



General model for studying the feasibility of heterogeneous extractive batch distillation

Laszlo Hegely, Vincent Gerbaud, Peter Lang

► To cite this version:

Laszlo Hegely, Vincent Gerbaud, Peter Lang. General model for studying the feasibility of heterogeneous extractive batch distillation. *Industrial and engineering chemistry research*, 2014, vol. 53 (No 45), pp. 17782-17793. 10.1021/ie502704w . hal-01093449

HAL Id: hal-01093449

<https://hal.science/hal-01093449>

Submitted on 10 Dec 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID: 12222

Identification number: DOI : 10.1021/ie502704w
Official URL: <http://dx.doi.org/10.1021/ie502704w>

To cite this version:

Hegely, Laszlo and Gerbaud, Vincent and Lang, Peter *General model for studying the feasibility of heterogeneous extractive batch distillation*. (2014) Industrial & Engineering Chemistry Research, vol. 53 (No 45). pp. 17782-17793. ISSN 0888-5885

Any correspondence concerning this service should be sent to the repository administrator:
staff-oatao@inp-toulouse.fr

General Model for Studying the Feasibility of Heterogeneous Extractive Batch Distillation

Laszlo Hegely,^{†,‡} Vincent Gerbaud,^{‡,§} and Peter Lang^{*,†}

[†]Faculty of Mechanical Engineering, Department of Building Services and Process Engineering, Budapest University of Technology and Economics, Muegyetem rkp. 3-9, H-1111 Budapest, Hungary

[‡]INP, UPS, LGC (Laboratoire de Génie Chimique), Université de Toulouse, 4 allée Emile Monso, F-31432 Toulouse Cedex 04, France

[§]LGC (Laboratoire de Génie Chimique), CNRS, F-31432 Toulouse Cedex 04, France

ABSTRACT: By extending our former model for batch heteroazeotropic distillation, a general model is developed for the batch heterogeneous extractive distillation. An entrainer-rich and an entrainer-lean phase are present in the decanter, where the holdup of both phases can be reduced, kept constant, or increased, thanks to batch operation mode. Any fraction of both phases can be refluxed or withdrawn as distillate. The entrainer is fed continuously either onto one of the plates of the column, or into the decanter. The still path equation is derived for both cases. A discussion is given on the literature occurrence and practical applicability of the 16 possible operational policies, and the effect of continuous entrainer feeding on the still path direction of all operational policies is determined. The still path directions are validated by rigorous simulations for multiple operational policies for the mixture of ethanol, water, and *n*-butanol.

1. INTRODUCTION

Batch distillation is a widely applied separation technology in the pharmaceutical and specialty chemical industries.¹ Azeotropic and close-boiling mixtures are often encountered, and the separation of these mixtures requires the application of a special distillation method, such as pressure swing, extractive, and heteroazeotropic distillation. The addition of a new component, the entrainer (E), might alter the relative volatilities of the original components favorably. In the case of homoazeotropic distillation, E is added to the charge in the still at the start of the process, and no heteroazeotrope is present.

If E is added to the charge, and a heteroazeotrope is present in the system, formed either by the entrainer and one of the original components or by two original components, the separation method is called *batch heteroazeotropic distillation* (BHAD). The original azeotropic composition can be crossed due to the separation of the two liquid phases by decantation. The BHAD is used in the industry only in batch rectifiers equipped with a decanter. In this configuration, the heteroazeotrope must be the unstable node of the residue curve map, so that the top vapor composition lies in the two-liquid-phase region.

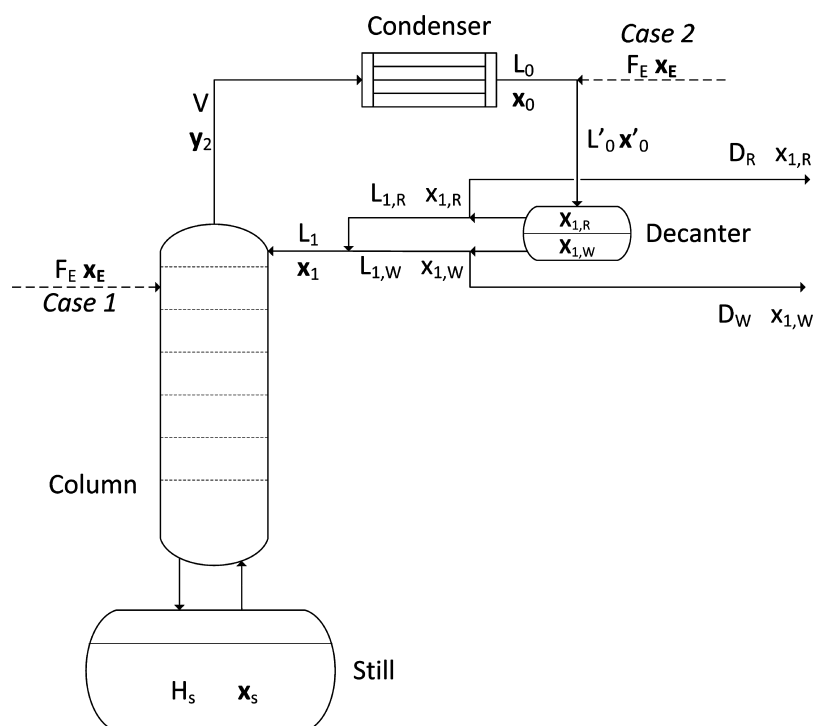
Two main types of BHAD can be distinguished, on the basis of whether distillation and the decantation of the two liquid phases occur sequentially (Mode I) or simultaneously (Mode II).^{2,3} By Mode I, the composition of the reflux and distillate is identical and the final distillate product is heterogeneous. By Mode II, since distillation and phase separation occurs simultaneously, the reflux usually has a different composition than that of the condensate, unlike batch homoazeotropic distillation. Skouras et al.^{2,3} distinguished two strategies for Mode II. The entrainer-rich phase is totally refluxed by Strategy A, and only partially refluxed by Strategy B. Rodriguez-Donis et

al.⁴ investigated the BHAD with variable E-rich phase decanter holdup. The E-lean phase had constant decanter holdup, and distillate was withdrawn only from this phase. The partial reflux of the E-lean phase is also allowed, as it can increase the recovery by maintaining the phase split longer. In the model of Lang and Modla,⁵ any fraction of either liquid phase can be refluxed (and withdrawn as distillate); however, the holdup of both phases is constant.

Hegely et al.⁶ proposed a general model of BHAD, where both liquid phases can be refluxed or withdrawn as distillate. Moreover, the holdup of both liquid phases in the decanter also can be increased, decreased, or kept constant. The still path equation was derived, and the possible operational policies were identified. Denes et al.^{7,8} suggested new, closed double-column configurations for BHAD. The charge is divided between the two reboilers, where the two original components are accumulated at the end of the process. The reflux strategy was Mode II, Strategy A.

In batch extractive distillation (BED), the entrainer is fed continuously to the column. The components do not form heteroazeotropes, or even if a heteroazeotrope is present, its existence is not exploited. The entrainer is conventionally chosen in industrial practice as a heavy component,^{9–12} and the separation is performed in a rectifier column. However, it is also possible to use a light or intermediate boiling component.^{13,14}

Lelkes et al.¹⁵ developed a method to study the feasibility of BED, by calculating feasible profiles of different column sections. Rodriguez-Donis et al.¹² published a general feasibility criterion for BED.



Based on industrial experiences of BED in a rectifier, where a very long start-up phase was observed, Lang et al.¹⁶ suggested a new operational policy, where entrainer feeding is started already during startup. Nonconventional variants of BED was also studied, e.g., BED in a middle-vessel column.^{17,18}

Koepler et al.¹⁹ was the first to mention BHED. The authors described the industrial application of the process; however, they did not present any theoretical analysis. Modla et al.^{20,21} extended the feasibility of Lelkes et al.¹⁵ to heterogeneous extractive distillation, and also performed rigorous simulations for the separation of dichloromethane and acetone using water as entrainer. The authors stated that the mixed addition (mixing to the charge and continuous feeding) of E provided the best results. Rodriguez-Donis et al.²² stated that BHED is particularly useful for mixtures where E forms a saddle azeotrope with one of the original components. By analyzing the isovolatility curves and the volatility order diagram, it is possible to predict the distillate, which can either be an original component (as in the case of BED), or a heterogeneous saddle azeotrope of the entrainer and an original component. In the latter case, a rectification section is not even required for the feasibility if the extractive stable node (and, thus, the overhead composition) lies in the VLLE region. Petlyuk²³ called the (continuous) heterogeneous extractive process as heteroextractive distillation. One of the phases in the decanter plays the role of the entrainer, but to allow the column section above the feed to function as an extractive one, an additional amount of entrainer, fed externally, is required. Van Kaam et al.²⁴ presented the experimental validation of the BHED process, where the saddle binary heteroazeotrope was withdrawn as the

Rodriguez-Donis et al.²⁶ investigated the feasibility of continuous heterogeneous extractive distillation with several feed point strategies for the entrainer stream and the main azeotropic feed. A stripping section is always present, and, depending on the feeding locations, the column might contain a rectifying or an extractive section, both, or none. In a batch rectifier column, the azeotropic feed—and, thus, the stripping section—is missing, but different feed-point strategies for the entrainer stream can be adopted for the batch process.

