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Time requirements for heteroazeotropic distillation in batch columns

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Abstract

Batch time requirements are provided for the separation of ternary heterogeneous azeotropic mixtures into three pure products in closed batch column configurations. The separations are performed in hybrid processes where distillation is combined with decantation for completing the separation task. Two multivessel column configurations, with and without vapour bypass, and a rectifier column, are compared in terms of time requirements. Three common classes of azeotropic systems were studied, classified under Serafimov's topological classes 1.0–2, 1.0–1a and 2.0–2b. The multivessel configurations were found to perform always better than the rectifier column, which requires from 29 to 88% more time in order to perform a given separation. The elimination of the vapour bypass in the multivessel column is either impractical or it has a negligible effect on the batch time requirements. Thus, the conventional multivessel-decanter hybrid, with the vapour stream bypassing the middle vessel, is proposed as the best candidate for heteroazeotropic mixtures.
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1. Introduction

Batch distillation has received renewed interest in the literature due to the great flexibility it offers. A single batch column can be used for separating multicomponent mixtures and frequent changes in the processed mixtures, the feed composition and the product specifications can be handled. Therefore, batch distillation is widely used in industries where the products demand and lifetime is both time varying and uncertain, e.g. the pharmaceutical and fine and speciality chemicals industry.

The most common batch column configuration is the so-called batch rectifier where the feed is charged to the reboiler and the products are taken from the top of the column sequentially one after the other during a rectification process. Lately, new column configurations, like the multivessel column, and non-conventional operation modes, like closed operations, have also received strong attention. The multivessel column can be viewed as a generalisation of a batch rectifier and a batch stripper. The column has both a rectifying and a stripping section and therefore it is possible to obtain a light and a heavy fraction simultaneously from the top and the bottom of the column. An intermediate fraction can also be recovered in the middle vessel. The new configuration was first mentioned by Robinson and Gilliland (1950) but the practical interest started after the work by Hasebe et al. (1992).

Several studies on the optimal operation of batch columns exhibited the superiority of the multivessel column compared to a batch rectifier with the same number of stages in terms of production rate, energy consumption and batch time requirements. The energy or mean rate energy consumption of the multivessel was almost half of that of a rectifier (Hasebe et al., 1997, 1999; Furlonge et al., 1999). The simultaneous optimal design and operation of the multivessel column was also addressed recently (Low & Sorensen, 2003). A novel genetic algorithm was used for solving the mixed integer dynamic optimisation problem and the annual profit was used as a performance index. The multivessel column had an annual profit twice as much as that of a batch rectifier and these economic benefits were becoming more prominent as the number of components separated was increasing. The study from Skouras and Skogestad (2004) has also verified the superiority of the multivessel column compared to the batch rectifier in the separation of zeotropic mixtures. Moreover, the slow composition dynamics of the middle vessel

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Nomenclature

F	feed (kmol)
L_{top}	liquid flows in the rectifying section of the multivessel column (kmol h^{-1})
L_{bot}	liquid flows in the stripping section of the multivessel column (kmol h^{-1})
LC	level controller
N	number of stages in the rectifier column
N_C	number of components (3 in all examples)
N_r	number of stages in the rectifying section of the multivessel column
N_s	number of stages in the stripping section of the multivessel column
N_T	total number of stages in the columns + number of product vessels
(s)	saddle
(sn)	stable node
TC	temperature controller
(un)	unstable node
V	vapour flows in the columns (kmol h^{-1})
x_B	composition in the bottom vessel
x_F	feed composition
x_{F1}	still composition at the beginning of Cycle 2 in the rectifier column
x_M	composition in the middle vessel
x_{M0}	composition in the middle vessel at the beginning of the decanting period
x_T	composition in the top vessel
x_{T0}	composition in the top vessel at the beginning of the decanting period

Fig. 1. Conventional multivessel-decanter hybrid column. Vapour bypass configuration. (a) Decanter in the middle; and (b) decanter in the top.

in a conventional multivessel column with a vapour bypass were highlighted. A modification of the multivessel column, first presented in Warter and Stichlmair (1999), with the vapour stream entering the middle vessel, was proposed for improving the dynamics in this vessel. The so-called modified multivessel required, in average, 30% less time to perform a given separation. However, as we point out later, such a modification can give rise to practical problems and is mostly of theoretical interest, at least for the mixtures studied here.

All the studies mentioned above are for zeotropic systems. However, the separation of azeotropic mixtures and more specifically heterogeneous azeotropic mixtures, which is the topic here, has been also addressed in batch columns. Koehler et al. (1995); Duessel and Stichlmair (1995); and Stichlmair and Fair (1998) have addressed heteroazeotropic distillation in batch rectifiers, while Rodriguez-Donis et al. (2001); Rodriguez-Donis et al. (2001); Rodriguez-Donis et al. (2002) have studied the separation characteristics in both rectifier and stripper configurations. Skouras and Skogestad (2004) presented simulation results for the process when the separation is performed in a multivessel-decan-
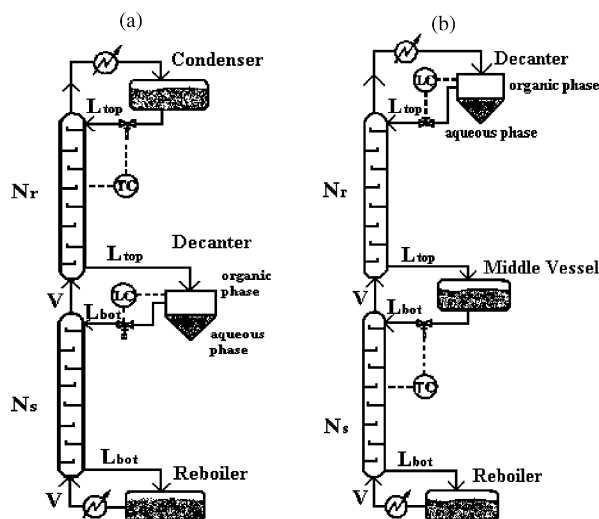
ter hybrid. Dynamic simulations for three common classes of azeotropic systems exhibited the feasibility of the process. Heteroazeotropic mixtures classified under Serafimov's topological classes 1.0–2, 1.0–1a and 2.0–2b (Hilmen et al., 2002; Kiva et al., 2003) were separated into pure products in the novel multivessel-decanter hybrid. The decanter was placed either in the middle or the top of the column depending on the mixture separated. When the heteroazeotrope was a saddle the decanter was placed in the middle vessel (Fig. 1a) and when the heteroazeotrope was an unstable node the decanter was placed in the top of the column (Fig. 1b).

