological classes with 2 binary azeotropes, namely classes 2.0-1, 2.0-2a, 2.0-2b and 2.0-2c. Topological class 2.0-2b is very common and represents 21% of all azeotropic mixtures reported in Reshetov (see Fig. 3). This class will be further studied and we will show that it can be separated in the closed multivessel column.

C) Topological class 2.0-2b

The system Ethyl Acetate-Water-1,4 Dioxane is an example of topological class 2.0-2b. Water and 1,4-Dioxane can not 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. One such entrainer can be ethyl acetate. The distillation line map of the ternary system formed is shown in Figure 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 original 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. 3. The left distillation region is an example of Cell II, while the right region is of Cell I type.

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 ethyl acetate 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 ethyl acetate will be the product in the middle vessel. The heteroazeotrope is accumulated at the top of the column and after decantation the organic (ethyl acetate 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 ethyl acetate. 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 Figure 5b. Simulations in 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 shows the potential of the idea of elementary cells in reducing the complexity of the numerous structures of VLE diagrams. However, a lot more work has still to be done in this area before general 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.
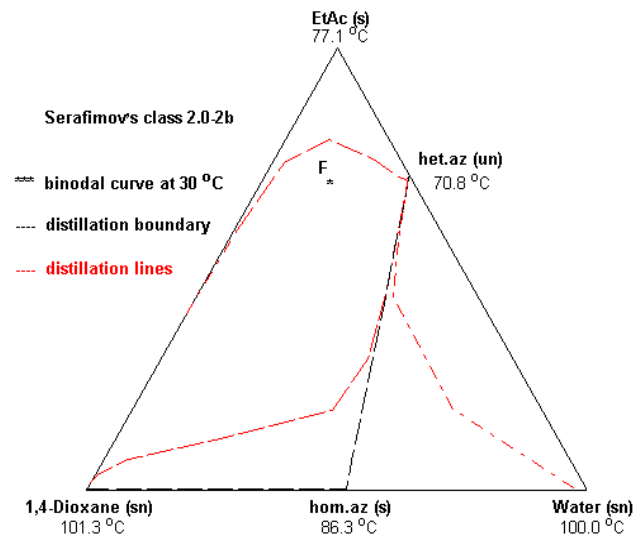

Figure 6: *Azeotropic mixture of Serafimov's topological class 2.0-2b*

3. SIMULATIONS

3.1 The model
The model used in our simulations consists of:
- Overall and component material balances
- Vapor-liquid equilibrium modeled by UNIQUAC equation [27] and liquid-liquid equilibrium based on experimental data [28,29]
- Indirect level control in the vessels with P temperature controllers. Direct level control in the decanter with a PI level controller
- Temperature estimations in the stages by a bubble point calculation under constant pressure, P=1.013 bar

The model is based on the following assumptions:
- Staged distillation column sections
- Equal constant molar vapor flows in both sections of the column
- Constant molar liquid holdup on all stages and negligible vapor holdup
- Perfect mixing and equilibrium in all stages and ideal vapor phase

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 by using the DAE solver ODE15s [30].

3.2 Procedure
The simulations were 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. [11] is applied. Two P temperature controllers are used for indirect level control in the top and middle vessel, as shown in Figure 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 Figures 4b and 5b. The controller makes sure that the organic phase formed in the decanter is refluxed 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.

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. Simulation and controller data are given in the Appendix.

3.3 Results

A) Topological class 1.0-2
The system Methanol-Water-1-Butanol is simulated.

<u>Step 1</u>. 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. Figure 7a 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.

