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Generalised model for heteroazeotropic batch distillation with variable decanter hold-up

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A B S T R A C T

A general model of batch heteroazeotropic distillation is proposed. Both liquid phases present in the decanter can be refluxed or withdrawn as distillate, their hold-up can be increased, decreased or kept constant, as well. By assuming maximal separation, that is, that the composition of the condensate always equals to that of the heteroazeotrope, the still path equation was derived. The still path directions are determined for all the 16 possible operational policies. It is possible to steer the still path in a desired direction by changing the operational parameters, which allows the recovery of a pure component in the still. The still path directions are validated by rigorous simulations for three policies not published yet using the mixture water – formaldehyde – propyl formate. From the 16 operational policies, 11 can be considered as useful in practice. To demonstrate the advantage of using a non-traditional policy, the separation of the mixture aniline – ethylene glycol – water was investigated, as well. By using a non-traditional operational policy with hold-up reduction in the decanter a higher purity of ethylene glycol was obtained in the still.

Keywords:

Heteroazeotropic batch distillation
Operational policies
Variable hold-up

1. Introduction

Batch distillation is a common separation technology in the pharmaceutical and specialty chemical industries [1], as it is capable of processing mixtures of varying composition and amount. However, for the separation of azeotropic and close-boiling mixtures special distillation methods have to be applied, such as pressure swing, extractive and heteroazeotropic distillation.

In some cases, the composition of the azeotrope changes with the pressure, and it might even disappear. These mixtures can be separated by *pressure swing distillation* (PSD), without the addition of a separation agent. Lewis [2] appears to be the first one to exploit the pressure sensibility for separating azeotropic mixtures. Knapp and Doherty [3] listed 26 pressure sensitive binary azeotropes. They presented a method by which non-pressure-sensitive binary azeotropes can be separated by using entrainers that form pressure-sensitive distillation boundaries. Wasylkiewicz et al. [4] developed an algorithm which allows the variation of the composition of azeotropes with pressure to be tracked. In the last decade several teams studied the realization of the PSD in batch. The separation of the pressure sensitive minimum boiling azeotrope acetonitrile – water with semicontinuous and batch pressure swing

distillation was investigated by simulation by Phimister and Seider [5]. Repke et al. [6] were the first to perform experimental investigations on the pressure swing batch distillation (PSBD). Modla and Lang [7] studied the feasibility of PSBD of binary mixtures in two novel double column configurations Modla et al. [8] studied the feasibility of the separation of ternary homoazeotropic mixtures with pressure swing batch distillation in one column and double column batch strippers and rectifiers). Modla and Lang [9] investigated the separation of an acetone-methanol mixture in a double column batch stripper, with and without thermal integration. Two versions of closed double-column systems for batch pressure swing distillation of binary homoazeotropic mixtures were investigated by Modla [10] with rigorous simulations. Recently, Modla [11] suggested a reactive PSBD process in a double column configuration for the production of ethyl acetate. Modla [12] proposed a triple-column configuration for the PSBD separation of a chloroform-acetone-toluene mixture. This novel configuration is the combination of a double column batch rectifier and a middle-vessel column.

In *batch extractive distillation* (BED), a new component, the entrainer (*E*) is fed continuously to the column, altering favourably the relative volatilities of the original components.

The batch extractive distillation with the application of a heavy solvent in a batch rectifier was studied among others by Yatim et al. [13], Lelkes et al. [14], and in a middle vessel column by Safrit et al. [15], Warter and Stichlmair [16], Cui et al. [17], Low and

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Sorensen [18], Warter et al. [19]. Hua et al., [20] proposed a two-reboiler batch rectifier configuration for batch extractive distillation. Lang et al. [21] suggested a new operational policy, with entrainer feeding during start-up, on the basis of industrial experiences obtained for the batch rectifier. Kotai et al. [22] compared the conventional batch extractive distillation with the hybrid process (absorption + distillation) suggested by Duessel and Stichlmair [23]. Acosta-Esquivarosa et al. [24] studied the sequential combination of liquid-liquid extraction and batch distillation both experimentally and by simulation. Steger et al. [25] proposed a new variant of batch extractive distillation, the inverse-fed batch extractive distillation, where the total amount of the entrainer is pre-loaded to the still, and the mixture to be separated is continuously fed to the column. If E forms a heteroazeotrope with one of the original components, the separation process is called heterogeneous batch extractive distillation. Barreto et al. [26] performed the optimization of seven operational policies of heterogeneous batch extractive distillation using genetic algorithm.

The effectiveness of an extractive distillation process relies on the *choice of the entrainer* also called solvent. Although many heuristics exist, based on the calculation of simple thermodynamic properties, like solvent selectivity or entrainer capacity, more systematic approaches combine them with computer-aided molecular design, e.g. [27,28]. The entrainer is conventionally chosen in industrial practice as a heavy component [29–32]. However, there are some cases when the use of high boiling entrainers is not recommended (e.g. heat sensitive mixtures). Indeed, it is possible to use light or intermediate entrainers, as demonstrated by the feasibility studies of Rodriguez-Donis et al. [33,34] following the general feasibility criteria published by Rodriguez-Donis et al. [31].

The book of Luyben and Chien [32] devotes a whole chapter to the batch distillation of azeotropes. They studied the separation of two mixtures by batch extractive distillation, using different operational policies. In most of the extractive distillation processes, the component withdrawn is a saddle point of the residue curve map, namely an intermediate boiling of the distillation region.

In the case of *azeotropic distillation*, the entrainer is not fed continuously into the column, but added to the still together with the charge at the start of the process. Unlike batch extractive distillation, whose feasibility assessment requires also the knowledge of volatility order regions, that of batch homoazeotropic distillation only relies upon residue curve map analysis. Residue curve map analysis is the basis of the design and synthesis of homoazeotropic distillation [35–37].

A simple method for the prediction of the behaviour, the feasibility and separation sequencing of multicomponent batch distillation has been developed by Bernot et al. [38]. Using the residue curve maps and global material balances, they identified the boundaries and distillation regions at infinite number of stages and high reflux ratio (“maximal separation”). The batch distillation regions were determined for ternary mixtures on the basis of only the temperatures of pure components and azeotropes, and azeotropic compositions by Foucher et al. [39] who also applied their method to the screening of entrainers. Later on, methods were suggested for the determination of batch distillation regions and product sequences for mixtures with arbitrary numbers of components requiring the knowledge of fixed point stabilities [40–42], or using only boiling point and composition information [43].

