

Syntheserahmenwerk zum Entwurf von destillativen Trennprozessen für azeotrope Vielstoffgemische (Kennziffer 2728)

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Summary

In the second part of the Max-Buchner research grant, rigorous optimization of complex large-scale heteroazeotropic distillation processes for multicomponent heterogeneous mixtures is achieved with outstanding robustness and efficiency through the initialization of the rigorous optimization by powerful shortcut methods and a reformulation as a continuous problem. The methods are demonstrated by two large-scale industrial case studies.

1. Introduction

The costs of a chemical process are often dominated by the costs for separation and purification of the products. Distillation, which is still the major separation and purification method, is an expensive unit operation in terms of capital and operating costs. It is therefore desirable to design economically optimized distillation processes, which can potentially save significant amounts of financial and energetic resources.

Distillation process design in industrial practice is usually conducted by tedious simulation studies which require detailed design specifications in an early design phase. Guided by heuristics, these iterative solution procedures result in a high manual effort and, in addition, no guarantee concerning the quality of the solution can be given. In order to achieve a systematic and optimization-based design procedure, a process synthesis framework for the efficient and robust design of distillation processes has been developed in our previous research work (c.f. Figure 1) [1]. The process synthesis framework combines shortcut methods for the conceptual design phase with rigorous optimization methods for the detailed design phase. With this combination of synthesis methods of increasing level of detail, separation processes for azeotropic multicomponent mixtures can be efficiently evaluated on the basis of rigorous thermodynamics and the optimal distillation flowsheet, the optimal process operating point and the optimal column specifications (number of trays, location of feeds and reboiler/condenser duties) can be determined.

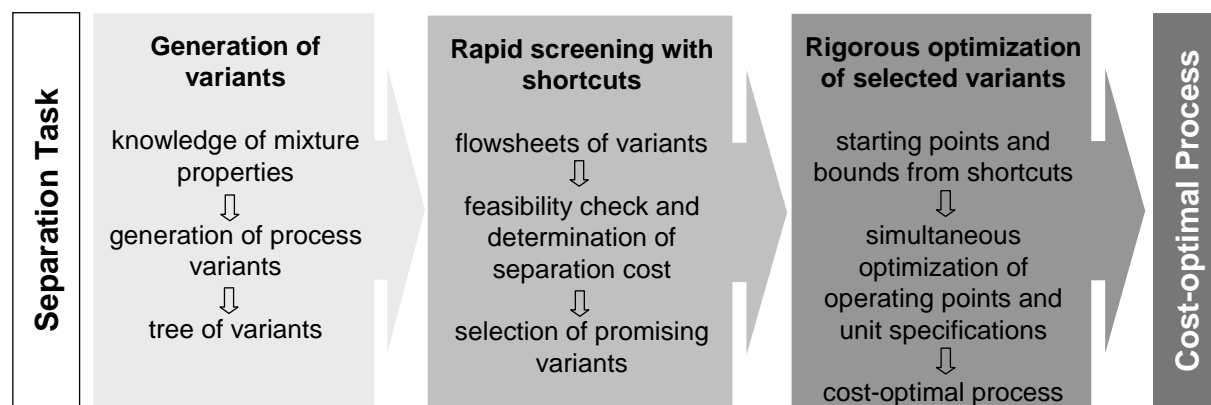


Figure 1: Process synthesis framework for the optimization based process design.

In the first step of the framework, possible flowsheet alternatives are generated. These flowsheet alternatives are screened with respect to feasibility and minimum energy demand in the second step. The application of shortcut methods like the rectification body method (RBM) [2] in this step allows for a robust and efficient evaluation of all alternatives. The most promising flowsheet variant can then be rigorously modelled and optimized in the third step with the help of bounds and initial values from the previous shortcut evaluation. By minimizing a cost function containing capital and operating costs the rigorous optimization step provides information about the optimal number of column trays and the optimal feed tray locations. Since these design variables are discrete variables while the energy duties, flowrates and compositions are continuous variables, a mixed-integer nonlinear optimization problem (MINLP) has to be solved. Considering the large scale and complexity of multichannel processes and the nonlinearity of the underlying nonideal thermodynamics, it is obvious that these MINLP problems are particularly hard to solve. We have presented the rigorous optimization of multichannel processes for homogeneous azeotropic multicomponent mixtures (see [1] and the interim report of the first funding period [3]). In these works, the robust and efficient solution of the MINLP problem is achieved by a favorable initialization strategy based on the results of the preceding shortcut evaluation and a reformulation as a purely continuous problem.

