

Separation of Azeotropic Mixtures in Closed Batch Distillation Arrangements

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Abstract

Batch time (energy) requirements are provided for the separation of ternary zeotropic and heteroazeotropic mixtures in three closed batch column configurations. Two multivessel column modifications (with and without vapor bypass) and a conventional batch column operated under the cyclic policy, were studied. The multivessel column performs always better than the conventional column and the time savings vary from 24% up to 54 %. Moreover, by eliminating the vapor bypass in the multivessel, additional time savings of 26% can be achieved for a zeotropic mixture. However, the multivessel with the vapor bypass should be used for the heteroazeotropic mixtures.

1. Introduction

The multivessel batch column is a combination 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, while an intermediate fraction may also be recovered in the middle vessel. Two modifications of the multivessel are studied here. First, the vapor bypass modification where the vapor from the stripping section bypasses the middle vessel and enters the rectifying section and second, a modification where both liquid and vapor streams enter the middle vessel. We refer to the first modification as conventional multivessel and to the second one as multivessel without vapor bypass. The third column configuration studied in this work is a conventional batch column (rectifier) operated with the cyclic policy. We refer to this column as cyclic column. The cyclic policy has been noted before in the literature by Sørensen and Skogestad (1994) and is easier to operate and control. All column configurations are shown in Fig. 1.

Batch time comparisons are provided for the separation of one zeotropic and two heteroazeotropic systems. We consider batch time as a direct indication of energy consumption since the boilup is constant for all columns. The columns are operated as closed systems. In the multivessel a ternary mixture is separated simultaneously in one such close operation and the final products are accumulated in the vessels (Wittgens et al, 1996). In the cyclic column the products are separated one at each time and for a ternary mixture a sequence of two such closed operations is needed. An indirect level control strategy based on temperature feedback control is implemented as proposed by Skogestad et al (1997).

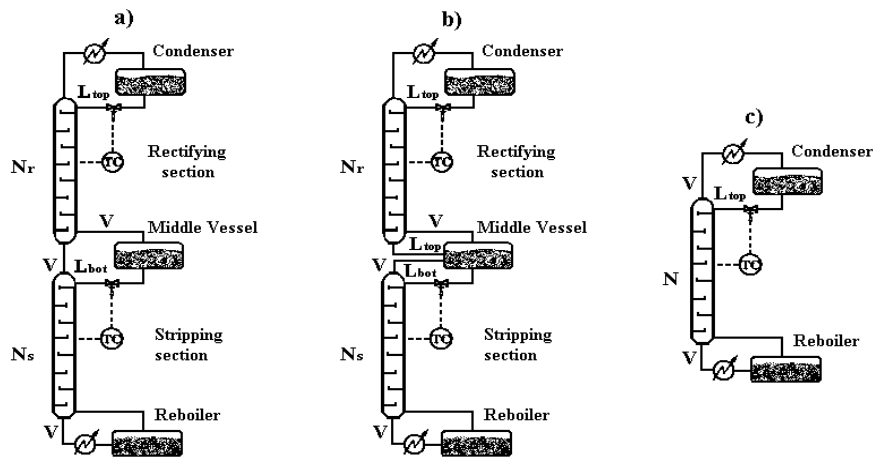


Figure 1. a, b) Multivessel batch column with and without vapor bypass
c) Cyclic batch column.

2. Simulations

2.1. Zeotropic systems

The zeotropic system of methanol-ethanol-1-propanol was studied.

Multivessel column: The zeotropic mixture is separated simultaneously in one closed operation. All three original components are accumulated in the three vessels at the end of the process, as shown in Figure 2a.

Multivessel column without vapor bypass: The separation is performed as mentioned above. With this modification the light component is depleted faster from the middle vessel. This leads to improved composition dynamics in the middle vessel and it can be advantageous for some separations, as we will show later.

Cyclic column: The separation is performed in two cycles that resembles to the direct split in continuous columns. During cycle 1 the light component (methanol) is accumulated in the top vessel (Fig 2b). Cycle 2 is almost a binary separation of the two components left in the still. The intermediate component (ethanol) is discharged from the top vessel, while the heaviest one (1-propanol) remains in the still (Fig 2c).