<u>Step 2</u>. 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 is accumulated in the middle vessel while the methanol stays at the top of the column. Figure 7b shows how the middle vessel is getting enriched in water. The water composition in the middle vessel starts at the heteroazeotropic point (x_{Mo}=0.782) and ends up at the composition of the aqueous phase determined by the liquid-liquid experimental data (x_M=0.98). At the end of the process all three original components are recovered in the vessels. The steady state vessel results are presented in Table 1.
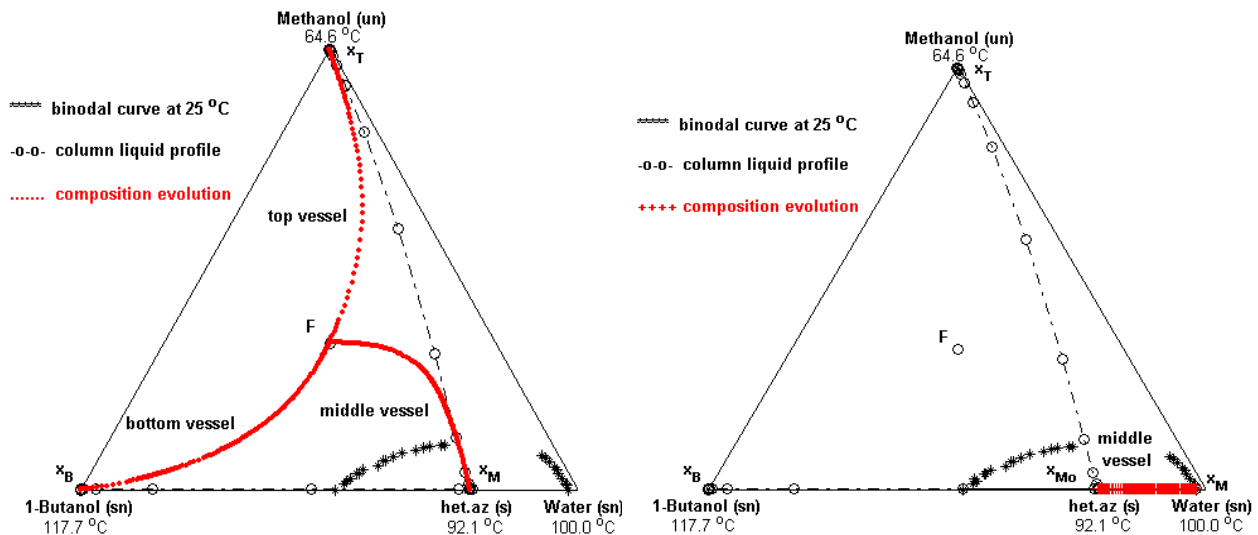

Figure 7: *Separation of the system Methanol – Water – 1-Butanol a) Step1 b) Step 2*

B) Topological class 1.0-1a
The system Ethyl Acetate-Water-Acetic Acid is simulated.

<u>Step 1</u>. 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 Figure 8a.

<u>Step 2</u>. 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 Figure 8b. 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 all three original components are recovered in the vessels (see Table 1).

***Table 1**: Steady state results for the three azeotropic systems simulated*

Class 1.0-2: Methanol – Water – 1-Butanol			
Holdup (kmol)	1.771	1.810	1.704
$X_{Methanol}$	**1.000**	0.000	0.000
X_{Water}	0.000	**0.981**	0.000
$X_{1-Butanol}$	0.000	0.019	**1.000**
Recovery (%)	98.7	98.9	94.9
Class 1.0-1a: Ethyl Acetate – Water – Acetic Acid			
Holdup (kmol)	1.095	3.139	1.052
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	97.2	97.7
Class 2.0-2b: Ethyl Acetate – Water – 1,4-Dioxane			
Holdup (kmol)	0.821	3.683	0.781
X_{EtAc}	0.016	**1.000**	0.000
X_{Water}	**0.984**	0.000	0.000
$X_{Dioxane}$	0.000	0.000	**1.000**
Recovery (%)	100	97.7	96.7

C) Topological class 2.0-2b
The system Ethyl Acetate-Water-1,4-Dioxane is simulated.