In section 2 of this report, we summarize the results of the case study for a homogeneous azeotropic multicomponent mixture, which was presented in the interim report for the first funding period. The extension of the rigorous process optimization to heterogeneous mixtures and heteroazeotropic distillation is shown in section 3. Two large-scale case studies for multichannel heteroazeotropic processes are then presented in section 4.

2. Rigorous optimization of a pressure swing process for a homogeneous azeotropic 5-component mixture

The case study in the interim report considers a pressure-swing three-column distillation process proposed by Wasykiewicz [4] for the complete removal of ethanol and benzene from the homogeneous azeotropic five-component mixture of acetone, chloroform, methanol, ethanol and benzene. The optimization model and results for this case study are given in [1] and [3] in detail. With the help of the shortcut evaluation step of the synthesis framework, we determined an optimal process operating point with a 25% lower minimum energy demand than the operating point proposed by Wasykiewicz [4]. In addition, a simplified and energy efficient two-column process could be identified.

The following rigorous optimization of the two-column and the three-column processes could be initialized robustly and efficiently with the results from the shortcut step. The discrete-continuous rigorous optimization model was reformulated as a continuous model, which resulted in significantly shorter solution times and convergence to better local optima when compared to the solution with common MINLP solvers.

3. Rigorous optimization of heteroazeotropic distillation processes

Many industrially relevant mixtures exhibit one or more immiscibilities between the components in the liquid phase. Moreover, in heteroazeotropic distillation the addition of an entrainer which exhibits immiscibilities with one of the components in the azeotropic feed allows for a crossing of distillation boundaries to produce pure component products. Hence, the distillation of heterogeneous mixtures occurs frequently in industrial practice and warrants the inclusion in the process synthesis framework. In typical heteroazeotropic designs, a

heterogeneous stream is produced at the top of the column and is split in a decanter into an entrainer-lean distillate and an entrainer-rich reflux. A thorough analysis of the properties of heteroazeotropic distillation has been given by Urdaneta et al. [5].

Heterogeneous mixtures pose additional challenges for the application of design methods. The methods for homogeneous systems cannot be applied without an adaptation to handle the decomposition of the liquid phase in the decanter and also on the trays within the column. Hence, there are very few publications on shortcut methods and rigorous optimization models for heterogeneous distillation systems; most of these consider immiscibilities only in the decanter. In these cases, the liquid profiles are either not allowed to enter the miscibility gap or the equilibrium is calculated by the Wilson model, which cannot model liquid phase splits. This practice, however, leads to miscalculations or the disregard of promising designs in many instances.

Recently, Kraemer et al. have developed novel shortcut methods (feed pinch method, FPM [6], and feed angle method, FAM [7]) which allow for an efficient and robust evaluation of heteroazeotropic distillation processes. In these works, possible liquid phase splits on the column trays are detected automatically by a computationally cheap but reliable liquid phase stability test [8]. The set of equilibrium equations is switched from the VLE to the VLLE case when a phase split is detected.