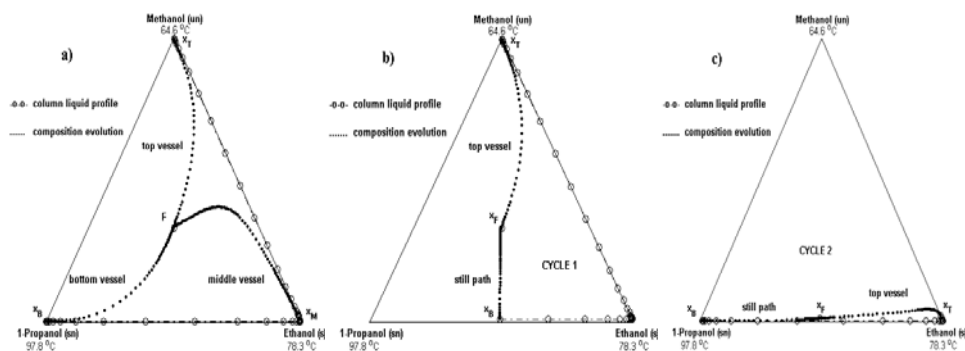


Figure 2. a) Simultaneous separation of a zeotropic mixture in the multivessel column
b, c) Separation of a zeotropic mixture in two cycles in the cyclic column

2.2. Azeotropic systems

Two classes of heteroazeotropic systems were studied, namely classes 1.0-2 and 1.0-1a. Skouras and Skogestad (2003) provided simulated results for the separation of different classes of heteroazeotropic systems in a closed multivessel-decanter hybrid.

2.2.1. Topological 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 stability of the stationary points of the system and the distillation line map modeled by UNIQUAC are shown on Figure 3a. One distillation boundary, running from methanol (unstable node) to the binary heteroazeotrope (saddle) divides the composition space in two regions. The system belongs to Serafimov's topological class 1.0-2 (Hilmen, 2002).

Multivessel column: For separating a heteroazeotropic mixture of this topological class a decanter has to take the place of the middle vessel. The mixture is separated simultaneously in one closed operation with an initial built-up period. During this period the composition profile is built-up and the heteroazeotrope accumulates in the middle vessel (Fig. 4a). At the second (decanting) period the heteroazeotrope is decanted and the organic phase is refluxed back in the column. The aqueous phase accumulates in the middle vessel, while methanol and 1-butanol are accumulated in the top and bottom vessel, respectively, as shown in Fig. 4b.

Cyclic column: The separation is performed in two cycles with a built-up period in between. During Cycle 1, methanol is accumulated in the top vessel (Fig 5a). Then a built-up period is needed where the heteroazeotrope accumulates in the top. Cycle 2 is a heteroazeotropic distillation with a decanter taking the place of the top vessel. The aqueous phase is gradually accumulated in the top vessel (see Fig. 5b) and the organic phase is refluxed back in the column. The still is getting enriched in 1-butanol (Fig. 5b).

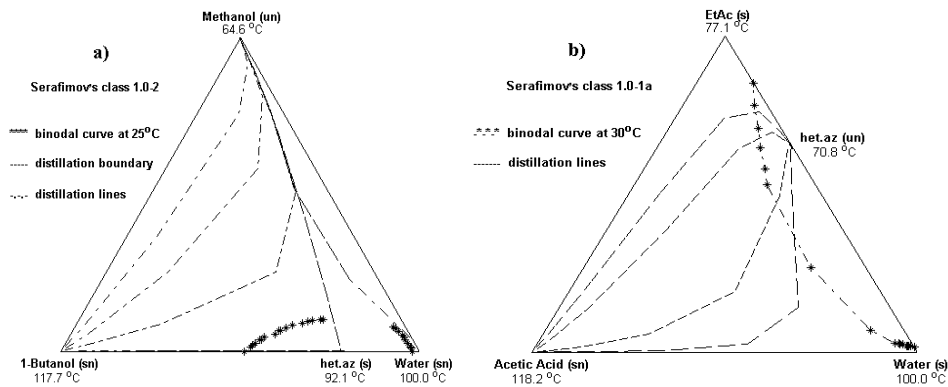


Figure 3. Azeotropic systems of a) topological class 1.0-2 and b) topological class 1.0-1a.