The aforementioned multivessel-decanter hybrid was realised for the most common multivessel configuration with the vapour stream bypassing the middle vessel. We call this configuration as the conventional multivessel-decanter hybrid. Alternatively, the process can be realised in the so-called modified multivessel where the vapour stream is entering the middle vessel, as shown in Fig. 2a and b. We call this configuration as the modified multivessel-decanter hybrid. The decanter is again placed either in the middle (Fig. 2a) or the top vessel of the column (Fig. 2b). Finally, the process can be realised in the batch rectifier with the decanter placed at the top of the column, as shown in Fig. 3. We refer to this column as the rectifier-decanter hybrid.

All columns are operated as closed systems. There are no distillate or bottom streams taken out from the columns. The final products are accumulated in the vessels and discharged when the specifications are satisfied. In the multivessel column a ternary mixture can be separated simultaneously in one such closed operation. In the rectifier column the separation is sequential. The products are separated one at a time and for a ternary mixture a sequence of two such closed operations is needed. The separation sequence resembles the direct split in continuous columns.
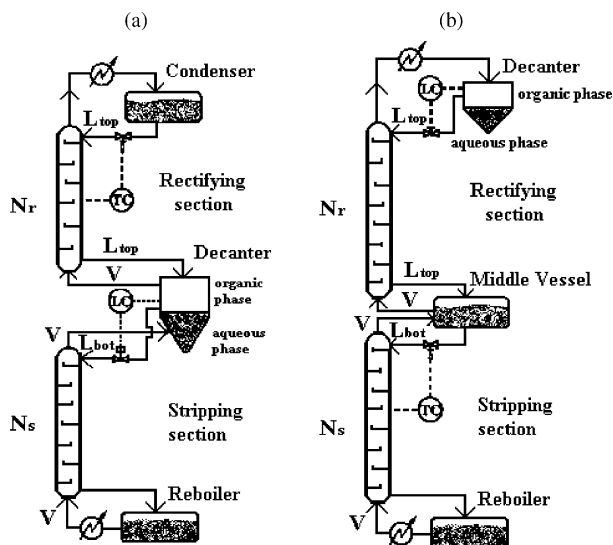
Fig. 2. Modified multivessel-decanter hybrid column. No vapour bypass configuration. (a) Decanter in the middle; and (b) decanter in the top.

From the practical point of view, closed operation modes are preferable over traditional open operation modes, like constant reflux or constant distillate or optimal reflux ratio policies. The closed operation mode requires minimum operator intervention and monitoring, there is a definite distinction between the product changeovers and it is easier to assure the product qualities (Sorensen & Prenzler, 1997). Moreover, closed operation modes can also exhibit advantages in terms of separation time requirements. Sorensen and Skogestad (1994) realised 30% time savings for difficult separations where a small amount of light product is to be recovered. The rectifier column was operated under the cyclic policy, which is characterised by repeating three periods: "filling up" of the reflux drum, "total reflux" (closed operation) of the column and finally "dumping" of the condenser hold-up. Noda et al. (1999) have also shown that the
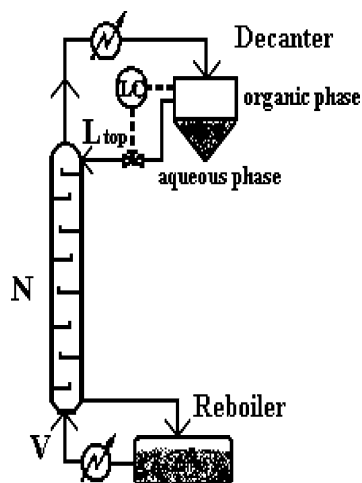

Fig. 3. Rectifier-decanter hybrid column with the decanter in the top vessel.

closed rectifier, called "total reflux column", performs equal or better than the rectifier or the stripper column, operated under traditional open policies, when the operation in all columns was optimised.

This work addresses the separation of ternary heteroazeotropic mixtures in the three hybrid column configurations shown in Figs. 1–3. The objective is to recover all three original components with acceptable purity. The emphasis is on the batch time requirements in the different columns in order to find the best column candidate for such separations. The study is structured as follows. First, the mathematical model of the processes is presented and the simulation procedure is explained. Then, three examples are presented for heteroazeotropic systems classified under Serafimov's classes 1.0–2, 1.0–1a and 2.0–2b. First, we explain how such mixtures can be separated in the hybrid columns and second, we provide, compare and discuss the batch time requirements in each column. The paper ends with some concluding remarks.

2. Simulations

2.1. The model

The mathematical model of the processes used in our simulations consists of overall and component material balances; vapour-liquid and liquid-liquid equilibrium modelled by NRTL activity coefficient model with binary parameters taken from the DECHEMA data series (Gmehling & Onken, 1977; DDBST Gmbh, 2002; Sorensen & Arlt, 1980), 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 vapour flows (boilup) in the column, constant molar liquid hold-up on all stages and negligible vapour hold-up, perfect mixing and equilibrium in all stages, ideal vapour phase, except in the second system studied (class 1.0–1a) where association (dimerisation) of the vapour phase is considered for acetic acid.

The resulting model takes the form of a set of differential and algebraic equations (DAE system) with a total of $N_T \times (N_C + 1)$ state variables, where N_T is the total number of stages in the column sections plus the vessels (3 for the multivessel configurations and 2 for the rectifier column) and N_C is the number of components. The resulting DAE system is solved in Matlab with the DAE solver ODE15s.

2.2. Simulation details

Batch time comparisons are provided for three common classes of heteroazeotropic systems. We consider batch time, as a direct indication of energy consumption since the heat input (boilup) in the reboiler is constant during the process.

Using such a simple comparison criterion (time requirements), instead of a more general one, e.g. annual profit (Low & Sorensen, 2004) limits the findings of this study. Moreover, the formulation of a more advanced optimisation problem could highlight the effect of issues like, number of stages, control parameters, operating conditions, etc, in the objective function and could give a more spherical view of the advantages of each column configuration. Such detailed optimisation studies were provided by Furlonge et al. (1999) and Low and Sorensen (2004), and are beyond the scope of this study.

The simple criterion of minimum batch time is used here in order to compare the separation performance. The economic benefits of doing so are obvious. Reduced batch time makes the equipment available for other separation tasks and reduces the energy consumption if we assume that the heat input in the column is constant. Moreover, reducing the batch time is a simple objective quite used in the industrial practice. In order to minimise batch time, all columns are operated at maximum boilup (reboiler capacity). The vapour flow is constant in each column and equal in all three columns. The ratio of the vapour flow relative to the initial feed (V/F) is a measure of how many times the feed is boiled every hour. This is chosen to be close to unity (once per hour).