In the second period of the Max-Buchner research grant, the extension of the rigorous optimization step of the process synthesis framework to heteroazeotropic distillation was achieved. The necessary extensions and adjustments to the rigorous optimization model are described in the following. The rigorous column optimization model for a single heteroazeotropic column is based on the model for a homogeneous column as given by Kraemer et al. [1]. We therefore list the heteroazeotropic column model only briefly in the following and refer to [1] for details:

$$0 = \sum_k b_{F,k,n} F_k z_{k,i} + L_{n-1} x_{n-1,i} + V_{n+1} y_{n+1,i} - L_n x_{n,i} - V_n y_{n,i} + b_{R,n} R x_{R,i} + b_{B,n} B y_{N_{max},i}, \quad n \in [2, N_{max}] \quad (1)$$

$$0 = \sum_k b_{F,k,n} F_k h_{f,k} + L_{n-1} h_{l,n-1} + V_{n+1} h_{v,n+1} - L_n h_{l,n} - V_n h_{v,n} + b_{R,n} R h_{l,R} + b_{B,n} B h_{v,N_{max}}, \quad n \in [2, N_{max}] \quad (2)$$

$$0 = \sum_k b_{F,k,n} F_k z_{k,i} + V_{n+1} y_{n+1,i} - L_{Cond} x_{n,i}, \quad n = 1, i \in I \quad (3)$$

$$0 = \sum_k b_{F,k,n} F_k h_{f,k} + V_{n+1} h_{v,n+1} - L_{Cond} h_{l,n} + Q_D, \quad n = 1 \quad (4)$$

$$0 = \sum_k b_{F,k,n} F_k z_{k,i} + L_{n-1} x_{n-1,i} - L_n x_{n,i} - V_n y_{n,i} - B y_{n,i}, \quad n = N_{max}, i \in I \quad (5)$$

$$0 = \sum_k b_{F,k,n} F_k h_{f,k} + L_{n-1} h_{l,n-1} - L_n h_{l,n} - V_n h_{v,n} - B h_{v,n} + Q_B, \quad n = N_{max} \quad (6)$$

$$0 = L_{Cond} x_{n,i} - R x_{R,i} - D x_{Dec,i}^I, \quad n = 1, i \in I \quad (7)$$

$$0 = L_{Cond} h_{l,n} - R h_{l,R} - D h_{l,Dec}^I, \quad n = 1 \quad (8)$$

$$\sum_i x_{n,i} = 1, \sum_i x_{n,i}^I = 1, \sum_i x_{n,i}^{II} = 1, \sum_i y_{n,i} = 1, \sum_i x_{R,i} = 1, \sum_i x_{Dec,i} = 1, \sum_i x_{Dec,i}^I = 1, \sum_i x_{Dec,i}^{II} = 1, \quad n \in N \quad (9)$$

$$y_{n,i} = K_n^I(\mathbf{x}_n^I, \mathbf{y}_n, T_n, p) x_{n,i}^I, \quad y_{n,i} = K_n^{II}(\mathbf{x}_n^{II}, \mathbf{y}_n, T_n, p) x_{n,i}^{II} \quad n \in N, i \in I \quad (10)$$

$$x_{n,i} = \varphi_n x_{n,i}^I + (1 - \varphi_n) x_{n,i}^{II}, \quad n \in N, i \in I \quad (11)$$

$$y_{Dec,i} = K_{Dec}^I(\mathbf{x}_{Dec}^I, \mathbf{y}_{Dec}, T_{Dec}, p)x_{Dec,i}^I, \quad y_{Dec,i} = K_{Dec}^{II}(\mathbf{x}_{Dec}^{II}, \mathbf{y}_{Dec}, T_{Dec}, p)x_{Dec,i}^{II}, \quad i \in I \quad (12)$$

$$x_{Dec,i} = \varphi_{Dec} x_{Dec,i}^I + (1 - \varphi_{Dec}) x_{Dec,i}^{II}, \quad i \in I \quad (13)$$

$$\sum_n b_{F,k,n} = 1, \quad \sum_n b_{R,n} = 1, \quad \sum_n b_{B,n} = 1, \quad V_{N_{max}} = 0, \quad L_1 = 0 \quad (14)$$

$$NT = N_{max} - \sum_n \sum_n^{N_{max}} b_{R,n} - \sum_n \sum_{n=1}^n b_{B,n} \quad (15)$$

$$D_{col} = \sqrt{\frac{4B}{2\pi}} \sqrt{\frac{RT_n \sum_i y_{n,i} M_i}{p}}, \quad n = N_{max} \quad (16)$$