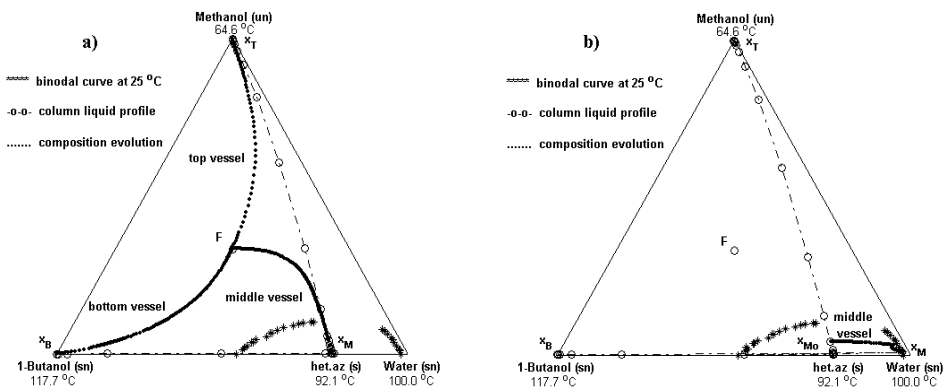


Figure 4. Separation in the multivessel column. a) Build up period b) Decanting period.

2.2.2. Topological class 1.0-1a

Ethyl acetate and water form a heterogeneous azeotrope and an immiscibility gap over a limited region of ternary compositions. The corresponding distillation lines map is shown in figure 3b. The system belongs to Srafimov's topological class 1.0-1a.

Multivessel column: For this class of heteroazeotropic systems the decanter has to be placed at the top of the column. The mixture is separated simultaneously in one closed operation after an initial built-up period. During this built-up period the heteroazeotrope accumulates in the top vessel. At the second (decanting) period the heteroazeotrope is decanted and the organic phase is refluxed back in the column. The aqueous phase accumulates in the top vessel, ethyl acetate in the middle vessel and acetic acid in the bottom. At the end of the process three pure products are accumulated in the vessels.

Cyclic column: The separation is performed again in two cycles but with a built-up period before the cycles. During this built-up period the heteroazeotrope accumulates in the top vessel. During Cycle 1 this heteroazeotrope is decanted and the organic phase is refluxed back in the column. The aqueous phase is accumulated in the top vessel. Cycle 2 is almost a binary separation between ethyl acetate and acetic acid. The first one is recovered at the top vessel while the second remains in the still.

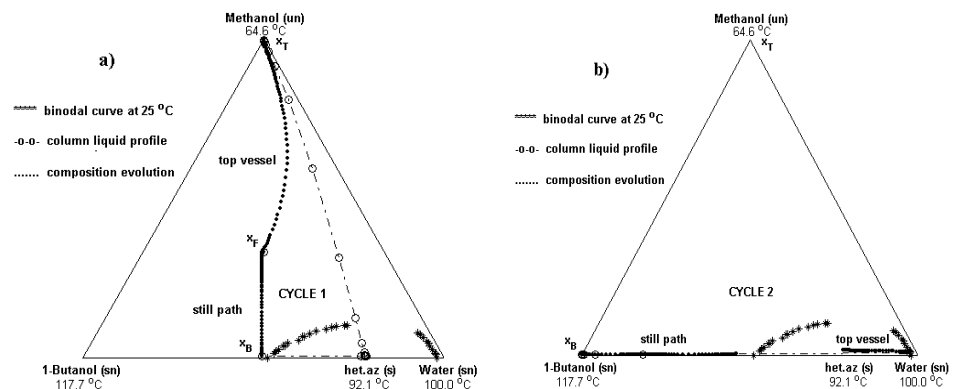


Figure 5. Separation in the cyclic column a) Cycle 1 b) Cycle 2.

3. Results

All simulations were terminated when the specifications in all vessels were fulfilled. Results are provided for two specification sets.

i) Zeotropic system: $x^1_{\text{spec}} = [0.99, 0.97, 0.99]$, $x^2_{\text{spec}} = [0.99, 0.98, 0.99]$

In the second set higher purity is required for the intermediate component.

ii) Azeotropic mixture of class 1.0-2: $x^1_{\text{spec}} = [0.99, 0.97, 0.99]$, $x^2_{\text{spec}} = [0.99, 0.98, 0.99]$

The heteroazeotrope is the intermediate 'component' (saddle). In the multivessel it is accumulated in the middle vessel/decanter. After decantation the aqueous phase is accumulated in the middle vessel. In the cyclic column the aqueous phase is the top product of Cycle 2. The specification for the aqueous phase ($x_{\text{aq}}=0.98$) in the second set is close to the equilibrium value ($x_{\text{aq}}^{\text{exp}}=0.981$) determined by the binodal curve at 25°C.