Rodriguez-Donis et al. [44] proposed a set of entrainer selection rules for homoazeotropic batch distillation in batch rectifiers and strippers. Safrit and Westerberg [45] presented a tool for generating batch distillation column sequences, when batch rectifying, stripping, middle vessel and extractive middle vessel columns are allowed.

Another possible method for the separation of azeotropic mixtures is the *batch heteroazeotropic distillation* (BHD), where either

the original components form a heteroazeotrope, or a heteroazeotrope is introduced by adding an entrainer to the mixture, leading to the formation of two liquid phases. By separating the two phases with decantation, it is possible to get through the original azeotropic composition. The top vapour composition to be decanted after condensation lies near the heteroazeotropic composition, which is an unstable node of the residue curve map. The method has been applied as early as 1902 [46] for the production of ethanol from its aqueous mixture using benzene as entrainer. The batch heteroazeotropic distillation is widespread in the industry. It is only reported to be performed in batch rectifiers equipped with a decanter, and in open operation mode, that is, with continuous distillate withdrawal.

Pham and Doherty [47] described the structure and properties of residue curve maps for ternary heterogeneous azeotropic mixtures. Entrainer selection rules for the heteroazeotropic batch distillation were published by Rodriguez-Donis et al. [48]. The batch heteroazeotropic distillation was investigated with variable decanter holdup by Rodriguez-Donis et al. [49]. However, they investigated the variation of the hold-up of the entrainer-rich phase only. The distillate came from the entrainer-lean phase only, which had a constant hold-up. In order to increase the recovery by maintaining the phase split longer time, the entrainer-lean phase could also be partially refluxed. Skouras et al. [50,51] distinguished two main types of batch heteroazeotropic distillation. By Mode I, distillation and the liquid-liquid phase split are applied sequentially, that is the composition of the reflux (and the distillate) equals that of the condensate (as by Pham and Doherty [47]), and the existence of two liquid phases is only exploited at subsequent separation of the distillate. Düssel and Stichlmair [23] presented a batch stripping process operated by Mode I for the separation of water and pyridine using toluene as entrainer. By Mode II, distillation and phase separation occurs simultaneously and the reflux has different composition than that of the condensate. For Mode II there are two separation strategies as presented by Koehler et al. [52] and Skouras et al. [50,51]. By Strategy A the entrainer-rich phase is totally, and by Strategy B only partially refluxed, respectively. Obviously more entrainer is required for Strategy B since a considerable part of it is removed from the column. Therefore it proves to be a competitive alternative to Strategy A only in the cases where the original mixture already contains the entrainer in sufficient quantity.

By extending the method of Pham and Doherty [47] Lang and Modla [53] suggested a general method for the calculation of the residue curves and for the determination of batch distillation regions relevant for the heteroazeotropic distillation. The method considers not only the VLLE, but operating parameters like reflux, as well. Any fraction of either liquid phase can be refluxed (and withdrawn as distillate), while the hold-up of both phases is constant. The authors suggested distinguishing two versions for both strategies of Mode II: Version 1, where the E-lean phase is not refluxed and Version 2 where this phase is refluxed partially (in order to increase the reflux ratio, if necessary).

The operation modes and strategies presented above are also discussed by Luyben and Chien [32]. They studied the dehydration of acetic acid via batch heteroazeotropic distillation by using isobutyl acetate and vinyl acetate as entrainer. They also suggested an overall control strategy for this process.

Skouras et al. [50,51] extensively studied the closed operation mode of the batch rectifier configuration and multivessel columns. Pommier et al. [54] developed a specific software architecture, which uses sequential quadratic programming and genetic algorithm to optimise batch columns. The efficiency of this tool was also demonstrated on a batch heteroazeotropic distillation process. The rigorous simulation of the separation of the azeotrope toluene – pyridine with water showed that the operation planned accord-

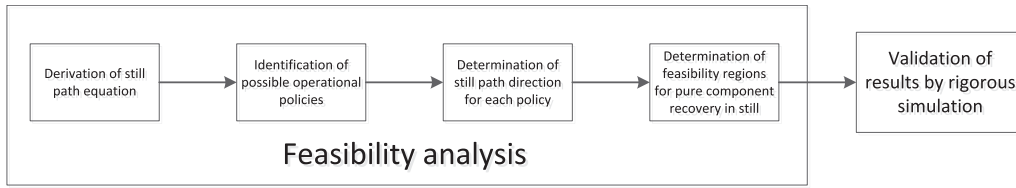


Fig. 1. The methodology used in the paper.

ing to Mode II Strategy A Version 1 (no accumulation in the decanter of the entrainer totally refluxed) was in fact behaving like Mode II Strategy B Version 1 (partial reflux of entrainer and its accumulation in the decanter) because of the change of the overhead vapour composition and the decanter phase split with time.

The batch heteroazeotropic distillation with continuous entrainer feeding (also known as heterogeneous batch extractive distillation) was investigated by Modla et al. [55,56], Rodriguez-Donis et al. [57], Van Kaam et al. [58] and Barreto [26].

Denes et al. [59] suggested a new double-column system operated in closed mode for heterogeneous batch distillation, which can produce both original components at the same time. The charge is divided between the two reboilers, where the two products are accumulated at the end of the process. The system is operated according to Mode II, Strategy A, Version 1. Denes et al. [60] proposed a generalised configuration of the above double-column system, which has more operational parameters and thus greater flexibility.

The behaviour of rectifying profiles and overlapping of distillation regions in heterogeneous mixtures were studied by Krolkowski et al. [61]. This paper contains a very comprehensive and detailed literature review about all aspects of the synthesis of distillation systems for the separation of homo- and heteroazeotropic mixtures, too.

The aim of this paper is to propose a general model of batch heteroazeotropic distillation, identify the possible operational policies and to confirm the results of the feasibility study. Its novelty is the general treatment of batch heteroazeotropic distillation, and the systematic identification of all the possible operational policies, including several policies previously not published. As in the model of Lang and Modla [53], any fraction of both liquid phases can be refluxed and distillate withdrawn can be withdrawn from both phases. This is combined with the possibility of varying the liquid hold-up of the entrainer-rich phase in the decanter proposed by Rodriguez-Donis et al. [49], however, the variation of the entrainer-lean phase is considered as well.

The paper is organised as follows: first, it presents the general model, then the equation describing the still path, which is defined as the trajectory of the still composition [38], is derived and the feasibility of directing the still path in different directions is investigated. Second, the possible operational policies are identified and discussed. Third, rigorous simulation of some operational policies are presented in order to validate the model and to demonstrate the benefits of using a non-traditional operational policy. Fig. 1 summarizes the methodology used in the present paper.