$$C_{op} = f(Q_B, Q_D), \quad C_{cap} = f(NT, D_{col}, A_{reb}, A_{con}) \quad (17)$$

$$\min TAC = C_{op} t_a + f_c C_{cap} \quad (18)$$

The streams to and from a column tray and the optimization superstructure of a heteroazeotropic distillation column with variable feed tray locations and variable reflux/reboil tray locations are shown in Figure 2. The mass and energy balances (eqs. (1)-(6)) for the rigorous optimization of distillation columns for homogeneous mixtures (see also Kraemer et al. [1]) were supplemented with mass and energy balances for a decanter at the top of the column (eqs. (7),(8)). A decanter at the bottom of the column or a decanter connected to the column by side streams can also be implemented with little changes in the model equations. Eqs. (15) and (16) calculate the number of column trays and the diameter of the column. The economic functions to determine the operating and capital costs are represented by eq. (17). The annualized total costs are minimized by means of the objective function in eq. (18).

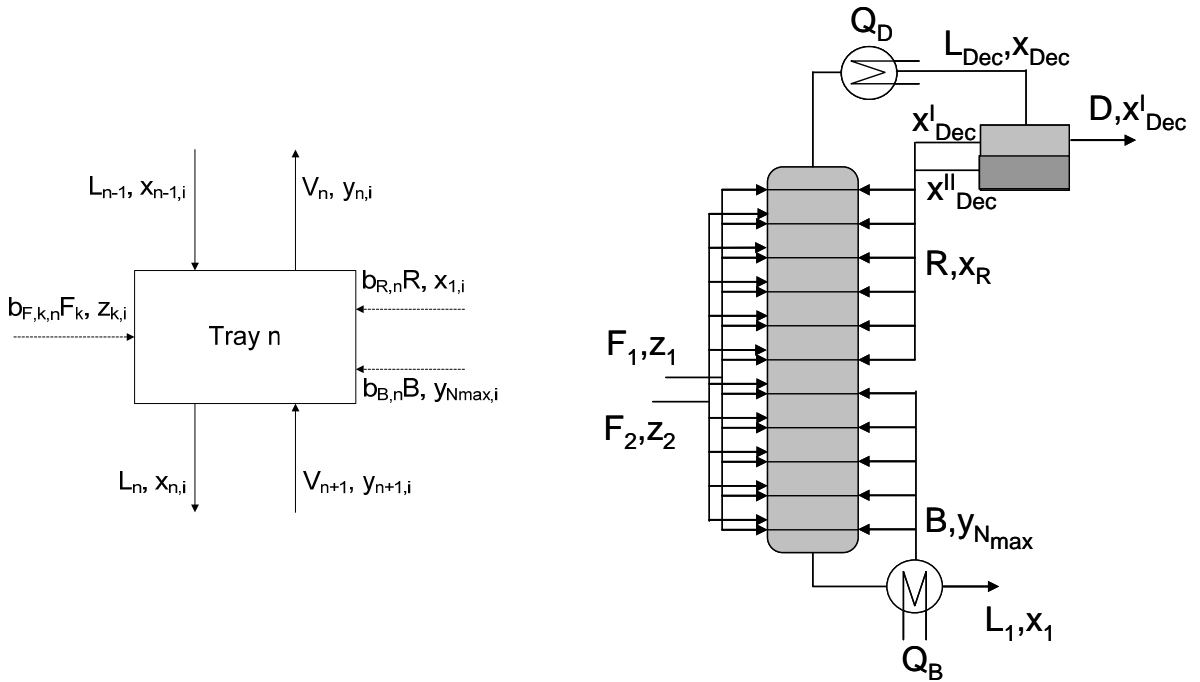


Figure 2: Equilibrium tray with streams and optimization superstructure of a heteroazeotropic distillation column.