The objective of this paper is to propose a general model of BHED, by extending our former model, which is valid for BHAD,⁶ and to study the effects of the entrainer feeding on the operational policies and still path directions. The entrainer can be fed onto any plate of the column, or mixed to the condensate stream, which is equivalent to feeding it into the decanter.

The paper is organized as follows. First, the general model and the equations describing the still path (the trajectory of the still composition) for two different entrainer feeding locations are presented. After that, the different operational policies of batch heterogeneous extractive distillation and the effect of entrainer feeding on the still path direction are discussed. Finally, rigorous simulation results obtained with the professional dynamic simulator of CHEMCAD for the separation of the mixture of water and ethanol with *n*-butanol by different operational policies are presented in order to validate the model.

2. THE EXTENDED MODEL FOR FEASIBILITY STUDIES

distillate, and the holdup of both phases can be increased, decreased or kept constant in the decanter. Throughout the paper, we use the same notation as that used by Hegely et al.⁶

In the feasibility analysis, the following simplifying assumptions are applied:

- (1) The composition of the condensate is constant and equals to that of the heteroazeotrope,
- (2) The overall liquid composition in the decanter equals that of the incoming stream (which might be the condensate, or the condensate mixed with the entrainer stream),
- (3) The vapor and liquid hold-ups of the column and of the condenser are negligible,
- (4) The entrainer is boiling point liquid,
- (5) Constant molar overflow.

It must be noted that the third assumption can even be omitted. In practice, during product withdrawal operation, the tray and condenser holdups are approximately constant. The material balances can be written for the still and the column together, and the results of the feasibility analysis will be valid for the average (still + column) hold-up composition, instead of the still composition.

Rodriguez-Donis et al.²⁶ presented four different possibilities for the entrainer feeding location for continuous heterogeneous extractive distillation. The entrainer could be (1) mixed with the azeotropic feed, (2) fed to the column at a point between the azeotropic feed and the reflux stream, (3) mixed with the refluxed stream, or (4) mixed with the condensate stream. In a batch process, the first case is not applicable, because there is no continuous azeotropic feeding. If the entrainer is fed to the column at a lower position than the top, a rectifying section exists above the feeding location and an extractive section below it. Feeding the entrainer at the top plate is equivalent to mixing it with the reflux stream. In this case, the column is only composed of an extractive section. During the feasibility analysis, as the column holdup is neglected, and constant molar overflow is assumed, the two latter configurations are treated together, as Case 1, since the existence of a rectifying section has no influence on our feasibility results. In Case 2, the entrainer stream is mixed with the condensate or, in a practical realization, fed directly into the decanter.

The top vapor of the column has a molar flow rate of V and molar composition of y_2 . Its condensate, a liquid stream with a flow rate of $L_0 = V$, and composition $x_0 = y_2$, is usually a two-phase liquid; however, in Case 2, a homogeneous condensate can also be feasible. For the following, the notations with an prime/accnt mark will denote variables related to Case 2. For example, in Case 2, after the mixing of the condensate and the entrainer stream, this mixed stream entering the decanter (decanter inlet stream) has a flow rate of L'_0 and a composition of x'_0 . Compositions x_0 (for Case 1) and x'_0 (for Case 2) lie in the heterogeneous region; that is, the condensate (Case 1) or the decanter inlet stream (Case 2) 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 of the condensate (η_R) is defined as the ratio of the flow rate of the E-rich phase and the total flow rate:

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

Taking into account the first two simplifying assumptions, the phase ratio (η_R) and the composition of the phases leaving the

decanter ($x_{1,R}$ and $x_{1,W}$) are also constant, although they may change during a real operation.²⁷

Hegely et al.⁶ introduced the operational parameters r_R (respectively r_W), defined as the ratio of the E-rich (respectively E-lean) phase entering the decanter and refluxed to the column:

$$r_R = \frac{L_{1,R}}{L_{0,R}} \quad (2)$$

$$r_W = \frac{L_{1,W}}{L_{0,W}} \quad (3)$$

where $L_{1,R}$ and $L_{1,W}$ are the flow rates of E-rich and E-lean phases refluxed, respectively. In Case 1, the liquid entering the decanter is the condensate; in Case 2, it is a mixture of the condensate and the entrainer stream. If the reflux ratio of the E-rich phase (R_R) is defined as the ratio of the flow rates refluxed and nonrefluxed,

$$R_R = \frac{L_{1,R}}{L_{0,R} - L_{1,R}} \quad (4)$$

r_R has the following relation with R_R :

$$r_R = \frac{R_R}{R_R + 1} \quad (5)$$

r_R is always non-negative, and if R_R tends to infinity, r_R approaches unity. If the flow rate of the E-rich phase refluxed is higher than the flow rate of this phase in the stream entering the decanter (which means that the holdup of the E-rich phase in the decanter is decreasing), R_R is a negative number and r_R is greater than unity.

Hegely et al.⁶ gives the differential total and component material balances of the still. H_S denotes the holdup and x_S represents the composition of the still. The total material balance of the still is given as

$$\frac{dH_S}{dt} = [(r_R - 1)\eta_R + (r_W - 1)(1 - \eta_R)]V \quad (6)$$

The component material balance of the still is given as

$$\frac{d(H_S x_S)}{dt} = [(r_R - 1)\eta_R x_{1,R} + (r_W - 1)(1 - \eta_R)x_{1,W}]V \quad (7)$$

From the above equations, the still path equation can be derived, which is a differential equation describing the evolution of the still composition in time:

$$\frac{dx_S}{dt} = \frac{V}{H_S} [(1 - r_R)\eta_R(x_S - x_{1,R}) + (1 - r_W)(1 - \eta_R)(x_S - x_{1,W})] \quad (8)$$

For the BHED process, the entrainer feeding must be included into the material balances. The equations have different forms, depending on the entrainer feeding location, so Cases 1 and 2 are treated separately.

2.1. Case 1. In Case 1, the entrainer is fed to the column either at an intermediate or at the top tray, or, alternatively, it is mixed to reflux stream. The flow rate of the entrainer stream is F_E , its composition is x_E . The variables and equations concerning the decanter are unchanged, compared to Hegely et al.,⁶ as the decanter is not directly influenced by the entrainer

feeding; however, the differential material balances of the still must be modified.

The total material balance of the still is given as

$$\frac{dH_S}{dt} = [(r_R - 1)\eta_R + (r_W - 1)(1 - \eta_R)]V + F_E \quad (9)$$

The component material balance is given as

$$\frac{d(H_S x_s)}{dt} = [(r_R - 1)\eta_R x_{1,R} + (r_W - 1)(1 - \eta_R)x_{1,W}]V + F_E x_E \quad (10)$$

The equation of the still path by applying the product rule of differentiation is given as

$$H_s \frac{dx_s}{dt} = \frac{d(H_s x_s)}{dt} - x_s \frac{dH_s}{dt} \quad (11)$$

$$H_s \frac{dx_s}{dt} = [(r_R - 1)\eta_R x_{1,R} + (r_W - 1)(1 - \eta_R)x_{1,W}]V + F_E x_E - [(r_R - 1)\eta_R x_s + (r_W - 1)(1 - \eta_R)x_s]V - F_E x_s \quad (12)$$

$$\frac{dx_s}{dt} = \frac{V}{H_s} [(1 - r_R)\eta_R (x_s - x_{1,R}) + (1 - r_W)(1 - \eta_R)(x_s - x_{1,W})] - \frac{F_E}{H_s} (x_s - x_E) \quad (13)$$

In eq 13, besides the first two terms, which represent the removal of the E-rich and the E-lean phase from the column, respectively, a new term appeared, compared to eq 8, which describes the effect of the continuous feeding of the entrainer (that is, a change in the still composition toward the entrainer composition). As stated by Hegely et al.,⁶ the removal of either liquid phase from the column can be realized by either withdrawing it as distillate, or accumulating it in the decanter. In the case of total reflux (no distillate, constant decanter holdup) of a liquid phase ($r_R = 1$ or $r_W = 1$), the corresponding term disappears from eq 13. Nevertheless, entrainer feeding also can be continued during total reflux operation, in which case the still composition is not constant, but rather approaches the entrainer composition.