2. Generalised model for feasibility studies

Fig. 2 shows the scheme of the batch heterogeneous distillation column of the generalised model.

In the feasibility analysis the following simplifying assumptions are applied:

- the composition of the condensate is constant and equals to that of the heteroazeotrope,
- the composition in the decanter equals that of the condensate,

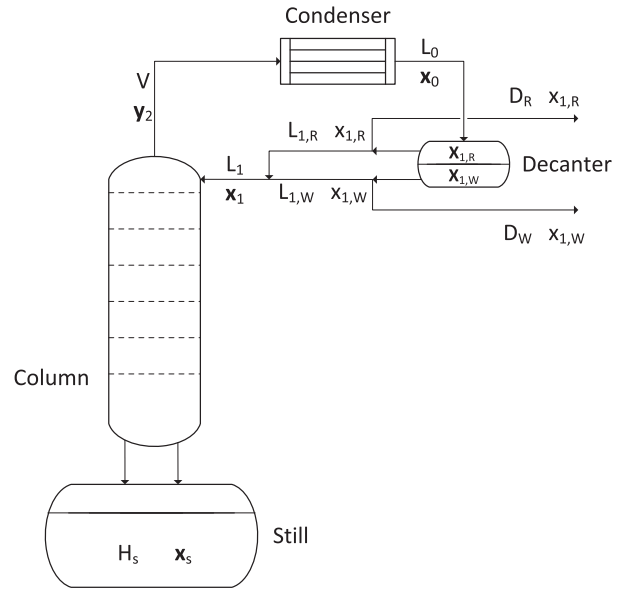


Fig. 2. Heteroazeotropic batch distillation column model.

- the vapour and liquid hold-ups of the column and of the condenser are negligible,
- constant molar overflow.

The condensate of the top vapour, which has a molar flow rate of V and molar composition of y_2 , gives rise to a two-phase liquid stream with a flow rate of L_0 , and composition x_0 . Considering that x_0 lies in the heterogeneous region, near the unstable node heteroazeotrope, the condensate is a heterogeneous liquid. $L_{0,R}$ and $L_{0,W}$ are the flow rates of the E-rich and E-lean (E-weak) phase in the condensate. The phase split ratio is η_R , which is defined as the ratio of the flow rate of the E-rich phase and the total flow rate of the condensate:

$$\eta_R = \frac{L_{0,R}}{L_0} \quad (1)$$

Accordingly, the ratio of the flow rate of the E-lean phase and the total flow rate is:

$$\frac{L_{0,W}}{L_0} = 1 - \eta_R \quad (2)$$

The first two of the simplifying assumptions also mean that the phase ratio (η_R), and the composition of the phases leaving the decanter ($x_{1,R}$ and $x_{1,W}$) are not changing with time, although they may change slightly during a real operation [54].

Both liquid phases can be refluxed or withdrawn as distillate. Besides, the hold-up of both phases can be increased, decreased or kept constant in the decanter. The change in the hold-up of the E-rich (E-lean) phase is characterised by the accumulation ratio a_R (a_W), which is defined as the ratio of the difference between the

E-rich (E-lean) phase flow rate entering and leaving the decanter and the flow rate of this phase entering the decanter:

$$a_R = \frac{L_{0,R} - (L_{1,R} + D_R)}{L_{0,R}} \quad (3)$$

$$a_W = \frac{L_{0,W} - (L_{1,W} + D_W)}{L_{0,W}} \quad (4)$$

where D_R and D_W are the flow rates of E-rich and E-lean phases withdrawn as distillate, $L_{1,R}$ and $L_{1,W}$ are the flow rates refluxed, respectively. If the value of the accumulation ratio is higher than zero, the incoming flow rate of the respective phase is higher than its flow rate leaving the decanter, thus this phase is accumulated in the decanter. If the accumulation ratio is lower than zero, the hold-up of this phase decreases in the decanter.

The reflux splitting ratios r_{S_R} and r_{S_W} characterise how the stream of the E-rich and E-lean phases leaving the decanter are divided into reflux and distillate. They are defined as the ratio of the flow rates refluxed and leaving the decanter:

$$r_{S_R} = \frac{L_{1,R}}{L_{1,R} + D_R} \quad (5)$$

$$r_{S_W} = \frac{L_{1,W}}{L_{1,W} + D_W} \quad (6)$$

Multiplying r_{S_R} with $(1 - a_R)$ (r_{S_W} with $(1 - a_W)$), we obtain r_R (r_W), the ratio of the flow rates refluxed and condensed:

$$r_R = (1 - a_R) r_{S_R} = \frac{L_{1,R}}{L_{0,R}} \quad (7)$$

$$r_W = (1 - a_W) r_{S_W} = \frac{L_{1,W}}{L_{0,W}} \quad (8)$$

where

$$1 - a_R = 1 - \frac{L_{0,R} - (L_{1,R} + D_R)}{L_{0,R}} = \frac{L_{0,R} - L_{0,R} + (L_{1,R} + D_R)}{L_{0,R}} \quad (9)$$

$$1 - a_W = \frac{L_{1,R} + D_R}{L_{0,R}} \quad (10)$$

The reflux ratio of the E-rich (E-lean) phase can be defined as the ratio of the flow rates refluxed and non-refluxed:

$$R_R = \frac{L_{1,R}}{L_{0,R} - L_{1,R}} \quad (11)$$

Similarly for the E-lean phase:

$$R_W = \frac{L_{1,W}}{L_{0,W} - L_{1,W}} \quad (12)$$

Compared to the traditional definition of the reflux ratio, the distillate flow rate is replaced with the non-refluxed one, in order to take into account the effect of hold-up change. The phase reflux ratio has a negative value, in the case of refluxing the decanter hold-up of the phase to the column. Through a series of transformations, we can obtain the relationship between r_R and R_R (r_W and R_W):

$$r_R = \frac{L_{1,R}}{L_{0,R}} = \frac{\frac{L_{1,R}}{L_{0,R} - L_{1,R}}}{\frac{L_{0,R}}{L_{0,R} - L_{1,R}} + 1} = \frac{R_R}{R_R + 1} \quad (13)$$

$$r_W = \frac{R_W}{R_W + 1} \quad (14)$$

r_R is always nonnegative, and for positive, finite R_R , its value is between one and zero. As R_R tends to infinity, r_R approaches unity. In the case of negative R_R , r_R is greater than unity.