In order to allow a liquid phase split everywhere in the column, VLLE equations were formulated for the decanter and for each column tray (eqs. (10)-(13)). Note that the VLLE equations reduce to the VLE case when only one liquid phase is present. Both liquid compositions are identical in this case. Within the miscibility gap VLLE solutions exist. Unfortunately, a multiplicity of solutions may also occur in the miscibility gap: the physically correct VLLE solution and a physically invalid VLE solution can be calculated. Without a reliable phase stability test, the correct VLLE solution may be omitted in favor of the invalid VLE solution, which then leads to an inaccurate column simulation. In order to identify the phase split within the mixing gap correctly, we supplemented the VLLE equations with an efficient phase stability test as implemented in the shortcut methods for heteroazeotropic distillation.

Unfortunately, we observed that the inclusion of the phase stability test resulted in very poor optimization behavior. Note that the liquid compositions on the column trays are variable in the optimization problem. The crossing of the binodal by the liquid tray compositions during the optimization apparently causes severe convergence issues. The phase stability test was therefore not included in the rigorous optimization of heteroazeotropic columns. The calculation of incorrect VLE solutions within the heterogeneous region was instead prevented by a combination of following measures:

- temperature bounds,
- accurate initialization of homogeneous and heterogeneous trays
- reduction of trays at the top and the bottom of the column in the optimization

A strict enforcement of temperature bounds leads to the elimination of VLE solutions in the heterogeneous region in most cases. This is due to the observation that incorrect VLE solutions usually exhibit boiling temperatures beyond the true minimum or maximum boiling temperature of the mixture everywhere in the heterogeneous region except in the vicinity of the binodal. In addition to the temperature bounding, an accurate initialization of the homogeneous and heterogeneous trays helped to prevent incorrect VLE solution. The accurate initialization of the heterogeneous trays was achieved by the tray-to-tray profiles of the shortcut evaluation step with the feed pinch method [6], which contains the phase stability test [8]. Furthermore, we modeled the column superstructure with variable reflux, reboil and feed trays as shown in Figure 2 such that the column trays can be cut off from the top and from the bottom. As a consequence, the column profile may cross the binodal between the same two trays irrespective of the reduction of column trays in the optimization.

The initialization strategy described by Kraemer et al. [1] was adopted for the case studies in this work with the only difference being that the tray-to-tray profiles of the feed pinch method [6] were used for the initialization of the heteroazeotropic columns instead of linear profiles from the rectification bodies. The discrete-continuous optimization model for heteroazeotropic columns was reformulated as a continuous problem in the same way as proposed for the homogeneous column model by Kraemer et al. [1]. As a consequence, the optimization problems could be solved as nonlinear programming problems (NLP) with common NLP solvers.

4. Case studies for the rigorous optimization of heteroazeotropic distillation

The rigorous optimization of heteroazeotropic distillation processes is illustrated by two large-scale case studies. The liquid activity coefficients for the K-values of the components in both case studies were calculated with the NRTL model. The pure component vapor pressure was determined by the extended Antoine equation. DIPPR equations are employed for the calculation of the enthalpies. Both optimization case studies were formulated and solved on

the optimization platform GAMS 22.7. The SQP-based solver SNOPT was employed for the solution of the continuously reformulated problems on a PC with a 2.66 GHz Quad-Core CPU (GAMS uses only one CPU core). External functions are used in GAMS to calculate the thermodynamic properties (liquid activity coefficients and enthalpies) and the required derivatives.

4.1. Separation of an isopropanol-water mixture with the entrainer cyclohexane

In this case study, an azeotropic mixture of isopropanol and water is separated into pure components with the help of the entrainer cyclohexane. The ternary mixture exhibits a large miscibility gap between water and cyclohexane as shown in Figure 3 as well as three binary azeotropes and one ternary heterogeneous azeotrope, which is the minimum boiler of the system. A heteroazeotropic distillation process was generated for the separation task as given in Figure 3 and Table 1 [9]. The fresh feed of the process and a recycle is given into a simple homogeneous column, which separates pure water at the bottom. The distillate of the homogeneous column is drawn off and fed into a heteroazeotropic column as saturated vapor. Pure isopropanol is produced as the bottoms product of the heteroazeotropic column and the distillate of the heteroazeotropic column is drawn off the water rich phase of the decanter, which is defined by a tie-line close to the minimum boiling ternary azeotrope. A mixture of both phases, mostly from the organic phase, is recycled back to the heteroazeotropic column as reflux. Note that the separation mass balance of this column crosses the distillation boundary between the ternary azeotrope and the binary azeotrope on the isopropanol-water edge. The vapor profile of the column is however entirely located in the upper distillation region since the vapor which is drawn off at the top of the column and sent to the decanter has a composition slightly above the ternary azeotrope. The overall mass balance around the setup of the column and the decanter is therefore able to cross the distillation boundary in a feasible heteroazeotropic separation.