Theoretically, the minimum batch time is achieved for infinite number of stages. In practice, in our simulations, each column section has sufficient number of trays for the given separation and therefore the time calculations are not depended on the number of stages. Same number of stages was used in both the conventional multivessel and the rectifier column for a fair comparison. Thus, the number of stages in the rectifier column is the sum of the stages in the two sections of the multivessel. The modified multivessel has one stage less than the conventional since the middle vessel is actually an additional equilibrium stage. Column and simulation data are given in Table A.1 in the Appendix.

The effect of the liquid column hold-up in the separation times is not addressed in this study. All columns have constant very small liquid hold-up negligible compared to the initial feed (total 2% of the charge). This means that the dynamics inside the column sections are negligible compared to that in the product vessels and all of the initial charge is recovered in the vessels at the end of the process.

The initial distribution of the feed in the vessels of the multivessel column affects the separation time and our simulation experience is that, in most cases, it is optimal or close to optimal to charge the feed in the reboiler. This statement holds, at least, for the systems and feed compositions studied here. In the multivessel column, 94% of the total charge is fed in the reboiler, 5% in the middle vessel and only 1% in the top vessel. In the rectifier column, 99% of the charge is fed in the reboiler and 1% in the top vessel. More detailed studies on this issue showed that the simple "feed in the reboiler" policy proved to be either optimal or close to optimal for the closed multivessel (Hasebe et al., 1999; Furlonge et al., 1999). Additionally, this feed policy resembles the one used in the rectifier where the feed is charged in the reboiler.

A simple indirect level control in the vessels of the multivessel column based on temperature feedback control loops is employed (Skogestad et al., 1997). The feasibility of this control strategy was also verified experimentally for the separation of a quaternary mixture (Wittgens & Skogestad, 2000). The same simple control approach is employed in the rectifier. This simple control strategy proved to be robust in anticipating uncertainties in the feed composition. The temperature measurements for the T-controllers are situated in the centre of the column section in both the multivessel and the rectifier column. The temperature setpoints are set to the average of the boiling point of the two pure components or azeotropes separated in this column section. In the decanters a direct level PI-controller is used instead of a temperature controller (Skouras & Skogestad, 2004). Same controller setpoints and tuning parameters were used in all columns for fair comparison and are given in Table A.2 in the Appendix.

The batch time calculations do not include charging of the columns, preheating, product discharging and shutdown. These are considered to be the same for both the multivessel and the rectifier column. The only exception is the product discharging period, which is higher for the rectifier because of the time required to discharge the top vessel hold-up between the two cycles (off-cut fractions). This is an additional advantage for the multivessel configurations.

3. Results

In this section we present three examples for the separation of ternary heterogeneous azeotropic mixtures in different column configurations. The first mixture is classified under Serafimov's topological class 1.0–2, the second one is an example of class 1.0–1a and the last one is a system representing class 2.0–2b. The feasibility of separating these three classes of heteroazeotropic systems in a closed multivessel-decanter hybrid was presented by Skouras and Skogestad (2004). The emphasis is now, not on how we actually perform the separation, even if it will be briefly illustrated, but on the time requirements for each separation.

3.1. Serafimov's topological class 1.0–2

Suppose that a ternary mixture of methanol/water/1-butanol is to be separated by batch distillation into three pure products. Water and 1-butanol form a heterogeneous azeotrope and an immiscibility gap over a limited region of ternary compositions exists. The distillation line map of the mixture, modelled by NRTL, is shown on Fig. 4. The stable nodes are noted as (sn), unstable nodes as (un) and saddles as (s). A system with such a distillation line (or residue curve) map is classified under Serafimov's topological class 1.0–2. A distillation boundary, running from methanol
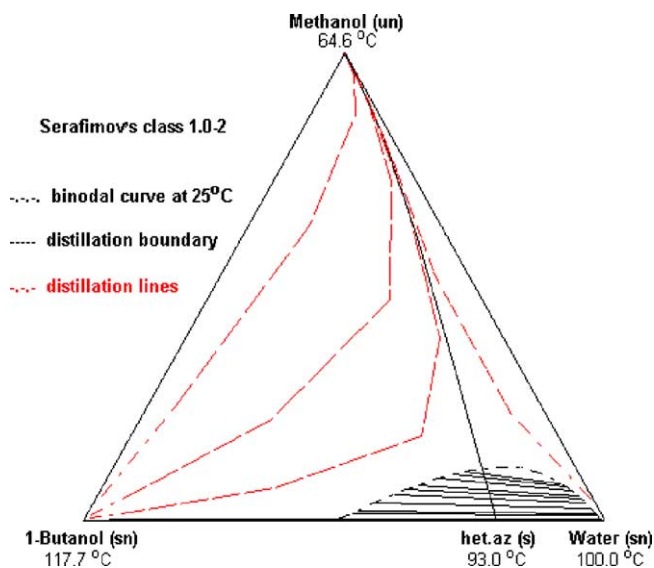
Fig. 4. Distillation line map of the mixture methanol/water/1-butanol. Serafimov's class 1.0–2.

(unstable node) to the binary heteroazeotrope (saddle) divides the composition space in two regions, thus limiting the feasible products under distillation. The heteroazeotrope is a saddle, which means that it behaves as the intermediate "component" under distillation. Therefore, in the multivessel column the heteroazeotrope is accumulated in the middle vessel. The decanter is then placed in the middle vessel of the multivessel configuration as shown in Figs. 1a and 2a. In the rectifier column there is no middle vessel and therefore the decanter is placed in the top vessel, as shown in Fig. 3.

In the multivessel column the mixture is separated simultaneously in one closed operation with an initial build-up period. During this period the composition profile is established, as shown in Fig. 5a. The methanol is accumulated in the top vessel and the butanol in the bottom vessel. The heteroazeotrope is accumulated in the middle vessel, thus, limiting the separation. A decanter in the middle vessel is then required to perform the liquid–liquid split and complete the separation task. This is the second step of the separation, called decanting period. During this step, the organic phase is refluxed back in the column and the aqueous phase is gradually accumulated in the middle vessel. Methanol stays in the top vessel and the butanol is accumulated in the bottom vessel. At the end of the process, all three original components are recovered in the vessels, as shown in Fig. 5b.

The separation in the modified configuration of the multivessel column, without the vapour bypass, is performed in the same way as in the conventional multivessel and it will not be described again.