2.2. Case 2. In Case 2, the entrainer is mixed to the condensate or fed to the decanter. In this way, the decanter is directly influenced by the entrainer feeding. The flow rate of the stream entering decanter is now given as

$$L'_0 = L_0 + F_E = V + F_E \quad (14)$$

By mixing the entrainer with the condensate, the global composition (x'_0) of the decanter no longer equals to that of the heteroazeotrope, but, assuming that the entrainer stream is the pure component, x'_0 still lies on the same edge of the composition triangle as the heteroazeotrope. Moreover, unless the entrainer flow rate does not exceed a critical value, the global composition is in the heterogeneous region and, thus, the composition of the phases is not changed:

$$x'_{1,R} = x_{1,R} \quad (15)$$

$$x'_{1,W} = x_{1,W} \quad (16)$$

However, the phase split ratio in the decanter has a different value:

$$\eta'_R = \frac{L'_{0,R}}{L'_0} \quad (17)$$

$L'_{0,R}$ can be calculated from the following equation, which describes the decanter inlet flow as the sum of its E-rich and E-lean phases:

$$L'_0 x'_0 = L'_{0,R} x'_{0,R} + L'_{0,W} x'_{0,W} = L'_{0,R} x_{1,R} + L'_{0,W} x_{1,W} \quad (18)$$

$$L'_{0,R} x_{1,R} = L'_0 x'_0 - (L'_0 - L'_{0,R}) x_{1,W} \quad (19)$$

$$L'_{0,R} (x_{1,R} - x_{1,W}) = L'_0 (x'_0 - x_{1,W}) \quad (20)$$

$$L'_{0,R} = L'_0 \frac{x'_0 - x_{1,W}}{x_{1,R} - x_{1,W}} \quad (21)$$

This means that the phase split ratio in the decanter can be written as

$$\eta'_R = \frac{x'_0 - x_{1,W}}{x_{1,R} - x_{1,W}} \quad (22)$$

A similar equation can be derived for the phase split ratio of the condensate:

$$\eta_R = \frac{x_0 - x_{1,W}}{x_{1,R} - x_{1,W}} \quad (23)$$

By subtracting eq 23 from eq 22, a relationship can be obtained between the two phase split ratios:

$$\eta'_R - \eta_R = \frac{x'_0 - x_{1,W} - (x_0 - x_{1,W})}{x_{1,R} - x_{1,W}} = \frac{x'_0 - x_0}{x_{1,R} - x_{1,W}} \quad (24)$$

From the component material balance of the mixing of the condensate and the entrainer, x'_0 can be expressed:

$$L'_0 x'_0 = L_0 x_0 + F_E x_E \quad (25)$$

$$x'_0 = \left(\frac{L_0}{L'_0} \right) x_0 + \left(\frac{F_E}{L'_0} \right) x_E = \left(\frac{L_0}{L_0 + F_E} \right) x_0 + \left(\frac{F_E}{L_0 + F_E} \right) x_E \quad (26)$$

By substituting eq 26 into eq 24, one obtains

$$\eta'_R - \eta_R = \frac{\left(\frac{L_0}{L_0 + F_E} \right) x_0 + \left(\frac{F_E}{L_0 + F_E} \right) x_E - \left(\frac{L_0 + F_E}{L_0 + F_E} \right) x_0}{x_{1,R} - x_{1,W}} \quad (27)$$

By rearranging eq 27, the decanter split ratio can be expressed as a function of the condensate split ratio:

$$\eta'_R = \eta_R + \left(\frac{F_E}{L_0 + F_E} \right) \left(\frac{x_E - x_0}{x_{1,R} - x_{1,W}} \right) \quad (28)$$

It can be seen that the phase split ratio of the decanter is always higher than that of the condensate, and increases with the entrainer flow rate. At a critical entrainer flow rate, η'_R reaches one.

In Case 2, according to their definition, the two operating parameters r_R and r_W have the following values:

$$r_R = \frac{L_{1,R}}{L'_{0,R}} \quad (29)$$

Table 1. Literature Examples for the 16 Possible Operational Policies of BHED

	r_R	r_W	reflux ^a	example in the literature
1	0	0	no reflux	
2	0	<1	E-lean phase (partial)	
3	0	1	E-lean phase (total)	
4	0	>1	E-lean phase (reintr.)	
5	<1	0	E-rich phase (partial)	
6	<1	<1	E-rich (partial) and E-lean phase (partial)	Van Kaam et al.: ²⁴ BHED experiment
7	<1	1	E-rich (partial) and E-lean phase (total)	
8	<1	>1	E-rich (partial) and E-lean phase (reintr.)	
9	1	0	E-rich phase (total)	
10	1	<1	E-rich (total) and E-lean phase (partial)	Koehler et al., ¹⁹ Rodriguez-Donis et al.: ²² mixture ethyl-acetate-ethanol–water Modla et al., ^{20,21} Rodriguez-Donis et al.: ²² mixture acetonitrile–water–butyl-acetate, Van Kaam et al., ²⁴ Barreto et al. ²⁵
11	1	1	E-rich (total) and E-lean phase (total)	
12	1	>1	E-rich (total) and E-lean phase (reintr.)	
13	>1	0	E-rich phase (reintr.)	
14	>1	<1	E-rich (reintr.) and E-lean phase (partial)	
15	>1	1	E-rich (reintr.) and E-lean phase (total)	
16	>1	>1	E-rich (reintr.) and E-lean phase (reintr.)	

^aThe abbreviation “reintr.” denotes reintroduction, a greater amount of liquid is refluxed than what leaves the condenser.

$$r_W = \frac{L_{1,W}}{L'_{0,W}} \quad (30)$$

The total material balance of the still is

$$\frac{dH_S}{dt} = L_1 - V \quad (31)$$

The reflux flow rate L_1 can be written as

$$L_1 = r_R L'_{0,R} + r_W L'_{0,W} \quad (32)$$

$$L_1 = r_R \eta'_R L'_0 + r_W (1 - \eta'_R) L'_0 \quad (33)$$

In this way, eq 29 has the following form:

$$\frac{dH_S}{dt} = [r_R \eta'_R + r_W (1 - \eta'_R)] L'_0 - V \quad (34)$$

The component material balance of the still is given as

$$\frac{d(H_S x_S)}{dt} = L_1 x_1 - V x_0 \quad (35)$$

The component flow rate of the reflux stream is given as

$$\begin{aligned} L_1 x_1 &= L_{1,R} x_{1,R} + L_{1,W} x_{1,W} \\ &= r_R \eta'_R L'_{0,R} x_{1,R} + r_W (1 - \eta'_R) L'_{0,W} x_{1,W} \end{aligned} \quad (36)$$

Meanwhile, the component flow rate of the top vapor can be expressed from the component material balance of the mixing of the condensate and the entrainer (eq 25), by taking advantage of the fact that $V = L_0$:

$$V x_0 = L'_0 x'_0 - F_E x_E \quad (37)$$

If we substitute $L'_0 x'_0$ from eq 18, we obtain

$$V x_0 = L'_{0,R} x_{1,R} + L'_{0,W} x_{1,W} - F_E x_E \quad (38)$$

$$V x_0 = L'_0 \eta'_{R,1,R} + L'_0 (1 - \eta'_{R,1,W}) - F_E x_E \quad (39)$$

Using eqs 36 and 39, the component material balance of the still is given as

$$\begin{aligned} \frac{d(H_S x_S)}{dt} &= r_R \eta'_R L'_{0,R} x_{1,R} + r_W (1 - \eta'_R) L'_{0,W} x_{1,W} - L'_0 \eta'_{R,1,R} \\ &\quad - L'_0 (1 - \eta'_{R,1,W}) + F_E x_E \end{aligned} \quad (40)$$

$$\frac{d(H_S x_S)}{dt} = (r_R - 1) \eta'_R L'_{0,R} x_{1,R} + (r_W - 1) (1 - \eta'_R) L'_{0,W} x_{1,W} + F_E x_E \quad (41)$$