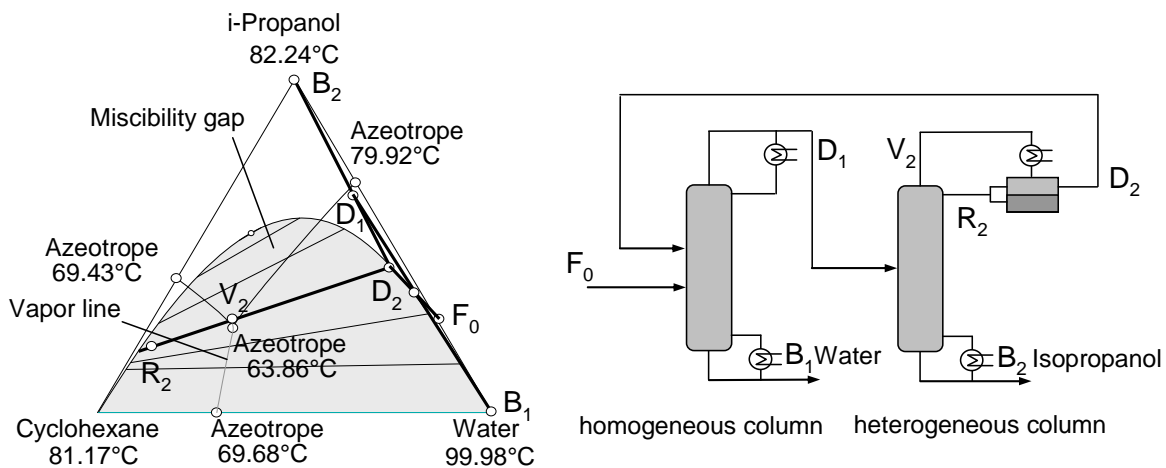


Figure 3: Topology of the isopropanol, water, cyclohexane system and heteroazeotropic distillation process to separate isopropanol and water.

Following the process synthesis framework (c.f. Figure 1), the heteroazeotropic flowsheet was evaluated by shortcut methods. Specifically, the minimum energy demand of the heteroazeotropic column was determined with the feed pinch method for highly nonideal separations [6]. The minimum energy demand of the homogeneous column was calculated with the rectification body method [2]. The process operating point for the shortcut evaluation

was chosen such that the recycle flow rate was minimal. The feed and recycle flowrates and compositions are given in Table 1.

An alternative column sequence where the fresh feed is introduced into the heterogeneous column was also evaluated within the shortcut step of the synthesis framework. This process, however, yielded a significantly larger minimum energy demand and was therefore discarded [9].

	Feed F_0	Recycle D_2
Flowrate	6.28 mol/s	2.9 mol/s
Composition $[x_P, x_W, x_C]$	[0.366, 0.634, 0]	[0.402, 0.571, 0.027]

Table 1: Feed and recycle flowrates and compositions for the first case study.

The rigorous optimization of the heteroazeotropic process was initialized with the operating point and profiles from the shortcut evaluation step. Specifically, the heteroazeotropic column was initialized with tray-to-tray profiles from the feed pinch method and the homogeneous column with linear profiles from the rectification body method. By this initialization, the top 10 trays of the heteroazeotropic column are initialized as heterogeneous trays with a liquid phase split.

In the rigorous optimization problem, the fresh and recycle feeds to the homogeneous column are introduced separately. The maximum tray numbers were set to 50 trays, yielding an optimization problem of about 4000 variables, including 300 binary decision variables. The solution of the optimization problem was carried out by the solution procedure proposed by Kraemer et al. [1]. The optimization results for the costs, number of column trays, feed tray locations and the process operating point are displayed in Table 2.