The separation in the closed rectifier column will be described more detailed. The products are separated one at a time in a sequence that resembles the direct split in continuous columns. The column has two vessels and thus, two
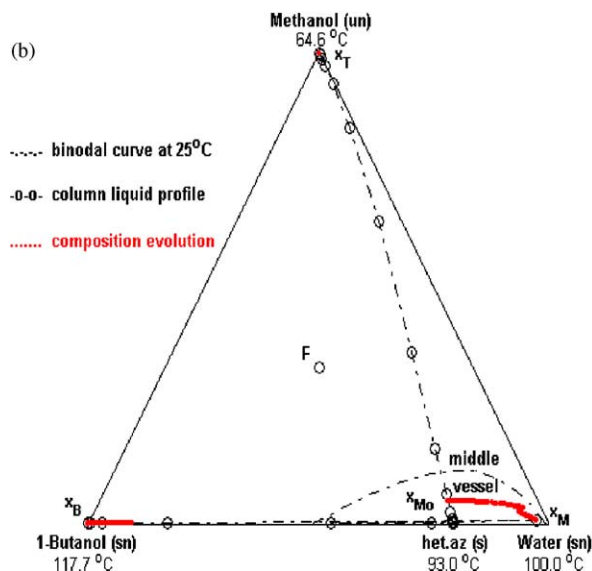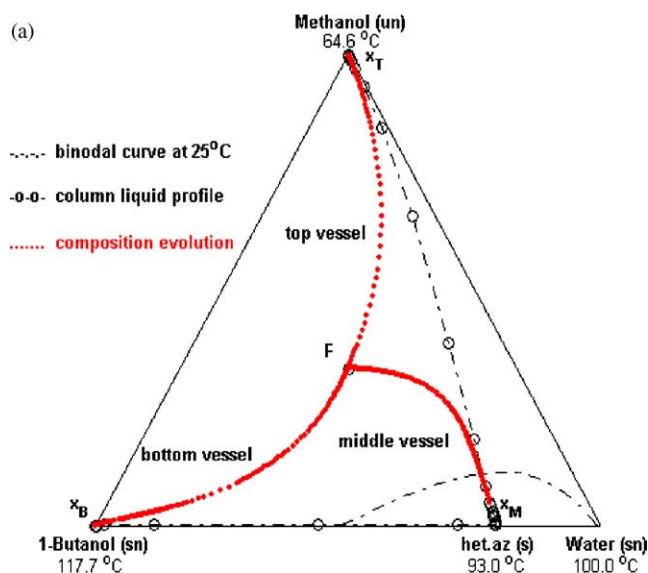

Fig. 5. Separation in the multivessel-decanter hybrid column. (a) Build up period (step 1 of the process); and (b) decanting period (step 2 of the process).

closed operations, called cycles, are needed for the separation of a ternary system. An off-cut fraction is also needed between the cycles.

For a mixture of class 1.0–2 the separation is performed in two cycles with a build-up period in between. Cycle 1 is a common rectification step in order to recover the light component (methanol) in the top vessel. Cycle 1 of the process is shown in Fig. 6a. The still (bottom vessel) is following a linear path away from the component (methanol) accumulated in the top vessel. Cycle 1 is terminated when the specification for methanol in the top vessel is fulfilled. Then, the vessel hold-up is discharged instantaneously. A small amount of methanol still remains in the column and can contaminate the products of Cycle 2. An off-cut fraction is then removed
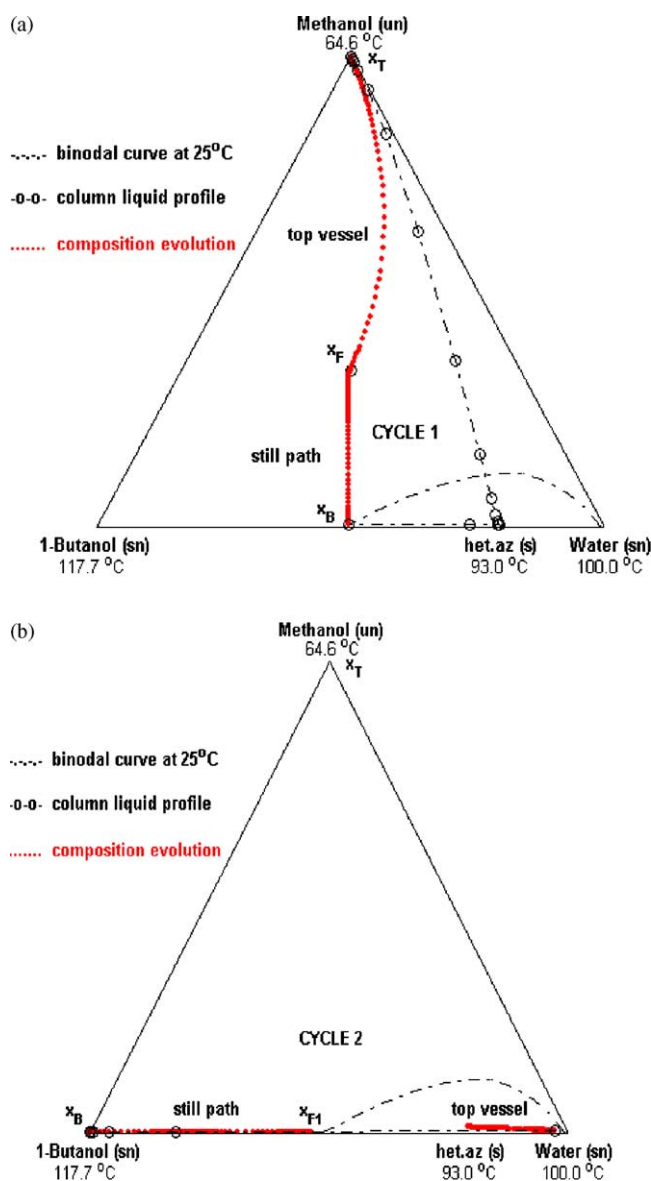
(a)

(b)

Fig. 6. Separation in the rectifier-decanter hybrid in two cycles. Cycle 1: recovering of methanol in the top vessel; Cycle 2: recovering of water in the decanter and 1-butanol in the reboiler.

during a closed operation operated for short time with the same indirect level control and control parameters same as for the second cycle. The off-cut fraction removed from the top vessel is equal to the total column's hold-up (0.1 kmol). Only two components are then left in the column, namely water and 1-butanol. A build-up period is needed in order to get some of the heteroazeotrope in the top vessel and afterwards Cycle 2 can start. Cycle 2 is a heteroazeotropic distillation step with a decanter placed in the top vessel. The two phases are decanted, the organic phase is refluxed back in the column and the aqueous phase is gradually accumulated in the decanter. Thus, during Cycle 2, the still is getting enriched in 1-butanol and the top vessel in water, as shown in Fig. 6b. For simplicity the off-cut fraction and

the build-up period between the two cycles are not shown in Fig. 6.