The equation of the still path is obtained by applying the product rule of differentiation (eq 11):

$$\begin{aligned} H_S \frac{dx_S}{dt} &= (r_R - 1) \eta'_R L'_{0,R} x_{1,R} + (r_W - 1) (1 - \eta'_R) L'_{0,W} x_{1,W} \\ &\quad + F_E x_E - [r_R \eta'_R + r_W (1 - \eta'_R)] L'_0 x_S + V x_S \end{aligned} \quad (42)$$

Using eq 14 to substitute V , and rearranging the equation, yields

$$\begin{aligned} H_S \frac{dx_S}{dt} &= (r_R - 1) \eta'_R L'_{0,R} x_{1,R} + (r_W - 1) (1 - \eta'_R) L'_{0,W} x_{1,W} + F_E x_E \\ &\quad - [(r_R - 1) \eta'_R + (r_W - 1) (1 - \eta'_R)] L'_0 x_S - F_E x_S \end{aligned} \quad (43)$$

The final form of the still path equation for Case 2 is

$$\begin{aligned} \frac{dx_S}{dt} &= \frac{V + F_E}{H_S} [(1 - r_R) \eta'_R (x_S - x_{1,R}) \\ &\quad + (1 - r_W) (1 - \eta'_R) (x_S - x_{1,W})] - \frac{F_E}{H_S} (x_S - x_E) \end{aligned} \quad (44)$$

The comparison of the still path equation of Case 2 to that of Case 1 (eq 13) reveals that while, the term describing the continuous entrainer feeding is the same, two differences occur:

- (1) The condensate phase split ratio is replaced by the decanter phase split ratio, which always has a higher value.

- (2) The influence of the first two terms (removal of either the E-rich or the E-lean phase) is increased, as V is replaced by $V + F_E$.

In the case of total reflux operation, the first two terms disappear, and the still path equation for Case 1 and Case 2 become identical.

3. THE EFFECT OF THE CONTINUOUS ENTRAINER FEEDING

In this section, the effect of continuous entrainer feeding on the possible operational policies and on the still path directions is discussed.

3.1. The Effect of Continuous Entrainer Feeding on the Operational Policies. The model has four independent operational parameters: r_R , r_W , V , and F_E . In BHAD, r_R and r_W determine the still path direction, and V only influences the speed of distillation;⁶ in BHED, the still path direction is also determined by the relative magnitude of F_E and V . A higher F_E/V ratio obviously diverts the still path in a more prominent way toward the entrainer composition. Hegely et al.⁶ distinguished 16 possible operational policies, depending on the values of r_R and r_W , categorized into four distinct intervals: zero (0), between zero and one (<1), one (1), and higher than one (>1). The continuous entrainer feeding does not change the classification of the operational policies, as the value of the entrainer flow rate cannot be divided into separate categories (assuming that it is higher than the minimum value necessary for process feasibility, and not so high as to render the decanter holdup homogeneous). The operational policies are listed in Table 1, along with literature examples for the different policies. The majority of the literature suggests either Policy 9 or Policy 10. Using Policy 9, the E-rich phase is totally refluxed, while the E-lean phase is not refluxed at all. The E-lean phase could be accumulated in the decanter or withdrawn as distillate; the latter one is applied in the literature examples. Using Policy 9, the reflux ratio is completely determined by phase split ratio in the decanter. If this reflux ratio is insufficient for a feasible separation, or if the liquid–liquid split must be maintained longer than is possible via Policy 9, Policy 10 can be applied. In this case, beside the total reflux of the E-rich phase, the E-lean phase also is partially refluxed. Policy 10 is practically realized in the following way. A portion of the vapor is condensed and refluxed, while the remainder is led to the decanter, from which the total amount of the E-rich phase is refluxed at a constant E-rich phase holdup. The E-lean phase is withdrawn as distillate. Van Kaam et al.²⁴ performed a BHED experiment, which was originally intended to be a realization of Policy 10. The top vapor was condensed and partially refluxed. The nonrefluxed part of the condensate was led to the decanter. Instead of refluxing the E-rich phase, the continuous entrainer feeding was increased to compensate for the loss of entrainer in the decanter. In this way, Policy 6 was realized, as both liquid phases were partially refluxed.

3.2. The Possible Still Path Directions. The still path direction is determined by the sum of the same three vectors (Figure 2) both for Case 1 (eq 13) and Case 2 (eq 44), which originate from x_S , the actual still composition and have a direction of $(x_S - x_{1,R})$, $(x_S - x_{1,W})$ and $(x_E - x_S)$, respectively. The first two vectors, whose magnitude depends on r_R and r_W , were already present in the BHAD. These vectors point away from (toward) the E-rich phase composition $x_{1,R}$ and the E-lean phase composition $x_{1,W}$, if the value of r_R and r_W is less (higher)

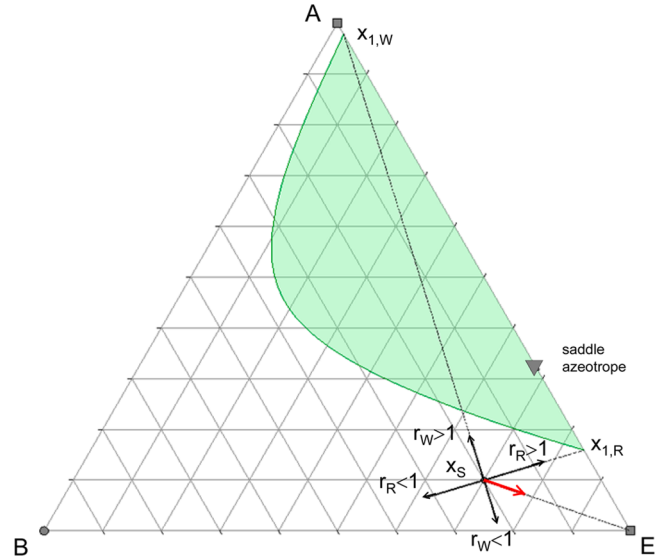


Figure 2. Possible directions of the vectors influencing the still path.

than one, respectively. However, a new vector appears that always points toward the composition of entrainer composition, and whose direction is proportional to the entrainer flow rate. The direction of the resultant vector of the first two vectors (which are related to the decanter) depends on the operational parameters r_R and r_W , that is, on the operation policy. This direction is modified by the addition of the vector of the entrainer feeding to an extent that was dependent on the relative magnitude of the vectors, that is, on all the four operational parameters (r_R , r_W , V , and F_E) and also on the split ratio of the condensate or in the decanter.

The results are illustrated for a mixture of A, B, and E. A and B can be a homoazeotropic (minimum or maximum) or a close boiling mixture, while A and E form a binary heteroazeotrope, which is a saddle point of the system. With an azeotrope A-B, a distillation boundary may exist, but this does not affect the feasibility of the separation.^{4,5}

The possible directions of the still path of BHAD can be classified into eight still path zones (see Figure 3a.⁶), covering in all possible directions. At least one operational policy belongs to each zone; that is, the still composition can be directed in any desired direction. Policy 11 (total reflux operation) is an exceptional case not belonging to any zone, as the still composition remains constant. Some zones, which point toward or away from the composition of one of the phases, only have one direction (Zones I, III, V, and VII), while the others span a set of directions.

The continuous E-feeding has the following effects on the still path zones. Comparing with the BHAD (Figure 3a), the still path zones are modified in the following way (see Figure 3b):

- The zones with only one direction are opening into the direction of the entrainer composition and every zone widens toward the entrainer feeding vector.
- As every zone has the entrainer feeding vector in common, every one of them are overlapping other zones. For example, the new Zone I partially overlaps with the new zones (Zones III, IV, and VIII).
- There are zones that disappear (in this case, Zones II and VII), because they have become identical to other zones (here, Zones I and VI, respectively).