The flow rate of the condensate is equal to that of the top vapour V :

$$L_0 = L_{0,R} + L_{0,W} = \eta_R L_0 + (1 - \eta_R) L_0 = V \quad (15)$$

The total flow rate of the reflux stream:

$$L_1 = L_{1,R} + L_{1,W} = r_R L_{0,R} + r_W L_{0,W} \quad (16)$$

$$L_1 = [r_R \eta_R + r_W (1 - \eta_R)] V \quad (17)$$

The total component flow rates in the reflux:

$$L_1 x_1 = L_{1,R} x_{1,R} + L_{1,W} x_{1,W} \quad (18)$$

The evolution of the still composition is described by a differential equation, which can be derived from the differential total and component material balances of the still pot.

The total material balance:

$$\frac{dH_S}{dt} = L_1 - V \quad (19)$$

$$\frac{dH_S}{dt} = [r_R \eta_R + r_W (1 - \eta_R) - 1] V \quad (20)$$

$$\frac{dH_S}{dt} = [(r_R - 1) \eta_R + (r_W - 1) (1 - \eta_R)] V \quad (21)$$

The component material balance of the still:

$$\frac{d(H_S x_S)}{dt} = L_1 x_1 - V x_0 \quad (22)$$

$$\frac{d(H_S x_S)}{dt} = [(r_R - 1) \eta_R x_{1,R} + (r_W - 1) (1 - \eta_R) x_{1,W}] V \quad (23)$$

By applying the product rule of differentiation, the equation of the still path:

$$H_S \frac{dx_S}{dt} = \frac{d(H_S x_S)}{dt} - x_S \frac{dH_S}{dt} \quad (24)$$

The final form of the equation describing the evolution of the still composition is:

$$\frac{dx_S}{dt} t = \frac{V}{H_S} [(1 - r_R) \eta_R (x_S - x_{1,R}) + (1 - r_W) (1 - \eta_R) (x_S - x_{1,W})] \quad (25)$$

The Eq. (25) consists of two terms, which represent the removal of the E-rich and the E-lean phase from the column, respectively, by either withdrawal as distillate, or accumulating in the decanter. When the assumption of constant condensate composition is valid, the two ways of removal have exactly the same effect. If one of the phases is completely refluxed (no distillate is withdrawn and the hold-up of the respective phase in the decanter is constant), the right hand side of Eq. (25) will only consist of the term related to the other phase, as either r_R (total reflux of E-rich phase) or r_W (total reflux of E-lean phase) equals one.

3. Operational policies

In this section, the possible operational policies are identified based on the operational parameters r_R and r_W , then the still path directions is determined for each policy, and the feasibility of recovering one of the original components in the still at the end of operation is discussed.

3.1. Identification of possible operational policies

The model has three independent operational parameters: r_R , r_W and V . While V , which is related to the heat duty of the still, only

Table 1

The possible operational policies (reintr.: reintroduction – a greater amount of liquid is refluxed than what leaves the column as condensate).

	r_R	r_W	Reflux	Example in the literature
1	0	0	No reflux	
2		<1	E-lean phase (partial)	
3		1	E-lean phase (total)	
4		>1	E-lean phase (reintr.)	
5	<1	0	E-rich phase (partial)	Mode II, Strategy B, Version 1 [50,53]; Mode II, Strategies 2' and 2'' [62]
6		<1	E-rich (partial) and E-lean phase (partial)	Mode II, Strategy B, Version 2 [53]
7		1	E-rich (partial) and E-lean phase (total)	
8		>1	E-rich (partial) and E-lean phase (reintr.)	
9	1	0	E-rich phase (total)	Mode II, Strategy A, Version 1 [50,53]; Mode II, Strategy 1 [62]
10		<1	E-rich (total) and E-lean phase (partial)	Mode II, Strategy A, Version 2 [53]
11		1	E-rich (total) and E-lean phase (total)	Total reflux operation
12		>1	E-rich (total) and E-lean phase (reintr.)	
13	>1	0	E-rich phase (reintr.)	Mode II, Strategy 3 [62]
14		<1	E-rich (reintr.) and E-lean phase (partial)	
15		1	E-rich (reintr.) and E-lean phase (total)	
16		>1	E-rich (reintr.) and E-lean phase (reintr.)	

influences the speed of the distillation, r_R and r_W determine the direction of the still path, as well. By changing the values of these two operational parameters, either by varying the decanter hold-up or the reflux splitting ratios, the direction of the still path can be changed. As the still composition is a very important characteristic of batch distillation, it is expedient to distinguish the possible operational policies on the basis of the values of the operational parameters r_R and r_W . The 16 different possible policies are shown in Table 1. If r_R (r_W) is zero, the E-rich (E-lean) phase is not refluxed. If r_R (r_W) is one, the E-rich (E-lean) phase is refluxed entirely. If r_R (r_W) is between zero and one, the respective phase is partially refluxed, while the remaining amount of the phase is either withdrawn as distillate or accumulated in the decanter. If r_R (r_W) is greater than unity, the amount of the E-rich (E-lean) phase refluxed is greater than what is removed from the column with the top vapour. To supply this difference in the flow rates, the hold-up of the respective phase must be decreased.

In Eq. (25), the reflux splitting ratios (r_{SR} and r_{SW}) and the accumulation ratios (a_R and a_W) are only present in the form of their products (r_R and r_W). That is, the same effect can be achieved either by accumulating one of the phases, or by its withdrawal as distillate. The practical realization of the withdrawal is of course easier, whereas a hold-up change of the phases in the decanter would require the application of a controller. However, accumulating one of the phases in the decanter may be useful, e.g. in order to maintain longer the existence of two liquid phases and to improve the final product recovery yield as shown by Rodriguez-Donis et al. [49]. The case is different if r_R or r_W is greater than unity, as this is only possible if the decanter hold-up is reduced, that is, a_R or a_W is greater than one.

3.2. The still path direction of the operational policies

As recalled by the general Eq. (25), the still path can be characterised by the direction of the sum of two other vectors with direction of $(x_S - x_{1,R})$ and $(x_S - x_{1,W})$, respectively, whose magnitude depends on r_R and r_W , respectively. If the value of r_R and r_W is positive, the two vectors, both starting at x_S , point away from $x_{1,R}$ and $x_{1,W}$, respectively. Their direction can be reversed, if r_R or r_W is greater than one. Therefore, the direction of the resultant vector depends on the operation policy through the value of the operational parameters r_R and r_W .