An equimolar feed x_F is processed and the simulations were terminated when the composition specifications for the products in the vessels were fulfilled. Batch time requirements are provided for two specification sets: $x_{spec}^1 =$ [0.99, 0.97, 0.99], $x_{spec}^2 =$ [0.99, 0.98, 0.99]. The specification for the aqueous phase ($x_{aq} = 0.98$) in the second set is close to the equilibrium value ($x_{aq}^{max} = 0.981$) determined by the binodal curve at 25 °C. This is the theoretically maximum concentration of water we can recover in the vessel in such a process and indicates the severity of the specification.

The batch time comparisons are summarised in Table 1. The time requirements in the conventional multivessel-decanter hybrid are used as a basis for the comparisons. A positive sign (+) in Table 1 indicates longer process times compared to the conventional multivessel. A negative sign (−) indicates shorter process times (time savings).

3.1.1. Conventional multivessel versus rectifier column

The results in Table 1 show that the conventional multivessel-decanter hybrid is faster than the rectifier-decanter hybrid. The rectifier requires from 29 to 41% more time depending on the specification set. The time advantages of the multivessel become more pronounced (from 29 to 41%) as the specification for the component recovered in the middle vessel (aqueous phase) becomes stricter. This is the opposite of what was observed by Meski et al. (1998) and also Skouras and Skogestad (2004) for zeotropic systems, where the multivessel column was becoming less advantageous as the specification in the middle vessel was becoming tighter.

This is explained by the different placement of the decanter in the two columns. In the multivessel column, the decanter is placed in the middle vessel and the components are separated simultaneously. This means that the decantation step in the middle vessel is performed in the presence of only small amounts of the light component, which mostly concentrates in the top stages of the column. In contrast, the separation in the rectifier column is done sequentially. First, the methanol is recovered during Cycle 1, and then Cycle 2 is a heteroazeotropic distillation step with a decanter in the top of the column. This sequential operation requires Cycle 1 to be run for long time in order to avoid excess amount of methanol entering the decanter during Cycle 2. Recall that the specification for the aqueous phase accumulated in the decanter in the second set (0.98) is very tight. Even small amounts of methanol left in the column before starting Cycle 2 make this specification infeasible. Cycle 1 has to be run for longer time than justified by the specification for methanol (0.99) and the column becomes proportionally less attractive for the second specification set. Thus, for heteroazeotropic systems of class 1.0–2, where the heteroazeotrope

Table 1
Batch time requirements and time savings (basis: conventional multivessel)

Specification	Conventional multivessel-decanter hybrid (h)	Modified multivessel-decanter hybrid (%)	Rectifier-decanter hybrid (%)
Class 1.0–2 $x_F = [1/3, 1/3, 1/3]$			
[0.99, 0.97, 0.99]	3.4	−35	+29
[0.99, 0.98, 0.99]	4.9	−33	+41
Class 1.0–1a $x_F = [0.6, 0.2, 0.2]$			
[0.97, 0.97, 0.99]	2.8	−7	+39
[0.98, 0.99, 0.99]	3.7	−11	+32
Class 2.0–2b $x_F = [0.45, 0.05, 0.5]$			
[0.97, 0.97, 0.99]	3.3	0	+61
[0.999, 0.999, 0.999]	4.3	0	+88

is a saddle, the multivessel is preferable over the rectifier even for strict specifications for the middle vessel product.

3.1.2. Conventional multivessel versus modified multivessel

By comparing the results in Table 1 for the two modifications of the multivessel column we see that the elimination of the vapour bypass leads to additional time savings of 33–35%. This result verifies the superiority of the modified multivessel without the vapour bypass reported earlier in the literature (Skouras & Skogestad, 2004). Moreover, we notice that the time savings in the modified multivessel are not strongly dependent on the specification set.

However, a modified multivessel with a vapour stream entering the decanter (middle) vessel, as shown in Figs. 1a and 2a, is not very wise from the practical point of view and is most of theoretical interest. Moreover, the decanter in our configurations is operated in 25 °C, which is significantly lower than that of the rest of the column. It is again impractical to have a hot vapour stream entering the decanter. Thus, for heteroazeotropic systems of class 1.0–2, the conventional multivessel of Fig. 1a seems to be the best alternative of all three columns.

3.2. Serafimov's topological class 1.0–1a

The task is to separate a ternary mixture of ethyl acetate/water/acetic acid, exhibiting a heterogeneous azeotrope in the binary edge ethyl acetate/water. An immiscibility gap over a limited region of ternary compositions exists and the distillation lines map modelled by NRTL is shown in Fig. 7 indicating a system of Serafimov's class 1.0–1a. There is no distillation boundary but from the shape of the distillation lines it is obvious that the products in the vessels depend on the feed region. There is only one stable node (acetic acid) acting as the heavy component and one unstable node (heteroazeotrope) acting as the light component. There are also two saddles (ethyl acetate and water) acting as the intermediate components depending on the

feed. In the upper left region of the ternary composition diagram, ethyl acetate will be the intermediate product while in the lower feed region water will be the intermediate product.

We place the feed in the upper region of Fig. 7 where ethyl acetate is a saddle. The heteroazeotrope is the unstable node and it will boil overhead in the column. Thus, the decanter has to be placed at the top of the column, as shown in Figs. 1b and 2b. In the multivessel column, the separation is performed simultaneously in one closed operation with an initial build-up period. The purpose of this initial period is to get some of the heteroazeotrope in the decanter (top) vessel, as shown in Fig. 8a. The second separation step (decanting period), where the heteroazeotrope is decanted and the organic phase is refluxed back in the column, can then start. The aqueous phase is gradually accumulated in the top vessel, the ethyl acetate in the middle vessel and the acetic acid in the bottom. At the end of the process, all three original components are recovered in the vessels, as shown in Fig. 8b. The separation is performed in the same
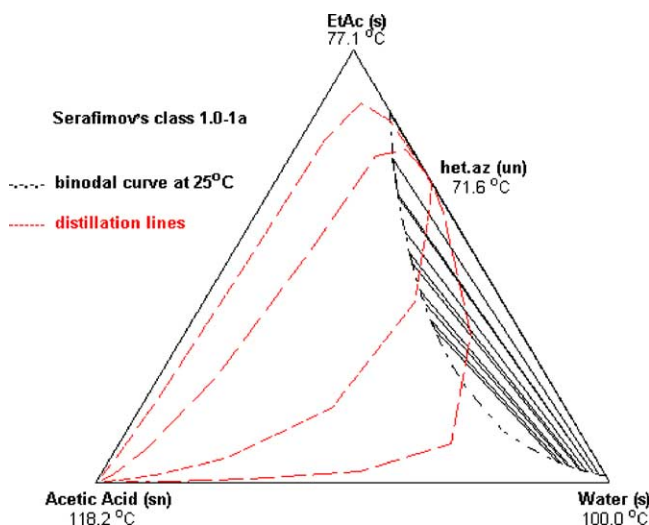