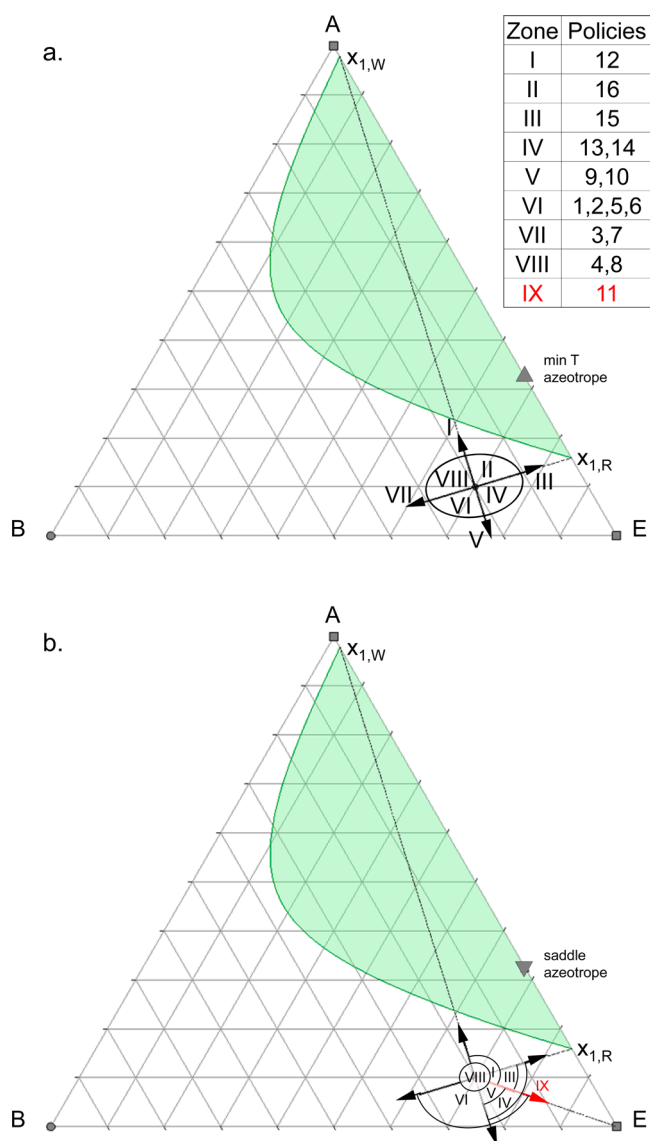


Figure 3. Direction of the still path for the different operational policies: (a) batch heteroazeotropic distillation (BHAD) and (b) batch heterogeneous extractive distillation (BHED).

- The operation under total reflux (Policy 11) appears as a new zone (Zone IX), pointing toward the entrainer composition. This is the only new zone with only one direction.

Because the new still path cover zones in all possible directions, similar to the BHAD, the still composition can be moved into any desired direction by varying the value of the parameters r_R and r_W .

It can be still mentioned that, despite the continuous E-feeding, the still composition can remain constant using Policies 4 and 8 (Zone VIII), if the direction of the resultant of vectors related to the operational parameters r_R and r_W is just opposite to the vector of E-feeding and their lengths are equal.

Similar to BHAD, it is possible to direct the still path to achieve a desired final still composition by applying an appropriate operational policy or a combination of multiple policies. Reaching the A–B edge, except where the purity requirement for the product B is satisfied, is unwanted as, in this way, the original mixture to be separated is obtained once

again. Using BHED, this problem is less likely to be encountered, because of the continuous feeding of the entrainer. Another objective could be to recover one of the original components (in this case, B) in the still, rendering a further separation step unnecessary. However, the concentration of E is increasing in the still, compared to that observed with BHAD, which can prevent recovering the original component.

3.3. The Practical Significance of the Operational Policies. Not all of the possible operational policies are of practical interest. The most conceptually straightforward one is Policy 9, the total reflux of the E-rich phase. If necessary, the reflux ratio can be increased by using Policy 10, that is, partially refluxing the E-lean phase besides the total reflux of the E-rich one. Policy 11, the total reflux of both phases, is applied in the start-up period, in order to obtain the heteroazeotrope as condensate. A desirable goal could be to reach the B–E edge, relatively far from the E vertex, so that B could be easily recovered in a second separation step. In order to reach this goal, the still path should be directed toward the B–E edge; that is, it should lie in one of the following zones (Figure 3b):

- Zone V (operation via Policy 9 or 10). These are the traditional operational policies. However, if the influence of the vector of E-feeding is large, they may result in a still path moving toward rather the E vertex than the B–E edge.
- Zone VI (operation via Policy 1, 2, 5, or 6). The two phases are not (or only partially) refluxed. If neither of the phases is refluxed, and the entrainer is fed into the column (Case 1), the column is operated according to the hybrid process. Policy 6 was already applied experimentally by Van Kaam et al.,²⁴ even if due to practical limitations of the experimental setup. By these policies, the still path can move directly toward the B–E edge, and can even move away from the E vertex. In order to compensate the influence of the continuous entrainer feeding, the vectors pointing away from the E-rich and E-lean phase composition, respectively, should be as long as possible (r_R and r_W as low as possible). A low r_R value moves the still composition toward lower E concentrations, while a low r_W value moves it toward the B–E edge. Since a certain amount of reflux is usually necessary for the feasibility of the separation, these operational parameters might have minimum values.

- Zone VIII (operation via Policy 4 or 8). In this still path zone, the holdup of the E-lean phase in the decanter is reduced. This results in a vector pointing toward the E-lean phase composition (away from the B–E edge); therefore, although the still path can still move toward the B–E edge using these policies, these policies are not recommended.

- Zone IV (operation via Policy 13 or 14). Because of the reduction of the E-rich phase holdup in the decanter, the still path moves even faster toward higher entrainer concentrations. Similar to Zone VIII, although the still path can theoretically move in the right direction, these policies are not recommended.

The reduction of the E-rich phase holdup (Policies 13–16) can be replaced with the continuous entrainer feeding, which is more efficient, since this latter is not limited by the original holdup of E-rich phase in the decanter. However, the composition of the E-rich phase and that of the entrainer feeding are different to an extent depending on the liquid–liquid equilibrium conditions. The smaller the difference between the composition of the E-rich phase and the entrainer, and the farther the still path is located from these points, the

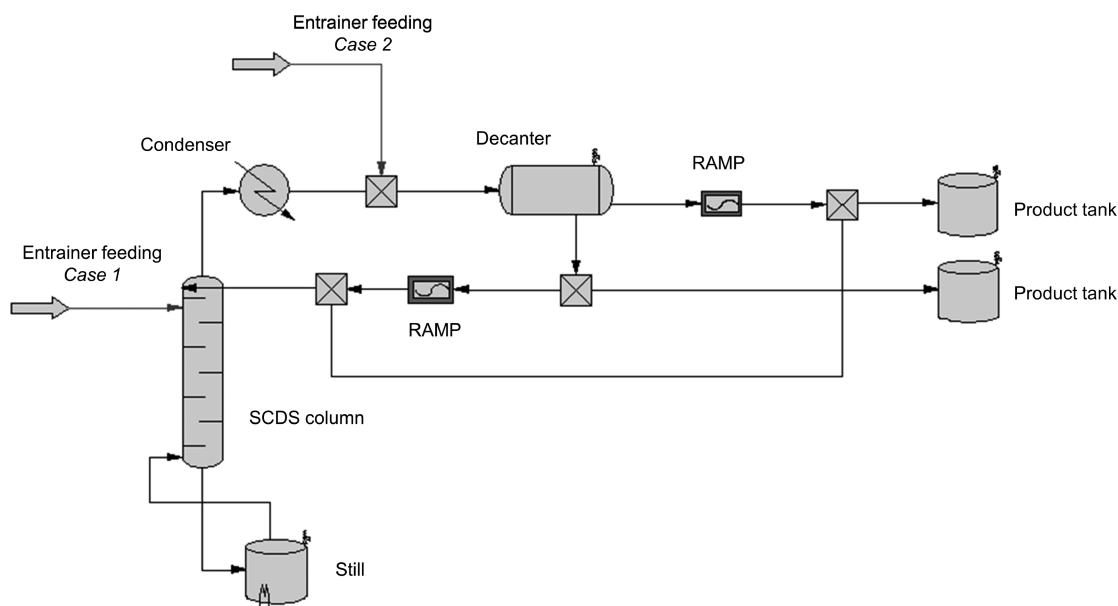


Figure 4. CHEMCAD model of the batch heterogeneous extractive column with variable liquid holdup.

more similar are the effects of the continuous entrainer feeding and of the reduction of the E-rich phase hold-up.

As seen above, although the variation of the holdup of the phases in the decanter is possible, its effect is smaller than that via BHAD, because of the usually strong influence of the continuous entrainer feeding.

4. RIGOROUS SIMULATION

The results of the feasibility analysis are validated by rigorous simulation calculations performed with the dynamic module (CC-DCOLUMN) of the professional flow sheet simulator CHEMCAD. Our goal is to study the applicability of new BHED operational policies.