The results are illustrated for a mixture of A, B and E. A and E form a binary heteroazeotrope, which is the only unstable node in the system. As the derivation of the equation did not exploit the type of the heteroazeotrope, the results are also valid for ternary heteroazeotropes. A and B can be a homoazeotropic (mini-

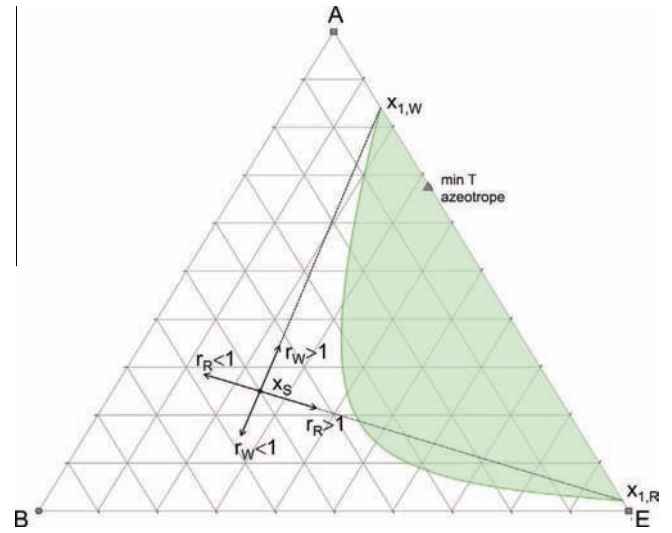


Fig. 3. The possible directions of the vectors influencing the still path.

mum or maximum) or a zeotropic mixture. With an azeotrope A-B, there may exist a distillation boundary, but as already hinted by Rodriguez-Donis et al. [49] and demonstrated through the distillation regions for heteroazeotropic batch distillation by Modla and Lang [53] this does not affect the separation feasibility.

The two vectors influencing the still path are presented in Fig. 3. Both vectors originate from x_S , the actual still composition. The vector corresponding to the E-lean phase points away from $x_{1,W}$ if $r_W < 1$, and towards it if $r_W > 1$, as the removal of E-lean phase ($r_W < 1$: less than total reflux of the phase) drives the still composition away from the E-lean phase composition. The other vector, corresponding to the E-rich phase points away from $x_{1,R}$ if $r_R < 1$, and towards it if $r_R > 1$. If r_R or r_W equals 1, the respective vector does not exist.

This is the case by the classical operational policy, Mode II, Strategy A, Version 1 (Policy 9 in Table 1), where $r_R = 1$ and $r_W = 0$, thus the single influencing vector points away from the composition of the E-lean phase.

The possible directions of the derivative vector, that is, the direction of the still path for every possible operational policy can be obtained by adding up the two vectors discussed earlier for each operational policy. The possible directions of the derivative vector calculated in this way can be classified into eight zones

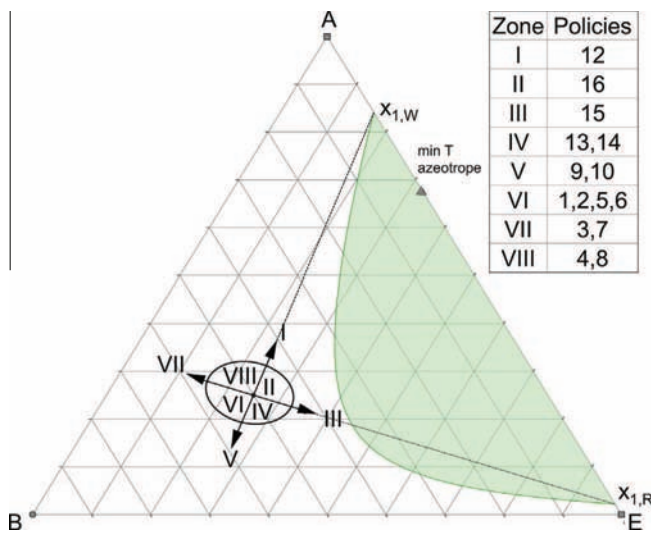


Fig. 4. The direction of the still path for the different operational policies.

(Fig. 4). The vector points either towards or away from the composition of one of the phases (Zones I, III, V and VII), or they are situated between these four main directions (Zones II, IV, VI and VIII).

It can be seen that the still composition can be changed in any desired direction. Zones I, II and VIII, where r_W is higher than one, correspond to directions, which were not reported previously. At least one operational policy belongs to every zone, as it is shown in Fig. 4. Policy 11 (total reflux operation) is an exception not belonging to any zone, as the still composition is constant.

3.3. Feasibility of recovering one of the original components in the still

Since the A-B mixture, azeotropic or zeotropic, is the one to be separated, the still path should not in practice end on this edge (except close to B, where the purity requirement is satisfied). By directing the still path appropriately, it can be possible to recover B in the still, thus eliminating the need of a further separation step, the separation of B and E. This requires the adjustment of the

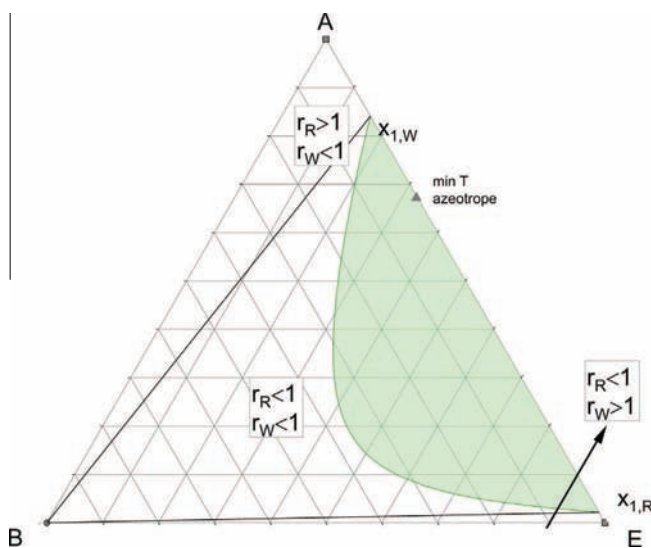


Fig. 5. Feasibility regions with the parameter values required to recover B in the still.

operational parameters r_R and r_W , since by using the traditional Policy 9 (refluxing the whole amount of E-rich phase only), the still path will reach either the A-B or B-E edge, depending on the composition of the charge and the heteroazeotrope.