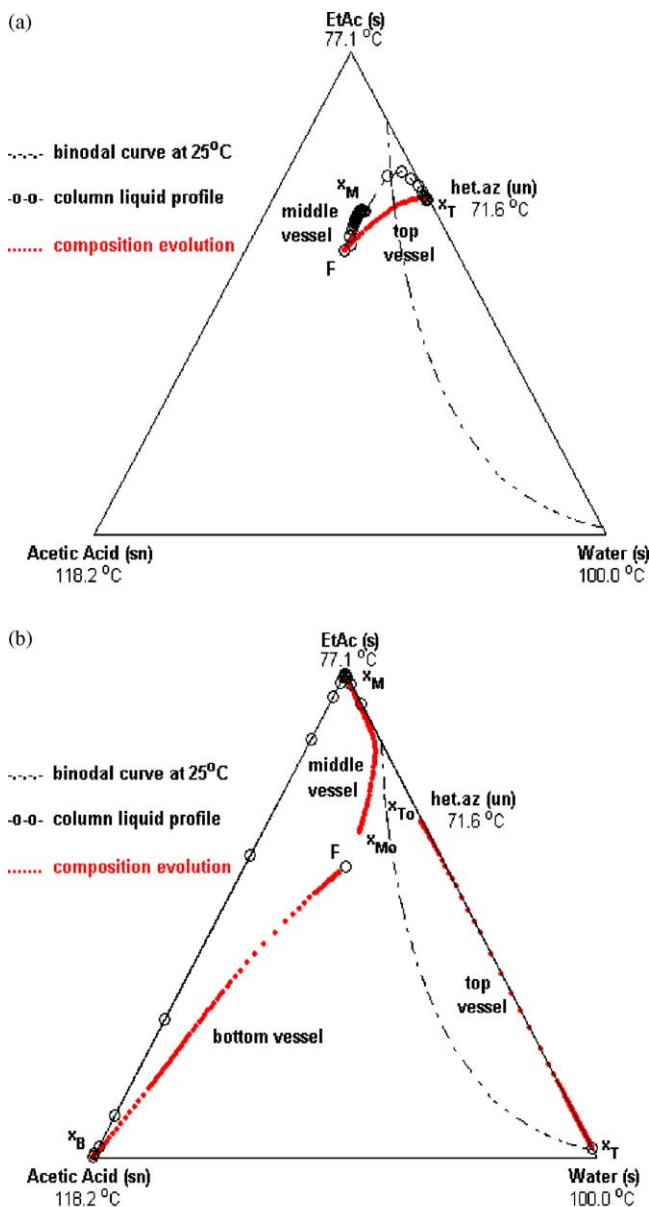Fig. 7. Distillation line map of the mixture ethyl acetate/water/acetic acid.

Fig. 8. Separation in the multivessel-decanter hybrid. (a) Build-up period (step 1 of the process); and (b) decanting period (step 2 of the process).
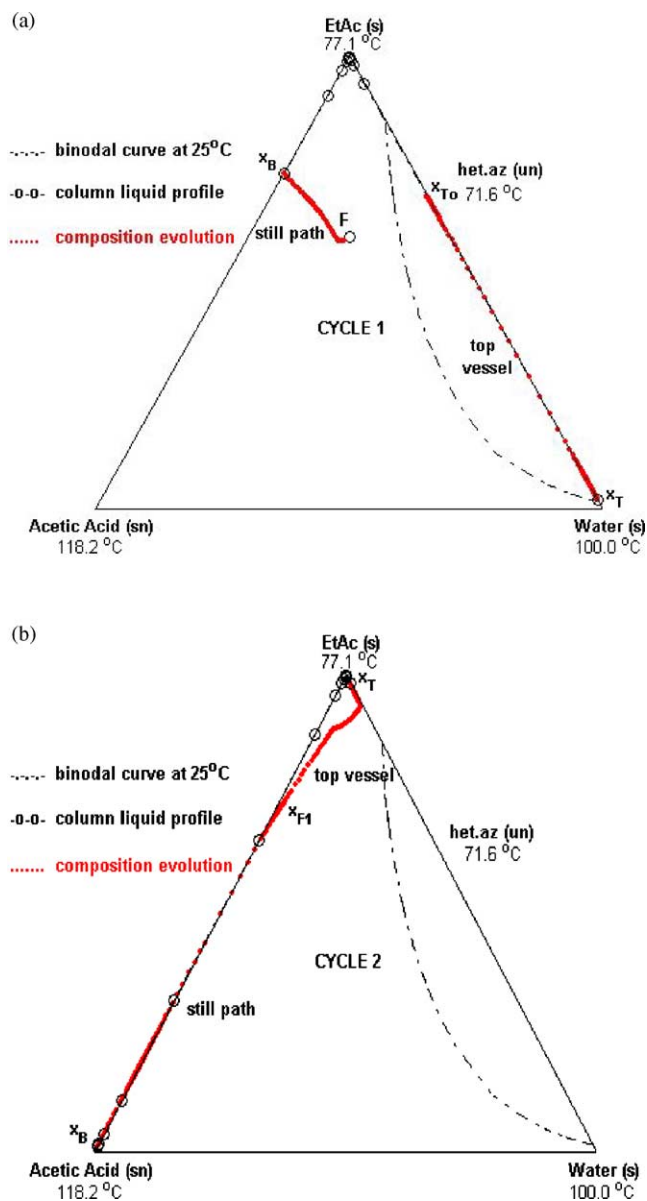

Fig. 9. Separation in the rectifier-decanter hybrid in two cycles. (a) Cycle 1: recovering of water in the decanter; and (b) Cycle 2: recovering of ethyl acetate in the decanter and acetic acid in the reboiler.

way in the modified multivessel column without the vapour bypass.

In the rectifier column the separation is again performed sequentially in two cycles with a build-up period before Cycle 1 and an off-cut fraction between the two cycles. Since for this azeotropic class (class 1.0–1a) the heteroazeotrope is an unstable node, Cycle 1 will be a heteroazeotropic distillation step. A build-up period is needed and the heteroazeotrope is accumulated in the decanter before Cycle 1 starts. During Cycle 1, the heteroazeotrope is decanted and the organic phase is refluxed back in the column. The aqueous phase is then gradually accumulated in the top vessel, as illustrated in Fig. 9.