For the rigorous simulation, simplifying assumptions of the feasibility analysis are replaced with the following, more realistic ones:

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

The calculations were performed with the CHEMCAD model (Figure 4), which comprises of the following parts. The column was modeled with a SCDS column equipped with a separate total condenser. One of the four Dynamic Vessels was the still, where a constant heat duty was applied; two other vessels were product tanks for the two liquid phases, while the fourth one served as the decanter. The two RAMP modules modified the liquid levels in the decanter with time, according to a piecewise linear function specified in the module.

The mixture studied is ethanol (A)–water (B) + *n*-butanol (E), which exhibit a minimum boiling point A-B homoazeotrope, while A and E form a saddle heteroazeotrope. The calculated residue curve map of the mixture along with the binodal curve at $T = 25\text{ }^{\circ}\text{C}$ is presented in Figure 5. The vapor–liquid–liquid equilibria were described with the NRTL model. The NRTL parameters used can be found in the Appendix.

The objective is the dehydration of the mixture by removing water from the decanter in the aqueous phase. First, Policy 9 is

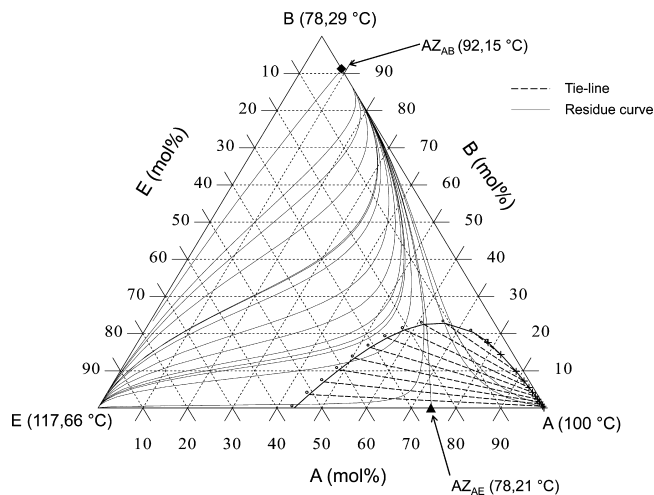


Figure 5. Residue curve map of the water (A)–ethanol (B)–*n*-butanol (E) mixture.

applied (total reflux of the E-rich phase only) after the startup. The composition of the charge (x_F) is 50 mol % A and 50 mol % B. The amount of charge is 100 mol (3.8 dm^3 at $25\text{ }^{\circ}\text{C}$) in the still pot, and 6.52 mol (0.25 dm^3 at $25\text{ }^{\circ}\text{C}$, which equals the maximum decanter holdup) in the decanter. The volume of decanter holdup has to be low, compared to that of the charge. The column has 50 theoretical trays; the heat duty applied is 2 kW. The holdup of the column is $0.01\text{ dm}^3/\text{plate}$. The column is operated for 82 min under total reflux; at the end of this period, the average (still + column) hold-up composition is $x_{S,0}$. The E-feeding (120 mol/h , $25\text{ }^{\circ}\text{C}$) is already started at $t = 8$ min into the column, that is, Case 1 of the entrainer feeding is applied. The feeding location is the second plate of the column (from the top), as a rectifying section of minimum one plate is required, if the decanter has been filled up before the start of the operation, in order to reach the two-liquid-phase region in the decanter. In the following, four examples are presented, which differ from each other in the policy applied after the start-up period. Table 2 gives an overview of the examples with

the operation policy applied, containing the material balances and the recoveries.

Table 2. Main Data and Results of the Examples

	Example 1	Example 2	Example 3	Example 4
operation policy	Policy 9	Policy 5	Policy 6	Policies 9 and 8
charge [mol]	106.52	106.52	106.52	106.52
entrainer [mol]	548	548	548	548
final residue [mol]	592.34	579.78	580.78	592.11
final decanter holdup [mol]	8.91	7.51	7.69	7.40
organic phase distillate [mol]	0	31.24	29.17	1.10
aqueous phase distillate [mol]	44.86	27.77	28.57	45.50
ethanol recovery [%]	93.9	81.3	83.3	93.5
water recovery [%]	83.6	51.6	53.8	85.20

4.1. Example 1. After the startup under $R = \infty$, the entire amount of aqueous (E-lean) phase is withdrawn as distillate (Policy 9). The holdups of the two phases are constant and equal (125 cm^3) in the decanter. In the simulations, the assumption of negligible column holdup is omitted, and results of the feasibility analysis are valid for the average (still + column) hold-up composition instead of the still composition.⁶ The hold-up path calculated is shown in Figure 6, along with the influencing vectors at two different times, at the end of the startup ($x_{S,0}$) and at 182 min ($x_{S,1}$). The vapor and liquid profiles are also presented, at the end of the startup and at the end of the operation ($t = 282 \text{ min}$). The liquid profiles start on the liquid–liquid envelope (composition of the reflux stream), and end at the still composition. The vapor profiles must always

start in the two-liquid region, in order to have a liquid–liquid split in the decanter.

The hold-up path moves into the direction predicted by the feasibility analysis, that is, between the vector pointing away from the E-lean phase composition ($x_{1,W}$) and that of pointing toward E. It must be noted that the E-lean phase composition is slightly changing during the operation, and always contains some ethanol. At the end of the operation, the still composition hardly contains water (0.53%). Since a large amount of E is needed for the separation, its concentration is high (91.55%) in the residue (see Table 2).

4.2. Example 2. The only difference between this and the previous examples is that Policy 5 (only partial reflux of E-rich phase) is applied after the startup instead of Policy 9. Ten percent (10%) of the E-rich phase is withdrawn as a distillate.

The hold-up path (Figure 7) is influenced not only by the two previous vectors, but also by a new vector pointing away from the point of E-rich phase ($x_{1,R}$), whose direction is toward the B-E edge in this case. Consequently, the still composition approaches better the B-E edge (0.39 mol % water in the residue (at 282 min)). However, the ethanol recovery (Table 2) is reduced compared to that of Example 1, as the E-lean phase distillate has to be considered a waste, since it contains a high amount of water.

4.3. Example 3. The only difference between this and Example 1 is that Policy 6 (partial reflux of both phases) is applied after the startup: 10% of the E-rich phase and 60% of the E-lean phase is withdrawn as distillate.

The still path is influenced by

- the vector of continuous entrainer feeding, which is unchanged,
- the vector of the E-lean phase, which gets shorter than that observed in Example 1, and

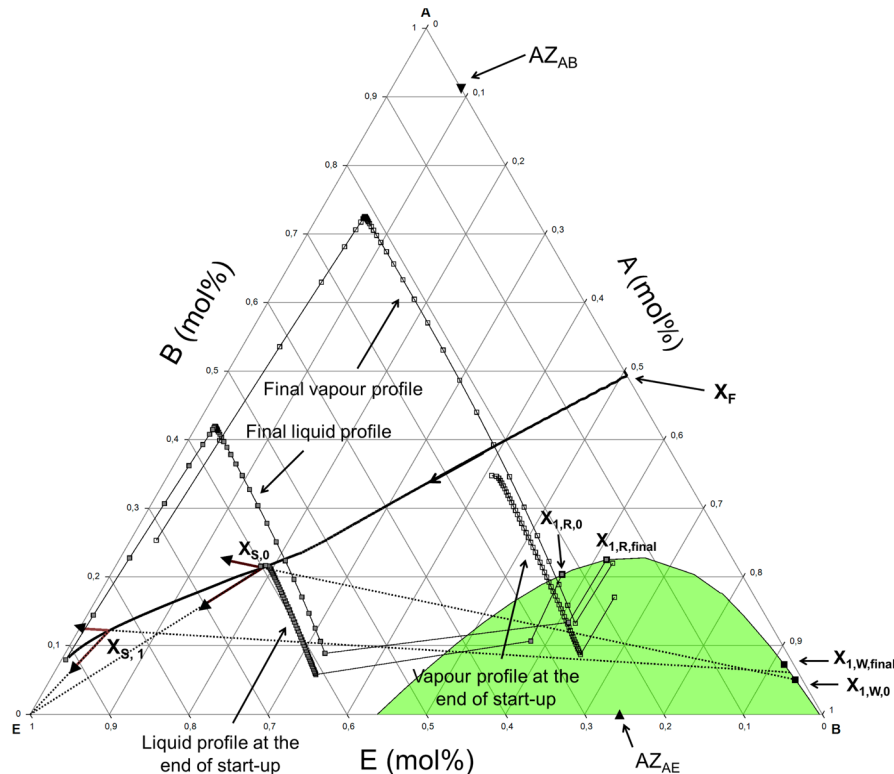


Figure 6. Hold-up path calculated for Policy 9.