	Heterogeneous column	Homogeneous column
Operating cost	24100 €a	39300 €a
Capital cost	60400 €a	42200 €a
Condenser duty	453 kW	82 kW
Reboiler duty	176 kW	362 kW
Number of trays	17	16
Feed tray	2	7
Recycle feed tray		7
Diameter	0.54 m	0.37 m
Recycle flowrate D_2	4.4 mol/s	
Recycle composition	$x_P=0.409$ $x_W=0.561$ $x_C=0.029$	

Table 2: Costs, column configurations and recycle for all columns of the first case study after rigorous optimization.

Due to the favorable initialization and the reformulation as a continuous problem, the rigorous optimization could be solved in only 143 seconds. Note that the process operating point shifted within the optimization: The minimum recycle flowrate of 2.9 mol/s, which served as the initial value, was raised to an optimal recycle flowrate of 4.4 mol/s.

4.2. Separation of multiple feeds in a complex heteroazeotropic distillation process

The task of this industrial case study is the separation of four feed streams, which contain different fractions of the components propargyl alcohol, monochlorobenzene and water, into pure components. The mixture topology and the compositions of the different feed streams are shown in Figure 4. Note that the column pressures are set to 0.23 bar for this case study, since the maximum allowed operating temperature in the distillation system is 85 °C in order to prevent a decomposition of propargyl alcohol.

	Feed F ₁	Feed F ₂	Feed F ₃	Feed F ₄	Recycle D ₁	Recycle D ₃
Flowrate	0.29 mol/s	0.17 mol/s	0.18 mol/s	0.11 mol/s	0.21 mol/s	0.037 mol/s
Composition [x _P , x _M , x _W]	[0.26, 0.74, 0]	[0.45, 0.1, 0.45]	[0.1, 0.86, 0.04]	[0.03, 0.93, 0.04]	[0.65, 0.3, 0.05]	[0.27, 0.01, 0.72]

Table 3: Feed and recycle flowrates and compositions for the second case study.

In earlier work [10], various alternative heteroazeotropic distillation flowsheets were generated and evaluated with shortcut methods. The process operating points in the shortcut evaluation were chosen such that the recycle flowrates were minimal. The flowsheet alternative which exhibited the lowest minimum energy demand is given in Figure 4. Mass balances of the three columns and two decanters at the minimal recycle flowrate are also shown in Figure 4. Flowrates and compositions of the feeds and the recycles are given in Table 3.