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

Step 2. A decanter in the top of the column is performing the liquid-liquid split and the organic phase (rich in ethyl acetate) is refluxed back in the column. The aqueous phase is gradually accumulated in the decanter, while the ethyl acetate is running down the rectifying section and enters the middle vessel. Dioxane is staying in the bottom of the column, as it is the stable node of the system. At the end of the process all three original components are recovered in the vessels. Figure 9b shows how the top decanter-vessel is getting enriched in water. The steady state results in the vessel are given in Table 1.
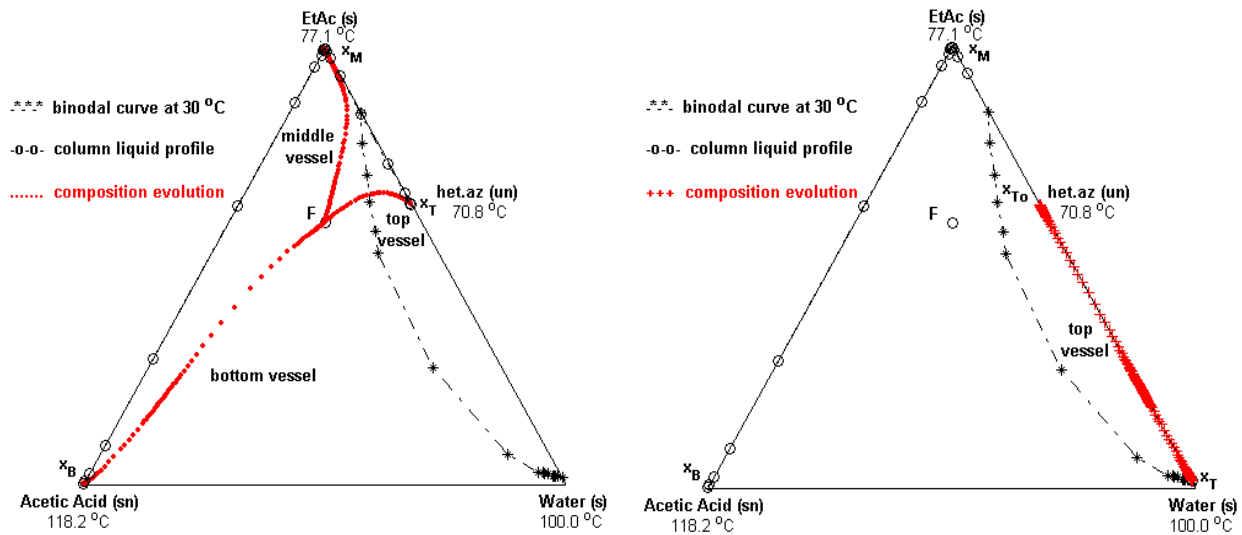

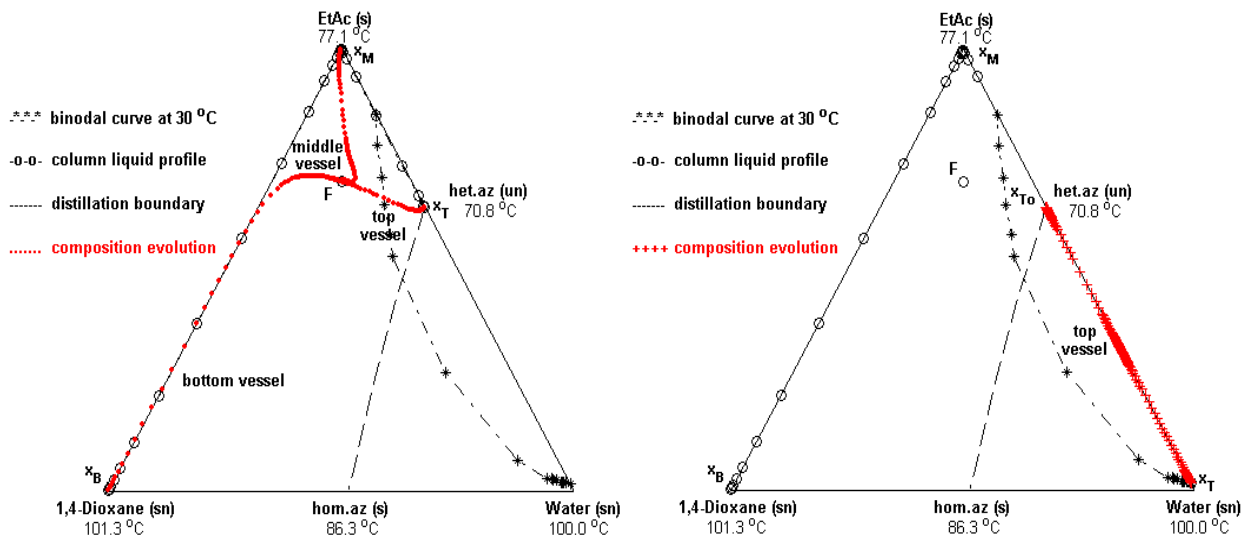**Figure 8:** *Separation of the system Ethyl Acetate – Water – Acetic Acid. a) Step1 b) Step 2*