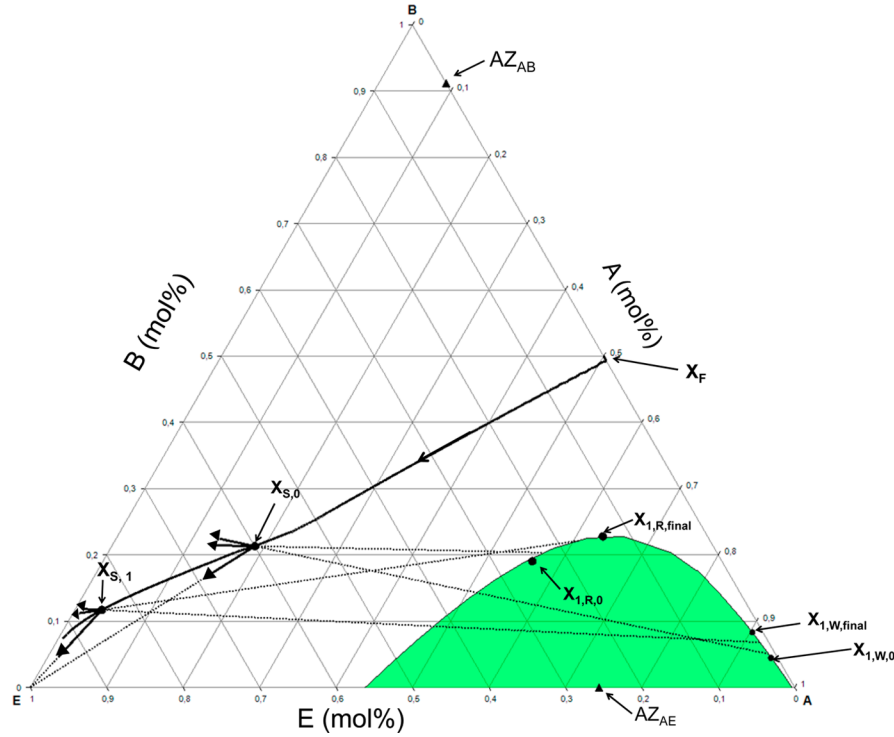


Figure 7. Hold-up path calculated for Policy 5.

- the vector of the E-rich phase (similarly to Example 2). (see Figure 8).

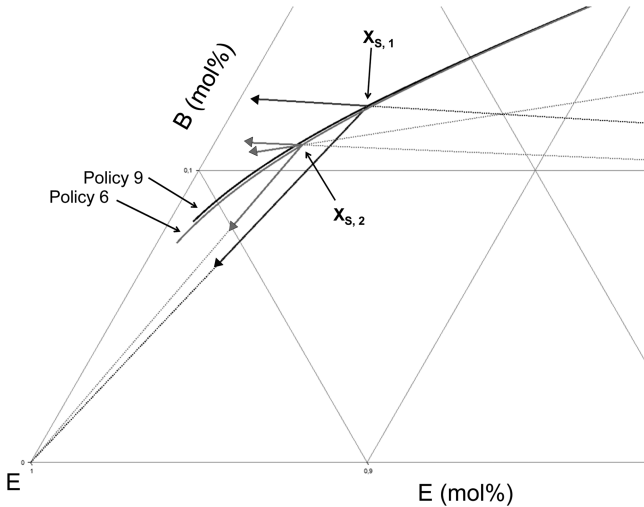


Figure 8. Comparison of the hold-up paths calculated for Policy 6 and Policy 9.

The resulting vector is located in Zone VI, and points less prominently in the direction of E; however, because of the large influence of the continuous entrainer feeding, the difference is not significant. Because of the fact that the vector of the E-rich phase also points toward the B-E edge, the final residue contains less water (0.42%) at the same time than in Example 1. The recoveries are slightly higher than those in Example 2 (see Table 2).

4.4. Example 4. The difference between this and Example 1 is that the hold-up reduction is applied by the combination of Policy 9 (total reflux of the E-rich phase) and Policy 8 (partial

reflux of E-rich phase, reduction of the holdup of the E-lean phase). Policy 9 is applied after the startup until the butanol content of the still exceeds 80 mol % (see Figure 9), then the

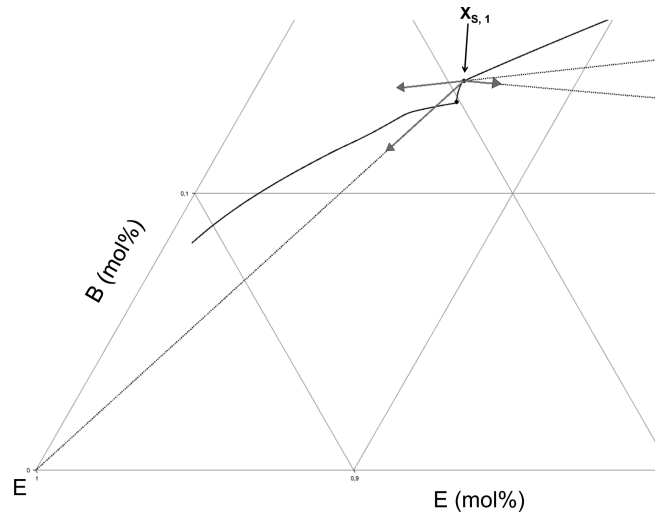


Figure 9. Hold-up path calculated for Example 4 (Policy 9 then Policy 8).

operation is continued by Policy 8. By Policy 8, 10% of the E-rich phase is withdrawn as distillate, and the E-lean phase holdup in the decanter is reduced by 75 cm³ (by 60%) during a period of 10 min.

During the application of Policy 8 (between $x_{S,1}$ and $x_{S,2}$), the direction of the hold-up path is in Zone VIII, and it clearly deviates from trajectory of Example 1. Because of the large influence of the continuous entrainer feeding, however, it moves rather toward the A-E edge than the B-E one, which is not advantageous. The water content of the residue (at 282

min) is 0.62 mol %, although the E-content (91.49%) is slightly less than that observed in Example 1. The ethanol recovery is slightly lower than in Example 1, while that of water is higher, because of the reduction of the E-lean phase holdup in the decanter (see Table 2).

We can conclude that the highest ethanol recovery was obtained by using Policy 9 (Example 1), while the recovery of the water was the highest by using a combination of Policies 9 and 8 (Example 4). The water content of the still residue was the lowest by using Policy 5 (Example 2).

The results of the rigorous simulations indicate that the still path directions are in accordance with the results of the feasibility analysis, and that batch heterogeneous extractive distillation can also be performed by new operational policies (e.g., Policy 5).

5. CONCLUSIONS

The model of Hegely et al.⁶ was extended to batch heterogeneous extractive distillation (BHED), by taking into consideration continuous entrainer feeding. The possibility of refluxing or withdrawing both liquid phases as distillate was maintained, as well as the variability of the hold-up of the phases in the decanter. Two different entrainer feeding locations are distinguished: in Case 1, the entrainer was fed into the column, whereas in Case 2, it was added to the decanter. The equation describing the evolution of the still composition was derived for both cases. Compared to batch heteroazeotropic distillation (BHAD), a new term, which is related to the continuous entrainer feeding, appeared, and by Case 2, the influence of the existing terms, which are related to the operation of the decanter, was increased.

Sixteen (16) operational policies can be distinguished on the basis of the two operational parameters r_R and r_W , which are the ratio of the flow rates of the E-rich and E-lean phase refluxed and condensed, respectively. The occurrence of the operational policies in the literature and potential practical applicability were discussed. The effect of the continuous entrainer feeding on the still path direction, which is now influenced by three vectors with magnitudes depending on the operational policy and the entrainer flow rate, was studied. The eight original still path zones of BHAD are modified: some of them disappear, and the remaining zones overlap each other. Beside the entrainer feeding, the still path zones still cover all possible directions (that is, by using an appropriate operational policy, it is possible to direct the still composition into any direction). In practice, however, the influence of the entrainer feeding is large, and it is difficult to move the still path away from the entrainer composition. For the same reason, the variation of the holdup of the phases in the decanter only has a small effect on the still path.

The still path directions were validated by rigorous simulation of the dehydration of the water–ethanol mixture, using *n*-butanol as an entrainer. Four examples were presented: operation by Policy 9 (total reflux of entrainer-rich phase only), Policy 5 (partial reflux of E-rich phase only), Policy 6 (partial reflux of both phases), and a combination of Policies 9 and 8 (partial reflux of E-rich phase, reduction of the E-lean phase hold-up in the decanter). The average (still and column) hold-up composition moved in accordance with the feasibility results. By using the new Policy 5, it was possible to slightly reduce the water content of the still residue that mainly contained ethanol and butanol.