The composition space can further be divided into three regions (Fig. 5), with different necessary values of r_R and r_W , to enable the recovery of B from the still compositions lying in the region in question. If the still composition lies in the region between $x_{1,W}$ and B, which coincides with Zone V, Policy 9 or 10, that is, $r_R = 1$ and $r_W < 1$ (total reflux of E-rich phase, partial or no reflux of E-lean phase), have to be used. In this way, the still composition will stay on this line, and approach B. Similarly, if the still composition lies on the line joining $x_{1,R}$ and B, which coincides with Zone VII, Policy 3 or 7, that is $r_R < 1$ and $r_W = 1$, (partial or no reflux of E-rich phase, total reflux of E-lean phase) have to be used. Between these two lines, the still path direction has to be in Zone VI, in order to move towards B. This means that both r_R and r_W have to be lower than one, that is, the phases are refluxed partially, or not at all. Outside this region, the still path direction must lie in either Zone IV (if the still composition is close to the A-B edge) or in Zone VIII (if the composition is close to the B-E edge). Thus, one of the parameters must be higher than one, which means the reduction of the hold-up of one of the phases. If the still composition is close to the A-B edge, this phase is the E-rich one ($r_R > 1$); if the composition is close to the B-E edge, it is the E-lean one ($r_W > 1$).

As the decanter hold-up is physically limited, it is usually necessary to combine the different operational policies. It must be noted that in real columns, the influence of the variation of the decanter hold-up is only significant in the case when the column (and condenser) hold-up is relatively small.

4. Rigorous simulation

In order to validate the results of the feasibility analysis by using fewer simplifying assumptions, and to illustrate the advantage of using a non-traditional operational policy, rigorous simulation calculations were performed with the dynamic module (CC-COLUMN) of the professional flowsheet simulator CHEMCAD.

For rigorous simulation, the following simplifying assumptions are applied:

- theoretical trays,
- constant volumetric liquid holdup on the trays and in the decanter,
- negligible vapour holdup.

All the calculations were performed with the same CHEMCAD model (Fig. 6). The column was modelled with a SCDS column with a separate total condenser. The still was a heated Dynamic Vessel. Two other Dynamic Vessels served as product tanks for the E-rich and E-lean phases, respectively, while a third one was used as a decanter with constant E-rich and E-lean liquid levels. The values of the liquid levels were supplied by two RAMP modules, which change the value of an operating parameter (in our case, the liquid levels) with time following a specified piecewise linear function.

Theoretical plate numbers were chosen in such a way that the distillate composition approached the heteroazeotropic one closely. The value of decanter hold-up was chosen to be high enough to enable the demonstration of the effect of phase hold-up variation, but low compared to the charge volume.

Out of the 16 possible operational policies, not all are of practical interest. For those, which were already published earlier, references are given in Table 1. The practically useful policies for regular operation are:

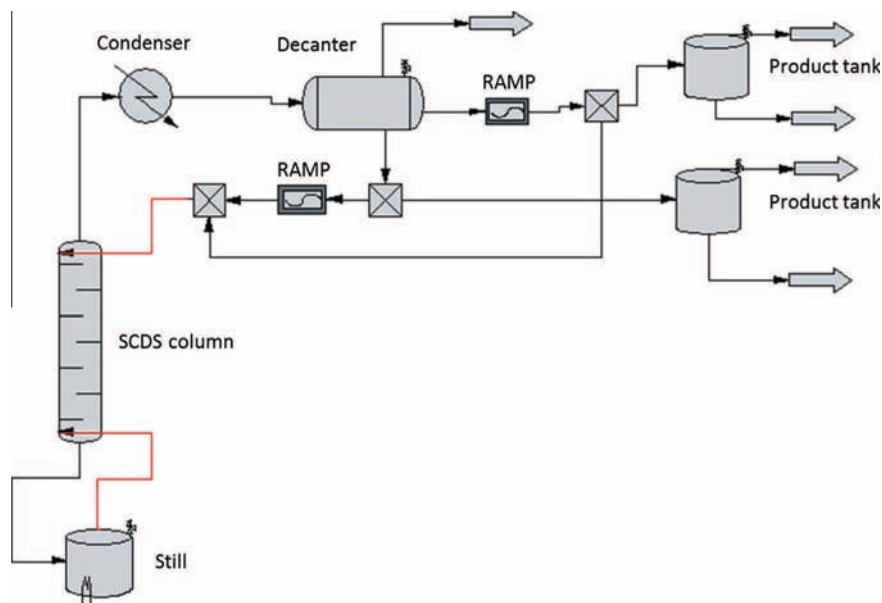


Fig. 6. The CHEMCAD model of the batch rectifier with variable liquid hold-up.

- Policy 9 with $r_R = 1$ and $r_W = 0$ is, what Lang and Modla [53] call Mode II, Strategy A, Version 1, where the E-rich phase is entirely refluxed, and the E-lean phase is withdrawn as distillate (or accumulated in the decanter). This is the traditional and conceptually most straightforward operational policy [51].
- Policy 5, where the E-rich phase is only partially refluxed and the E-lean phase is not refluxed (Mode II, Strategy B, Version 1), results in a deviation of the still path in the direction pointing away from the E-rich phase composition (Zone VI), compared to the still path of Policy 9.
- Policy 13 shows a similar deviation to Policy 5, but towards the E-rich phase composition (Zone IV).
- If necessary, the reflux ratio can be increased by partially refluxing of the E-lean phase, without changing the still path direction, but at the cost of an increased operation time. By applying partial E-lean phase reflux to the three policies presented above, Policies 10, 6 and 14 are obtained, respectively.
- Policies 7 and 8 are useful if the still composition is located between the line joining the E-rich phase composition (x_R) and the original component miscible with E (B in Fig. 4), and the B-E edge of the composition triangle.

There are some policies, which do not seem to be of practical interest:

- Policies 3 and 4 provide the same still path as the above two operational policies, but without the partial reflux of the E-rich phase. With the resulting increased E-loss, the condensate can become homogeneous after a shorter period of time, therefore Policies 3 and 4 are not recommended.
- Policies 1 and 2 are not recommended either, as the still path has the same direction as by Policies 5 and 6, but the lack of reflux (Policy 1), or that the E-lean phase is only partially refluxed (Policy 2), is likely to cause problems in the practical operation.

There are also a few policies, which can be useful only for special purposes, but not for the regular operation of the column:

- Policies 12 and 15 are similar to each other: one of the phases (12: E-rich, 15: E-lean) is entirely refluxed, while the hold-up of the other phase is reduced through refluxing it to the column. These policies could be used for a short time (as the decanter hold-up is limited) to quickly change the still composition towards the E-lean (Policy 12) or the E-rich (Policy 15) phase composition, respectively.
- Finally, Policy 11 is the total reflux operation, where both r_R and r_W equal one, normally applied during the start-up of the column.