Most of the water is removed during Cycle 1 and the still (bottom vessel) consists almost of only ethyl acetate and acetic acid. A small off-cut fraction is needed after Cycle 1 in order to remove the remaining water. Cycle 2 is then an almost binary rectification of ethyl acetate (top product) and acetic acid (bottom product), as shown in Fig. 9.

In our simulations an initial feed $x_F = [0.6, 0.2, 0.2]$ is processed and the process was terminated when the specifications for the products in the vessels were fulfilled. Two specification sets were considered also in this case: $x_{spec}^1 = [0.97, 0.97, 0.99]$ and $x_{spec}^2 = [0.98, 0.99, 0.99]$. The specification in the second set is stricter both for the aqueous

phase in the top vessel and for the product (ethyl acetate) recovered in the middle vessel. Moreover, the specification ($x_{aq} = 0.98$) for the aqueous phase is close to the maximum equilibrium value ($x_{aq}^{max} = 0.984$) determined by the binodal curve at 25 °C. The batch time requirements for the process and the comparisons for different column configurations are given in Table 1.

3.2.1. Conventional multivessel versus rectifier column

The results in Table 1 show that, also for class 1.0–1a, the rectifier column requires more time than the conventional multivessel in order to perform a given separation. The rectifier column requires 39% more time for the first specification set and 32% for the second tighter set, which indicates a weak dependence on the specification set. Intuitively, we would expect that the time advantages of the multivessel column would be much more reduced when the specification in the middle vessel is becoming tighter from 0.97 to 0.99. This intuition is based on the slow dynamics in the middle vessel of a conventional multivessel pointed out by Skouras and Skogestad (2004) for zeotropic systems. However, the results are not verifying our intuition and the reason is the presence of the decanter in the top vessel. In such distillation-decanter hybrids, the dynamics in the decanter play an important role, as important as the dynamics in the other vessels. The specification in the second step is stricter in both the decanter (from 0.97 to 0.98) and in the middle vessel from 0.97 to 0.99). The "middle vessel effect" (slow dynamics in the middle vessel) in favour of the rectifier column, is overweighed by the "decanter effect" (slow dynamics in the decanter) in favour of the multivessel column. Thus, the multivessel column is again preferable over the rectifier column even for high specifications in the middle vessel, for this class of heteroazeotropic systems.

3.2.2. Conventional multivessel versus modified multivessel

When we compare the conventional multivessel with the modified multivessel, a rather surprising result is observed since the former does not exhibit any significant advantage over the latter. The time savings in the modified multivessel are significantly reduced to 7–11% compared to 33–35% in the first example. The decisive factor here is again the dynamics in the decanter in the top of the column. Recall that the only difference between the two multivessel configurations is the vapour stream from the stripping section to the rectifying section, which can bypass or not the middle vessel. In the latter case the dynamics in the middle vessel are significantly improved and the separation task is accomplished faster in the modified multivessel column. However, in the multivessel-decanter hybrids the dynamics of the decanter are also a decisive factor. Thus, improving the dynamics of the middle vessel by avoiding the vapour bypass is not that important anymore. The "decanter effect" (slow decanter dynamics) outweighs the "middle ves-
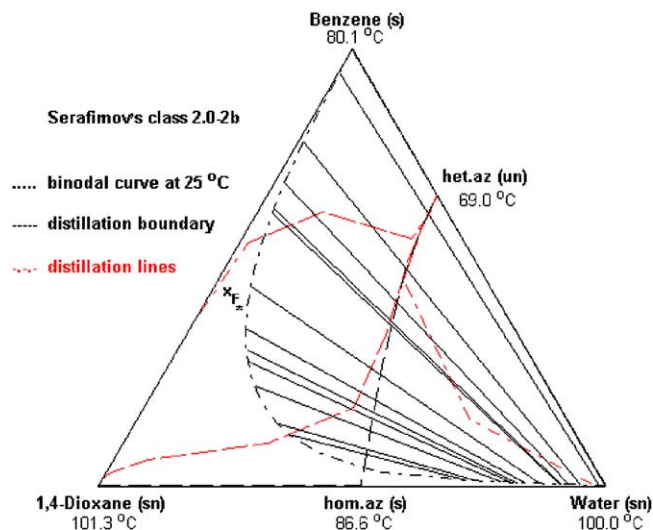

Fig. 10. Distillation line map of the mixture benzene/water/1,4-dioxane.

sel effect" (fast middle vessel dynamics) and the modified multivessel is only marginally better than the conventional one.

We note here that we can improve the dynamics in the decanter vessel by employing more "aggressive" level control. In practice this would mean to increase the flow of the organic phase refluxed back in the column so as the accumulation of the aqueous phase would become faster and the specification would be reached in shorter time. However, such an increase in the reflux rate would not be without drawbacks. By looking at the shape of the binodal curve in Fig. 7 we see that the organic phase still contains a large amount of water (around 15% at 25 °C). A more aggressive reflux policy would force a large amount of water re-entering the rectifying section and consequently entering also the middle vessel. There is obviously a trade-off between the time we save by sending faster the organic phase back in the column and the time we lose by the redistribution effect (re-mixing water and ethyl acetate) in the middle vessel.

In conclusion, the conventional multivessel-decanter hybrid is proposed for azeotropic class 1.0–1a, since there are only marginal time savings to be gained by eliminating the vapour bypass.

3.3. Serafimov's topological class 2.0–2b

The last ternary mixture studied is an example of topological class 2.0–2b and is the mixture benzene/water/1,4-dioxane. The distillation line map of the mixture is shown in Fig. 10. The heteroazeotrope is the unstable node, dioxane is the stable node while the homoazeotrope and benzene are the two saddles of the distillation line map. There is one distillation boundary running from the heteroazeotrope to the homoazeotrope, thus dividing the composition space in two distillation regions.

An initial feed $x_F = [0.45, 0.05, 0.50]$ as shown in Fig. 10 is to be processed in batch columns. The heteroazeotrope is the unstable node and thus, the decanter has to be placed at the top of the multivessel column, as shown in Figs. 1b and 2b. The separation process for class 2.0–2b resembles the process for class 1.0–1a and therefore it would be briefly described but not illustrated with figures.

In the multivessel column the mixture is separated simultaneously in one closed separation with an initial build-up period in order to get some of the heteroazeotrope in the decanter (top) vessel. The decanting period can then start. The heteroazeotrope is decanted, the organic phase is refluxed back in the column and the aqueous phase is gradually accumulated in the top vessel. At the end of the process, all three original components are recovered in the vessels. The separation is performed similarly in the modified multivessel without the vapour bypass.

Two cycles are required for the separation in the rectifier column. In addition, a build-up period before Cycle 1 and an off-cut fraction between the two cycles is required. The purpose of the build-up period is to obtain some of the heteroazeotrope in the top vessel.