■ APPENDIX: VALUE OF THE PARAMETERS USED FOR THE PHASE EQUILIBRIA CALCULATIONS

The NRTL parameters for the mixture A–B–E (where A is ethanol, B is water, and E is *n*-butanol), are given in Table A1.

Table A1. NRTL Parameters for the Water (A)–Ethanol (B)–*n*-Butanol (E) Mixture

<i>i</i>	<i>j</i>	B_{ij} [K]	B_{ji} [K]	α
A	B	670.441	−55.1681	0.3031
A	E	1468.34	215.427	0.3634
B	E	19.1588	−16.5768	0.3038

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +3614631707. E-mail: lang@mail.bme.hu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by TÁMOP (No. 4.2.2.B-10/1-2010-0009) and The Hungarian Scientific Research Fund (Országos Tudományos Kutatási Alapprogramok, OTKA) (Project No. K-106286).

■ NOMENCLATURE

- A = low boiling original component
- AZ = azeotrope
- B = high boiling original component
- B = NRTL binary interaction parameter, K
- BED = batch extractive distillation
- BHAD = batch heteroazeotropic distillation
- BHED = batch heterogeneous extractive distillation
- D = distillate molar flow rate, mol/h
- E = entrainer
- F = feed flow rate, mol/h
- H = holdup, mol
- L = liquid molar flow rate, mol/h
- R = reflux ratio
- r = the ratio of the flow rates of the refluxed and condensed streams
- t = time, min
- V = vapor molar flow rate, mol/h
- VLE = vapor–liquid–liquid equilibrium
- x = liquid mole fraction, mol/mol
- y = vapor mole fraction, mol/mol

Greek Letters

- α = NRTL parameter
- η = phase split ratio, mol/mol

Subscripts

- 0 = condensate; end of total reflux period
- 1 = decanter
- 2 = top vapor
- D = distillate
- E = entrainer
- i = component i
- j = component j
- R = entrainer-rich phase
- S = still
- W = entrainer-lean (entrainer-weak) phase

■ REFERENCES

- (1) Mujtaba, I. M. *Batch Distillation: Design and Operation*; Imperial College Press: London, 2004.
- (2) Skouras, S.; Kiva, V.; Skogestad, S. Feasible separations and entrainer selection rules for heteroazeotropic batch distillation. *Chem. Eng. Sci.* **2005**, *60*, 2895–2909.
- (3) Skouras, S.; Skogestad, S.; Kiva, V. Analysis and control of heteroazeotropic batch distillation. *AIChE J.* **2005**, *51*, 1144–1157.
- (4) Rodriguez-Donis, I.; Gerbaud, V.; Joulia, X. Feasibility of heterogeneous batch distillation processes. *AIChE J.* **2002**, *48*, 1168–1178.
- (5) Lang, P.; Modla, G. Generalised method for the determination of heterogeneous batch distillation regions. *Chem. Eng. Sci.* **2006**, *61*, 4262–4270.
- (6) Hegely, L.; Gerbaud, V.; Lang, P. Generalised model for heteroazeotropic batch distillation with variable decanter hold-up. *Sep. Purif. Technol.* **2013**, *115*, 9–19.
- (7) Denes, F.; Lang, P.; Modla, G.; Joulia, X. New double column system for heteroazeotropic batch distillation. *Comput. Chem. Eng.* **2009**, *33*, 1631–1643.
- (8) Denes, F.; Lang, P.; Joulia, X. Generalised closed double-column system for batch heteroazeotropic distillation. *Sep. Purif. Technol.* **2012**, *89*, 297–308.
- (9) Luyben, W. L.; Chien, I.-L. *Design and Control of Distillation Systems for Separating Azeotropes*; Wiley-VCH: New York, 2010.
- (10) Seader, J. D.; Henley, E. J. *Separation Process Principles*; Wiley: New York, 1998.
- (11) Lang, P.; Yatim, H.; Moszkowicz, P.; Otterbein, M. Batch extractive distillation under constant reflux ratio. *Comput. Chem. Eng.* **1994**, *18*, 1057–1069.
- (12) Rodriguez-Donis, I.; Gerbaud, V.; Joulia, X. Thermodynamic Insights on the Feasibility of Homogeneous Batch Extractive Distillation. 1. Azeotropic Mixtures with a Heavy Entrainer. *Ind. Eng. Chem. Res.* **2009**, *48*, 3544–3559.
- (13) Rodriguez-Donis, I.; Gerbaud, V.; Joulia, X. Thermodynamic Insights on the Feasibility of Homogeneous Batch Extractive Distillation. 3. Azeotropic Mixtures with Light Entrainer. *Ind. Eng. Chem. Res.* **2012**, *51*, 4643–4660.
- (14) Rodriguez-Donis, I.; Gerbaud, V.; Joulia, X. Thermodynamic Insights on the Feasibility of Homogeneous. Batch Extractive Distillation. 4. Azeotropic Mixtures with Intermediate Boiling Entrainer. *Ind. Eng. Chem. Res.* **2012**, *51*, 6489–6501.
- (15) Lelkes, Z.; Lang, P.; Benadda, B.; Moszkowicz, P. Feasibility of extractive distillation in a batch rectifier. *AIChE J.* **1998**, *44*, 810–822.
- (16) Lang, P.; Kovacs, G.; Kotai, B.; Gaal-Szilagyi, J.; Modla, G. Industrial application of a new batch extractive distillation operational policy. In *Distillation and Absorption 2006*; Sørensen, E., Ed.; IChemE Symposium Series 152; The Institution of Chemical Engineers: Rugby, U.K., 2006; pp 830–839.
- (17) Saifrit, B. T.; Westerberg, A. W.; Diwekar, U.; Wahnschafft, O. M. Extending continuous conventional and extractive distillation feasibility insights to batch distillation. *Ind. Eng. Chem. Res.* **1995**, *34*, 3257–3264.
- (18) Warter, M.; Demicoli, D.; Stichlmair, J. Operation of a batch distillation column with a middle vessel: Experimental results for the separation of zeotropic and azeotropic mixtures. *Chem. Eng. Process.* **2004**, *43*, 263–272.
- (19) Koehler, J.; Haverkamp, H.; Schädler, N. Zur Diskontinuierlichen Rektifikation Azeotroper Gemische mit Hilfsstoffeinsatz. *Chem. Ing. Technol.* **1995**, *67*, 967–971.
- (20) Modla, G.; Lang, P.; Molnar, K. Batch heteroazeotropic rectification of a low relative volatility mixture under continuous entrainer feeding: Feasibility studies. In *Proceedings of the 6th World Congress of Chemical Engineering* [CD-ROM]; Schallcross, D. C., Ed.; Institution of Chemical Engineers in Australia: Melbourne, Australia, 2001.
- (21) Modla, G.; Lang, P.; Kotai, B.; Molnar, K. Batch heteroazeotropic rectification of a low relative volatility mixture. *AIChE J.* **2003**, *49*, 2533–2552.
- (22) Rodriguez-Donis, I.; Equijarosa, J. A.; Gerbaud, V.; Joulia, X. Heterogeneous batch-extractive distillation of minimum boiling azeotropic mixtures. *AIChE J.* **2003**, *49*, 3074–3083.
- (23) Petlyuk, F. B. *Distillation Theory and Its Application to Optimal Design of Separation Units*; Cambridge University Press: Cambridge, U.K., 2004.
- (24) Van Kaam, R.; Rodriguez-Donis, I.; Gerbaud, V. Heterogeneous extractive batch distillation of chloroform-methanol-water: Feasibility and experiments. *Chem. Eng. Sci.* **2008**, *63*, 78–94.
- (25) Barreto, A. A.; Rodriguez-Donis, I.; Gerbaud, V.; Joulia, X. Optimization of Heterogeneous Batch Extractive Distillation. *Ind. Eng. Chem. Res.* **2011**, *50*, 5204–5217.
- (26) Rodriguez-Donis, I.; Papp, K.; Gerbaud, V.; Joulia, X.; Rev, E.; Lelkes, Z. Column Configurations of Continuous Heterogeneous Extractive Distillation. *AIChE J.* **2007**, *53*, 1982–1993.
- (27) Pommier, S.; Masseur, S.; Kotai, B.; Lang, P.; Baudouin, O.; Gerbaud, V. Heterogeneous batch distillation processes: Real system optimization. *Chem. Eng. Process.* **2008**, *47*, 408–419.