The new policies 8, 12 and 16, proposed for the first time here, were applied in order to demonstrate that the still path can be turned into directions previously not reported, that is, towards the E-lean phase. The test mixture studied is water (A) – formic acid (B) – propyl formate (E), where propyl formate is the entrainer. The calculated residue curve map of the mixture along with the binodal curve at $T = 25^\circ\text{C}$ is presented in Fig. 7. The vapour-liquid-liquid equilibria were described with the NRTL model. The NRTL parameters used can be found in Appendix A. The mixture A-B exhibits a maximum boiling-point homoazeotrope, while A and E form a heteroazeotrope, enabling the separation of the A-B mixture.

The column had 50 theoretical trays; the heat duty applied is 2 kW. The hold-up of the decanter was 0.5 dm^3 ; that of the column was $0.01\text{ dm}^3/\text{plate}$. The charge had a molar amount of 160 mol (5.08 dm^3) and a composition of 52.5 mol% A, 40.5 mol% B and 7% E. The column was operated for 40 min under total reflux, after which one of the policies previously mentioned was applied. The decanter was empty at the start of the operation; at the end of the total reflux period, the volumes of liquid phases inside it were equal (0.25 dm^3). The values of the operational parameters are shown in Table 2, while the respective still paths are presented in Fig. 8. Each path starts from the composition at the end the total reflux period ($x_{s,0}$). For Policy 12, the still composition moves towards that of the E-lean phase, while for Policies 8 and 16, the path deviates from this direction as predicted: towards the edge A-B (Zone VIII, Policy 8) or vertex E (Zone II, Policy 16). That is, the still

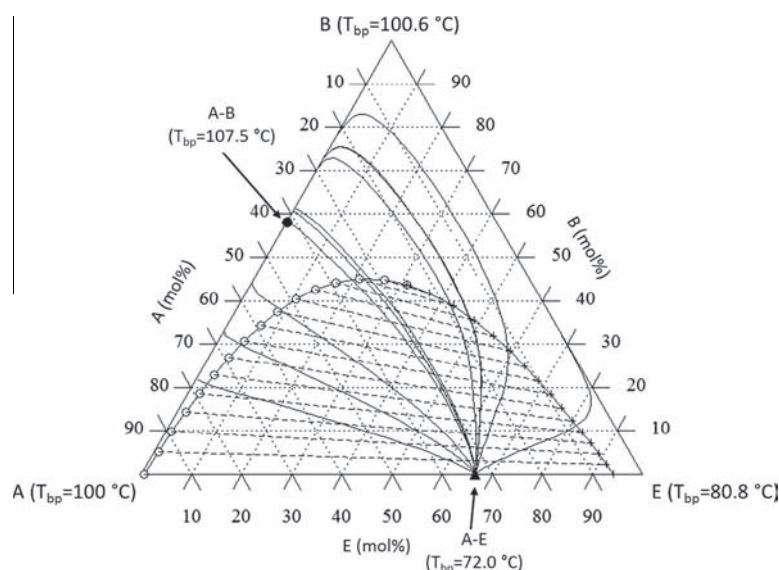


Fig. 7. The residue curve map of the mixture water (A) – formic acid (B) – propyl formate (E).

Table 2

The operational parameters of the policies investigated.

Policy	r_R	r_W
8	0.986	1.21
12	1.0	
16	1.014	

path directions are in accordance with the results of the feasibility analysis.

To demonstrate the advantage of using a non-traditional policy, two production processes (Productions 1 and 2) were investigated, as well. The calculations were carried out for the mixture aniline (A) – ethylene glycol (B) – water (E). The vapour–liquid–liquid equilibria were described with the NRTL model. The model parameters can be found in Appendix A. A–B form a minimum boiling-point homoazeotrope, while A and E form a heteroazeotrope, thus enabling the separation of the mixture A–B. The column had 50 theoretical plates, and the hold-up was 0.01 dm³/plate. The volume of the decanter was 0.75 dm³, the hold-up of both phases at the end of the total reflux period was 0.125 dm³. The heat duty applied was 2 kW. The charge had a molar amount of 100 mol (6.54 dm³) and a composition x_F of 47.5 mol% A, 32.5 mol% B and 20% E. The

goal of the separation was to obtain ethylene glycol in the still with a minimum purity of 97 mol%, while withdrawing the E-lean phase (aqueous aniline) as distillate.

Production 1 consisted of a total reflux period for 30 min, required to fill up the decanter, and subsequent operation by the traditional Policy 9, that is, the entire E-rich phase was refluxed ($r_R = 1$, $r_W = 0$). Fig. 9 shows the trajectory of the average composition of the still and column hold-ups. The still path equation (Eq. (25)) was derived with the assumption of negligible column hold-up. If this assumption is omitted, and the average hold-up composition is used instead of the still composition, the equation will have the same form. This means that the results on the still path direction presented in Section 3 will be valid for the hold-up path, instead of the still path. During the total reflux period, the decanter hold-up was built-up, and the hold-up composition, starting at x_F , moved away from the A–E azeotrope. After this initial period, the E-rich phase was refluxed, the E-lean phase was withdrawn as distillate, so the hold-up composition moved away from the composition of the E-lean phase, which was now the aqueous aniline, as predicted by the feasibility analysis. As the hold-up composition approached the A–B edge, that is the hold-up was depleted in E, B started to appear in the two liquid phases in the decanter and finally the liquid phases changed place: the E-lean phase, which used to be the lighter phase, became the heavier

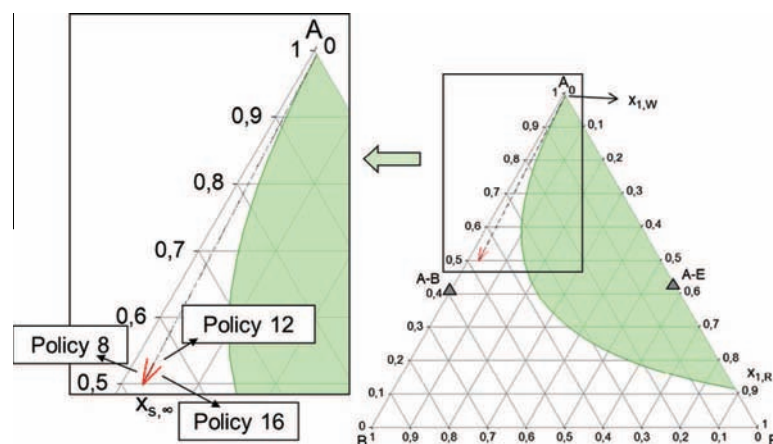


Fig. 8. The calculated evolution of still composition (Policies 8, 12, 16).