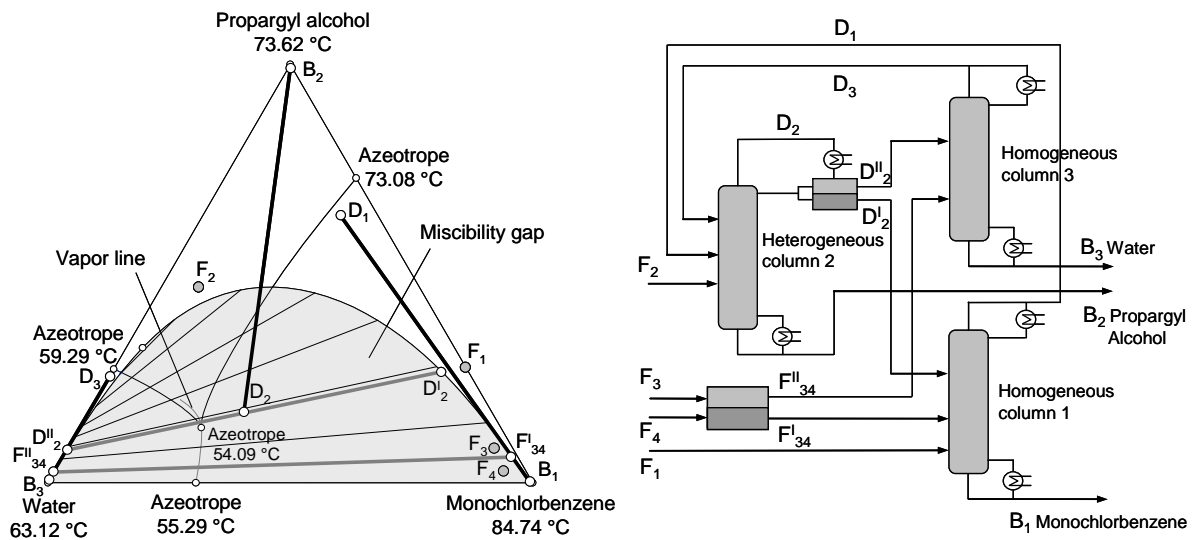


Figure 4: Topology of the propargyl alcohol, chlorobenzene, water system and heteroazeotropic distillation process to separate multiple feeds into pure components.

The rigorous optimization of this heteroazeotropic process is highly demanding not only due to the non-ideal thermodynamics and the liquid phase split but also due to the manifold of feeds, columns and recycles. Still, this rigorous optimization problem could be solved with satisfying robustness and efficiency because of the initialization with the results from the shortcut evaluation and the reformulation as a continuous NLP problem. As in the first case study, the heteroazeotropic column was initialized by tray-to-tray profiles from the feed pinch method (with 13 heterogeneous trays) and the homogeneous columns were initialized by

linear profiles from the rectification body method. The maximum tray numbers were set to 50, 40 and 20 trays for columns 1, 2 and 3, respectively, yielding an optimization problem of about 4500 variables, including 460 binary decision variables. All column feeds were fed separately into the columns. Note that the recycles are both drawn off as saturated vapor as a measure of heat-integration. Again, the solution of the optimization problem was carried out by the solution procedure proposed by Kraemer et al. [1]. The optimization results for the costs, number of column trays, feed tray locations and the process operating point are displayed in Table 4.

	Heterogeneous column 2	Homogeneous column 1	Homogeneous column 3
Operating cost	3110 €/a	3120 €/a	440 €/a
Capital cost	23000 €/a	14100 €/a	2920 €/a
Condenser duty	38 kW	13 kW	2.1 kW
Reboiler duty	23 kW	28 kW	3.8 kW
Number of trays	27	10	9
Feed trays	9 / 13 / 17	4 / 4 / 8	3/6
Diameter	0.21 m	0.24 m	0.05 m
Recycle flowrate D_1	0.306 mol/s		
Recycle composition D_1	$x_P=0.514$ $x_M=0.442$ $x_W=0.044$		
Recycle flowrate D_3	0.04 mol/s		
Recycle composition D_3	$x_P=0.249$ $x_M=0.005$ $x_W=0.746$		

Table 4: Costs, column configurations and recycles for all columns of the second case study after rigorous optimization.

The computational time for the rigorous optimization of this complex large-scale problem was only 456 seconds. Again, the process operating point shifted within the optimization: The cumulated minimum recycle flowrate of 0.247 mol/s, which served as the initial value, was raised to an optimal recycle flowrate of 0.346 mol/s.

5. Conclusions

We have shown in the second part of the Max-Buchner grant that the rigorous optimization of complex large-scale heteroazeotropic distillation processes for multicomponent heterogeneous mixtures can be accomplished robustly and efficiently when integrated into a process synthesis framework and reformulated as a continuous problem. The model for the rigorous optimization of distillation processes for homogeneous azeotropic mixtures of Kraemer et al. [1] was extended such that heteroazeotropic distillation processes for heterogeneous azeotropic mixtures could be rigorously optimized. Two case studies were presented, where heteroazeotropic processes were generated and evaluated by the minimum energy demand with the help of powerful shortcut methods. The results of the shortcut evaluations were used for the initialization of rigorous optimization problems. In this step, optimal number of trays, optimal feed tray locations and optimal operating points were determined by a minimization of an economic objective function. The complex discrete-continuous optimization problems could be solved with satisfying robustness and efficiency by a reformulation as continuous problems.

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