Figure 9: *Separation of the system Ethyl Acetate – Water – 1,4-Dioxane a) Step1 b) Step 2*

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.

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 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, simulated results were presented. Simulations verified the theoretical findings from the first part of the paper and proved the feasibility of separating classes 1.0-2, 1.0-1a and 2.0-2b in the novel column.

All separations were performed in a distillation-decanter hybrid. 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. Pure components are recovered from the vessels at the end of the process.

5. NOTATION

N   Number of stages
M   Liquid holdup (kmol)
X   Liquid compositions
R   Recoveries (%)
K_c Controller gains (kmol/hºC)
τ_I Integration time (h)
T_{sp} Temperature setpoints (ºC)
1,2   Process steps

Subscripts
F   Feed
T   Top vessel
M   Middle vessel
B   Bottom vessel
R   Rectifying section
S   Stripping section
o   Initial values

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APPENDIX

Table 1: Simulation and 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	$M_{F0} = 0.250$ 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 2: Initial feed and controller data

Class 1.0-2: Methanol – Water – 1-Butanol

$\mathbf{x}_{F0} = [1/3, 1/3, 1/3]$
Step 1: Two P temperature controllers
$K_{c,r} = 0.182$ kmol/h°C $T_{sp,r} = 78.35$ °C
$K_{c,s} = 0.195$ kmol/h°C $T_{sp,s} = 104.9$ °C
Step 2: One P temperature controller and one PI level controller
$K_{c,r} = 0.182$ kmol/h°C $T_{sp,r} = 78.35$ °C
$K_{c,s} = 10$ kmol/h°C $\tau_I = 0.5$ 1/h $M_{sp,s} = 0.001$ kmol

Class1.0-1a: Ethyl Acetate – Water – Acetic Acid

$\mathbf{x}_{F0} = [0.6, 0.2, 0.2]$
Step 1: Two P temperature controllers
$K_{c,r} = 0.794$ kmol/h°C $T_{sp,r} = 73.95$ °C
$K_{c,s} = 0.122$ kmol/h°C $T_{sp,s} = 97.65$ °C
Step 2: One PI level controller and one P temperature controller
$K_{c,r} = 10$ kmol/h°C $\tau_I = 0.5$ 1/h $M_{sp,s} = 0.001$ kmol
$K_{c,s} = 122$ kmol/h°C $T_{sp,s} = 97.65$ °C

Class 2.0-2b: Ethyl Acetate – Water – 1,4-Dioxane

$\mathbf{x}_{F0} = [0.7, 0.15, 0.15]$
Step 1: Two P temperature controllers
$K_{c,r} = 0.794$ kmol/h°C $T_{sp,r} = 73.95$ °C
$K_{c,s} = 0.207$ kmol/h°C $T_{sp,s} = 89.2$ °C
Step 2: One PI level controller and one P temperature controller
$K_{c,r} = 10$ kmol/h°C $\tau_I = 0.5$ 1/h $M_{sp,s} = 0.001$ kmol
$K_{c,s} = 0.207$ kmol/h°C $T_{sp,s} = 89.2$ °C