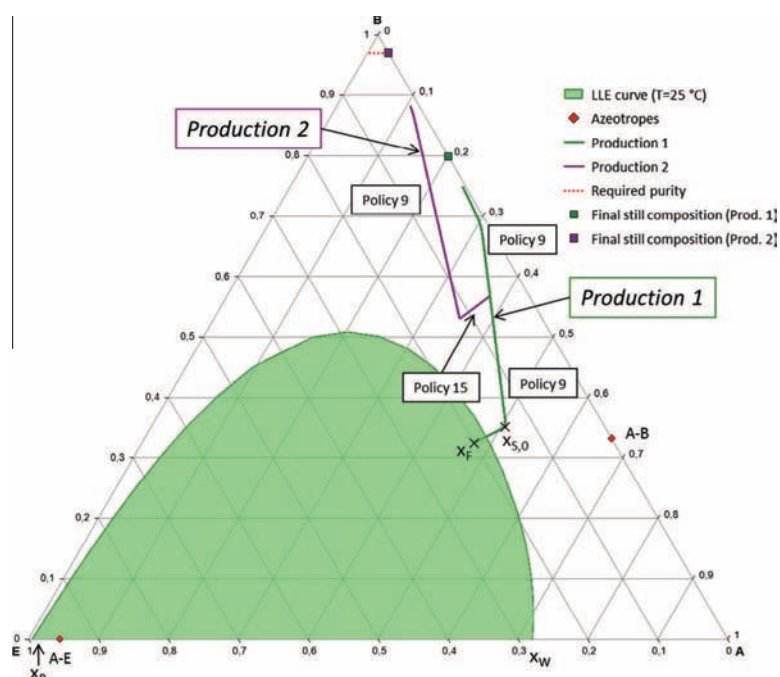


Fig. 9. The hold-up paths and final still compositions of Productions 1 and 2 for the separation of aniline (A) – ethylene glycol (B) with water (E).

one. Eventually, this also led to the disappearance of the liquid–liquid split. The operation is stopped after 427.5 min, immediately before the phase interchange. At this point the final still composition was 79.9 mol%, which stayed below the prescribed value.

Production 2 was identical to Production 1 during the first period of operation (396 min). At this point, instead of continuing the operation by Policy 9, Policy 15 was applied for 10 min: the hold-up of the E-rich phase was reduced ($r_R > 1$), and the E-lean phase was entirely refluxed ($r_W = 1$). The E-rich phase hold-up was reduced by 60%, that is, 75 cm³ of this phase was refluxed to the column, corresponding to $r_R \approx 1.133$. The predicted effect of using Policy 15 can be clearly seen in Fig. 9, as the movement of the average hold-up composition towards the E-rich phase composition. After 10 min, the operation was continued by Policy 9, and the average hold-up path moved away once more from the E-lean phase composition. At the end of the operation, an acceptable B purity (97.0%) and a high recovery (91.6%) was reached in the still. The total operation time was 553 min. If the operation was continued, the same phase interchange phenomenon described at Production 1 would be encountered at 560 min. By using a non-traditional operational policy, the liquid–liquid phase split could be maintained longer in the decanter for Production 2 than for Production 1, allowing to reach a higher purity in the still.

The results of the rigorous simulations indicate that the still path directions are in accordance with the results of the feasibility analysis, and that the application of non-traditional operational policies can render such separations feasible, which are infeasible by the traditional policies.

5. Conclusions

A general model of batch heteroazeotropic distillation was proposed. Both liquid phases can be refluxed or withdrawn as distillate. Their hold-up in the decanter can be increased, decreased or kept constant, as well. Two operational parameters r_R and r_W were introduced, defining the ratio of the flow rates of the E-rich and E-lean phase refluxed and condensed, respectively. By assuming

maximal separation, that is, that the condensate is always the heteroazeotrope, the still path equation was derived. Depending on the values of the parameters r_R and r_W , 16 possible operational policies were distinguished.

The direction of the still path is determined by the sum of two vectors, whose magnitude depends on the value of the operational parameters. The still path direction can lie in eight different zones, which cover all the possible directions. By determining the still path direction for every operational policy, we found that every zone corresponds to at least one policy, that is, still path compositions can be changed in any desired direction by choosing the right values of r_R and r_W . By using appropriate operational policies, it is also possible to recover a pure component in the still, thus eliminating the need for a further separation step. From the 16 operational policies, 11 can be considered as useful in practice. The composition space can be divided into three regions, with different values of r_R and r_W required to recover the least volatile pure component in the still from the still compositions lying in the region in question.

The still path directions for three new operational policies were validated by rigorous simulation for the mixture water – formic acid – propyl formate. The benefit of using a non-traditional operational policy with hold-up reduction in the decanter was demonstrated, as well. The recovery of ethylene glycol in the still from an ethylene glycol – aniline mixture by using water as entrainer was infeasible with the traditional policy of entirely refluxing the entrainer-rich phase. By combining this policy with a short period of a non-traditional one, where the hold-up of the entrainer-rich phase in the decanter was reduced by refluxing it, and the entrainer-lean phase was completely refluxed, the liquid–liquid phase split could be maintained longer, and thus it was possible to obtain ethylene glycol of required purity in the still.

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Table A1

NRTL parameters for water (A) – formic acid (B) – propyl formate (E) mixture.

<i>i</i>	<i>j</i>	B_{ij} (K)	B_{ji} (K)	α (–)	A_{ij} (–)	A_{ji} (–)	C_{ij} (–)	C_{ji} (–)
E	A	–327.315	–6253.91	0.2	33.8478	124.491	–5.51839	–17.4194
E	B	78.3303	127.613	0.3013	0	0	0	0
A	B	–362.885	342.424	0.2921	0	0	0	0

Table A2

NRTL parameters for aniline (A) – ethylene glycol (B) – water (E) mixture.

<i>i</i>	<i>j</i>	B_{ij} (K)	B_{ji} (K)	α (–)
A	B	256.926	343.831	0.29
A	E	–245.828	1790.56	0.1617
B	E	–338.073	405.263	0.2977

Appendix A. The value of the parameters used for the phase equilibria calculations

The NRTL parameters used for the calculations presented in Section 4, for the mixtures water – formic acid – propyl formate and – aniline – ethylene glycol – water, respectively, are given in Tables A1 and A2.

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