During Cycle 1 the heteroazeotrope is decanted and the organic phase is refluxed back in the column. The aqueous phase is then gradually accumulated in the decanter. An off-cut fraction is removed after Cycle 1 and the excess water is removed from the column. Cycle 2 is an almost binary distillation between benzene and dioxane with the first one recovered at the top vessel and the heavy dioxane recovered from the still.

The simulations were stopped when the composition specifications for the products in the vessels were fulfilled. Two specification sets were studied: $x^1_{spec} = [0.97, 0.97, 0.99]$, $x^2_{spec} = [0.999, 0.999, 0.999]$. The second specification set is very tight in all the vessels. The miscibility of benzene and water is negligible and therefore the aqueous phase is almost pure water and the specification for the aqueous phase can be set as high as 99.9%. The batch time comparisons for the process are given in Table 1.

3.3.1. Conventional multivessel versus rectifier column

The results for class 2.0–2b in Table 1 verify once again that the rectifier column is more time consuming than the multivessel column. The rectifier requires 61–88% more time and, moreover, it becomes relatively less attractive as the specifications in the vessels become stricter. This case study represents the ultimate example in favour of the multivessel column. The reason is the large amount of the heavy component in the initial feed (50% dioxane in the feed). The heavy component will be accumulated at the bottom vessel and, thus, the whole process is governed by the dynamics in this vessel. The same was observed by Skouras and Skogestad (2004) for a zeotropic system with a feed rich in the heavy component. Thus, the multivessel column is highly recommended over the rectifier column in this case.

3.3.2. Conventional multivessel versus modified multivessel

In the previous case of class 1.0–1a we show that the elimination of the vapour bypass was not so important in the case of distillation-decanter hybrids where the decanter is placed in the top of the column. The decisive factor was the dynamics of the decanter that play an important role and lessens the improved middle vessel dynamics of the modified multivessel. The results are even more pronounced in this case, where we observe no difference in the time requirements between the two multivessel configurations. Both multivessel columns require exactly the same time to fulfil the specifications. In this case it is the bottom vessel that governs the dynamics of the process and outweighs completely the faster middle vessel dynamics. Thus, improving the dynamics of the middle vessel by avoiding the vapour bypass is not at all important.

4. Conclusions

We presented batch time requirements for the separation of ternary heterogeneous azeotropic mixtures in closed batch distillation-decanter hybrids. Three systems were studied, each one representing a different topological class in Serafimov's classification, namely classes 1.0–2, 1.0–1a and 2.0–2b. All separations were performed in closed hybrid processes were distillation is combined with decantation in order to enhance the separation task. The column arrangements under consideration were a conventional multivessel column with the vapour stream bypassing the middle vessel, a modified multivessel with the vapour stream entering the middle vessel and a rectifier column. The decanter was placed either in the top or in the middle vessel of the multivessel configurations depending on the nature (class) of the system separated.

The results, for all three cases presented, verified that multivessel configurations perform always better than the rectifier column, in terms of batch separation times. This result, which is well justified in the related literature for zeotropic systems, showed to be also valid for heteroazeotropic mixtures studied here. The elimination of the vapour bypass in the modified multivessel column, proposed in the literature for enhancing the dynamics of the conventional multivessel, is not justified by the results for the hybrid version of the column with the decanter. Moreover, practical issues make the idea of eliminating the vapour bypass in heteroazeotropic distillation rather unattractive. Thus, the conventional multivessel-decanter hybrid is recommended for the separation of heteroazeotropic systems.

Appendix

See Appendix in Tables A.1 and A.2.

Table A.1
Column and simulation data

	Conventional multivessel-decanter hybrid	Modified multivessel-decanter hybrid	Rectifier decanter hybrid
Stages per section	$N_r = 25$, $N_s = 25$	$N_r = 25$, $N_s = 24$	$N = 50$
Initial feed (kmol)	$M_F = 5.385$	$M_F = 5.385$	$M_F = 5.385$
Initial condenser hold-up (kmol)	$M_{T0} = 0.035$	$M_{T0} = 0.035$	$M_{T0} = 0.035$
Initial middle vessel hold-up (kmol)	$M_{F0} = 0.250$	$M_{F0} = 0.250$	No middle vessel
Initial reboiler hold-up (kmol)	$M_{B0} = 5.000$	$M_{B0} = 5.000$	$M_{B0} = 5.250$
Trays hold-up (kmol)	$M_i = 1/500$	$M_i = 1/500$	$M_i = 1/500$
Vapour flow (kmol/h)	$V = 5$	$V = 5$	$V = 5$

Table A.2
Initial feed and controller data

Example 1: Serafimov's topological class 1.0-2 (methanol/water/1-butanol)

Step 1 or Cycle 1: two P temperature controllers
$K_{c,r} = 0.176\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,r} = 78.80\,°C$
$K_{c,s} = 0.202\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,s} = 105.35\,°C$

Step 2 or Cycle 2: one P temperature controller and one PI level controller
$K_{c,r} = 0.176\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,r} = 78.80\,°C$
$K_{c,s} = 10\,\mathrm{h^{-1}}$ $ô_I = 0.5\,\mathrm{h}$ $M_{sp,s} = 0.001\,\mathrm{kmol}$

Example 2: Serafimov's topological class1.0–1a (ethyl acetate/water/acetic acid)

Step 1 or Cycle 1: two P temperature controllers
$K_{c,r} = 0.909\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,r} = 74.35\,°C$
$K_{c,s} = 0.122\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,s} = 97.65\,°C$

Step 2 or Cycle 2: one P temperature controller and one PI level controller
$K_{c,r} = 10\,\mathrm{h^{-1}}$ $ô_I = 0.5\,\mathrm{h}$ $M_{sp,s} = 0.001\,\mathrm{kmol}$
$K_{c,s} = 0.122\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,s} = 97.65\,°C$

Example 3: Serafimov's topological class 2.0–2b (benzene/water/1,4-dioxane)

Step 1 or Cycle 1: two P temperature controllers
$K_{c,r} = 0.451\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,r} = 74.55\,°C$
$K_{c,s} = 0.236\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,s} = 90.7\,°C$

Step 2 or Cycle 2: one P temperature controller and one PI level controller
$K_{c,r} = 10\,\mathrm{h^{-1}}$ $ô_I = 0.5\,\mathrm{h}$ $M_{sp,s} = 0.0001\,\mathrm{kmol}$
$K_{c,s} = 0.236\,\mathrm{kmol\,h^{-1}\,°C^{-1}}$ $T_{sp,s} = 90.7\,°C$

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