iii) Azeotropic mixture of class 1.0-1a: $x^1_{\text{spec}}=[0.97, 0.97, 0.99]$, $x^2_{\text{spec}}=[0.98, 0.97, 0.99]$

The heteroazeotrope is the light 'component' (unstable node). After decantation the aqueous phase is accumulated in the top vessel/decanter in the multivessel column. In the cyclic column the aqueous phase is the top product of Cycle 1. The specification for the aqueous phase ($x_{\text{aq}}=0.98$) is close to the experimental equilibrium value ($x_{\text{aq}}^{\text{exp}}=0.985$) determined by the binodal curve at 30°C.

Charging of the column, preheating, product discharging and shutdown are not included in the time calculations. All these time periods would be the same for both the multivessel and the cyclic column. The only exception is the product discharging period, which is higher for the cyclic column, since the products are separated one at each time and they have to be discharged twice. All columns have sufficient number of trays for the given separation. Same number of stages was used in both the multivessel and the cyclic column on order to be fair in our time comparisons.

A modified multivesesel without a vapor bypass (Fig 1b) was studied. The conventional multivessel (Fig 1a) with the vapor bypass has an inherent inability to 'boil away' the light component from the middle vessel. The idea behind the modified multivessel is that the vapor stream entering the middle vessel will help the light component to be boiled off faster, thus, improving the composition dynamics in the middle vessel.

The results in Table 1 prove that this is true. For the zeotropic mixture the modified multivessel is 26% faster. The improvement is more pronounced for the separation of the first heteroazeotropic mixture of class 1.0-2, where the time savings go up to 37%. This is because the accumulation of the aqueous phase takes place in the middle vessel (for this class of mixtures) and it is very time consuming. Therefore, the improved middle vessel dynamics have a greater effect on the separation of a heteroazeotropic mixture of class 1.0-2 than on a zeotropic mixture.

A rather surprising result is the one observed for the separation of the heteroazeotropic system of class 1.0-1a. The modified multivessel does not exhibit any significant advantage over the conventional one (7% time savings for specification set 1) and it can be even slower (6% more time consuming for specification set 2). The explanation is simple. For systems of class 1.0-1a the heteroazeotrope is the unstable node and it is accumulated in the top vessel. Therefore the liquid-liquid split and the accumulation of the aqueous phase is taking place in a decanter in the top. The dynamics of the top

vessel dominates the separation. The improved dynamics of the middle vessel in the modified multivessel are not playing an important role anymore.

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

Zeotropic system	Conventional multivessel (with vapor bypass)	Modified multivessel (w/o vapor bypass)	Cyclic column
[0.99,0.97,0.99]	3.6 hr	-26%	+53%
[0.99,0.98,0.99]	3.9 hr	-26%	+46%
Heteroazeotropic systems			
<i>Class 1.0-2</i>			
[0.99,0.97,0.99]	3.1 hr	-29%	+28%
[0.99,0.98,0.99]	4.6 hr	-37%	+24%
<i>Class 1.0-1a</i>			
[0.97,0.97,0.99]	2.6 hr	+7%	+54%
[0.99,0.98,0.99]	3.7 hr	-6%	+44%

However, a modified multivessel for the separation of heteroazeotropic mixtures is problematic from the practical point of view. It is not practical to have a decanter where a vapor phase is bubbled through. Also the decanter is operated in a temperature lower than that of the column and a hot vapor stream entering the decanter is not very wise.

A look to all the results presented in this work reveal that the multivessel column is in all cases preferable over the cyclic column in terms of batch time (energy) savings. For the separation of azeotropic mixture the modified multivessel without the vapor bypass seems to be the best choice, with time savings up to 52% compared to the cyclic column. For the separation of heteroazeotropes, time savings and practical considerations lead to the choice of the conventional multivessel with the vapor bypass. Time savings vary from 25% up to 50% depending on the mixture separated. Beside the time savings achievable by multivessel distillation one should also mention its much simpler operation compared to the cyclic column. The final products are accumulated in the vessels at the end of the process and there is no need for product change-overs.

4. Conclusions

The multivessel column is superior to the cyclic column, in terms of batch time (energy) consumption, for all separations studied here. A modified multivessel column without vapor bypass is proposed for the separation of zeotropic systems. However, the conventional multivessel configuration with vapor bypass is proposed for the separation of heterogeneous azeotropic systems.

5. References

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