

A Framework for the Systematic Design of Hybrid Separation Processes*

Wolfgang Marquardt**, Sven Kossack and Korbinian Kraemer

Process Systems Engineering and Center for Computational Engineering Science, RWTH Aachen University, D-52064 Aachen, Germany

Abstract The design of optimal separation flow sheets for multi-component mixtures is still not a solved problem. This is especially the case when non-ideal or azeotropic mixtures or hybrid separation processes are considered. We review recent developments in this field and present a systematic framework for the design of separation flow sheets. This framework proposes a three-step approach. In the first step different flow sheets are generated. In the second step these alternative flow sheet structures are evaluated with shortcut methods. In the third step a rigorous mixed-integer nonlinear programming (MINLP) optimization of the entire flow sheet is executed to determine the best alternative. Since a number of alternative flow sheets have already been eliminated, only a few optimization runs are necessary in this final step. The whole framework thus allows the systematic generation and evaluation of separation processes and is illustrated with the case study of the separation of ethanol and water.

Keywords process synthesis, distillation design, rectification body method, mixed-integer nonlinear programming

1 INTRODUCTION

Large scale purification of reaction products in a chemical plant is typically accomplished through distillation. The costs associated with these separation steps are often the dominating factor in the total cost of a chemical process. For a cost-effective process the design of an efficient separation sequence is therefore important. Finding and evaluating the best possible distillation column setup has already generated a lot of scientific interest. Most of this previous research work, however, is related to non-azeotropic or even ideal mixtures [1].

Progress for the synthesis of distillation based separation processes for azeotropic mixtures has been made from the application of the analysis of residue curve maps from the group of Doherty and Malone [2]. Their methods, however, are limited by the fact that most of their methods rely on visual inspections of the column profile in the composition triangle, which effectively limits the methods to ternary mixtures.

Recent developments in our and other research groups overcome these limitations for most applications by employing algebraic criteria to determine feasibility and minimum energy demand. Besides covering distillation using simple and complex columns or homogeneous and heterogeneous entrainers, these approaches could be extended to hybrid separations including membranes and crystallization.

In the next section the traditional approaches to separation process design are out-lined. In Section 3 we then give a brief overview on recent developments in the synthesis of separation processes for non-ideal and azeotropic mixtures and on our contributions to this challenging field. A framework for the systematic design of separation sequences is presented which integrates existing and new approaches. The main focus is on distillation based separation while other separation techniques are also mentioned. Since the objective of this text is to give a broad overview of

existing methods, only key features are outlined below while a more detailed presentation of the technical details can be found in the cited literature.

The presented framework is illustrated by the separation example of ethanol and water in Section 4 before we close with a summary and conclusion.

2 SEPARATION PROCESS DESIGN

Broadly speaking the proposed design methods for separation processes can be grouped into three main areas: simulation studies, shortcut calculations and optimization based approaches.

In industrial practice simulation studies are the most common design method for chemical processes. Here, an initial flow sheet design, which is usually found through heuristics [3] or thermodynamic analysis of the residue curve map [2, 4], is fixed. The feasibility and the cost of the proposed process is then determined by repetitive simulation studies. In this step the different feasible alternatives are also manually optimized. These simulation studies are very time consuming and tedious, therefore only a small number of possible flow sheets can be evaluated; a problem is further aggravated by the fact that the use of heuristics often leads to a non-systematic generation of flow sheets. The design of the most cost-effective process using this design practice cannot be guaranteed.

Shortcut procedures such as the well known Underwood method [5] can be used to determine the minimum energy demand of a previously specified separation for zeotropic [5] and azeotropic [6–9] mixtures. They also allow an approximate evaluation of the feasibility of a desired split. Since shortcut methods have been specifically developed for the design of separation processes, they are the most important building block of the synthesis framework. The drawback of these methods is that they usually do not provide any detailed information on the optimal column design.

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** To whom correspondence should be addressed. E-mail: Wolfgang.Marquardt@avt.rwthachen.de

Such an optimal design of a distillation column can be computed by rigorously optimizing a column model. Here the design variables are usually optimized with mixed-integer nonlinear programming (MINLP) techniques [10–12], for which, in the general case, complex superstructures [10] need to be defined. These superstructures have to account for all possible splits and column configurations and are therefore difficult to set up and solve. The optimization runs are furthermore computationally expensive and the quality of the final solution depends strongly on the initial values because of the nonlinearity and non-convexity of the problem [11]. These drawbacks of rigorous MINLP optimization have so far prohibited their use in industrial practice. In the next section a solution is presented, which overcomes these difficulties.

3 SYSTEMATIC FRAMEWORK

As can be inferred from the discussion in the previous chapter, the use of flow sheet simulators, which have been designed to work as an analysis tool, as a design tool cannot be recommended. Instead, special design tools such as shortcut calculations or MINLP optimization are better suited for the design of separation processes. They have, however, also important weaknesses, which can be overcome by a combination of these tools in a systematic synthesis framework.

The envisioned synthesis framework is depicted in Fig. 1 and is illustrated later with the example separation of ethanol and water (this case study is presented in more detail in Section 4). The framework starts at the top left with the given separation problem. In the first step, possible splits are generated. The generated alternatives are then evaluated with the help of shortcut calculations in the second step. The results are then exported to a rigorous optimization model, where they are used for an efficient initialization and tight bounding of the optimization variables [13]. This handover can be automated, so that no manual intervention is necessary once the shortcut calculations are completed. It should be noted that a large number of alternatives can typically be discarded after the shortcut step, so that only a few alternatives remain for a detailed optimization in this last step.

In the following the individual steps are described in the order they appear in Fig. 1. It should be noted, however, that in most cases this framework does not prescribe a linear workflow. Iterations, especially between the generation of alternatives (step 1) and the shortcut evaluations (step 2), are expected, because the shortcut methods usually allow the design engineer to get a better understanding of the thermodynamic behavior of the process.

3.1 Generating possible flow-sheet alternatives

In industrial practice, a flow-sheet is often pragmatically fixed first using heuristics from the literature, solutions of similar problems, experience and intuition. Furthermore, analysis of residue curve maps is usually used in industrial practice even though only ternary subproblems can be analyzed this way [2, 4]. It should

be noted that all presented methods require vapor-liquid equilibrium parameters, as a first guess UNIFAC may be used in case no database parameters are available. It is nevertheless advisable to use parameters regressed from measured data as soon as they are available.

Although there are some attempts to automate this step, most notably Jacaranda (<http://www.homepages.ucl.ac.uk/~ucecesf/Jacaranda/>) and PROSYN (<http://www.process-design-center.com/2.3.1-prosyn.htm>), we think that this step still requires the creativity of an expert engineer to provide good solutions. There are however some tools available that may help the engineer in designing a flow-sheet especially for multi-component mixtures where visualization is impossible.

For azeotropic multi-component mixtures, adjacency and reachability matrices introduced by Rooks *et al.* [14] offer a completely equation-based approach to determine the structure of distillation regions for homogeneous mixtures. In our experience the procedure shows some numerical difficulties when the residue curve map is analyzed using numerical integration of residue curves originating close to singular points (pure components or azeotropes). A possible work-around that is currently explored within our group is the combination of the reachability matrices with the pinch distillation boundaries (see Section 3.3) to overcome these difficulties. These methods can be used to generate process alternatives, and according to Rooks *et al.* [14], there is usually a surprisingly large number of alternatives for the separation of azeotropic mixtures.

Several techniques exist to break azeotropes. The first heuristic rule suggests to check the pressure sensitivity of the azeotropic composition [3]. Should the pressure sensitivity be large, a pressure swing process might be feasible. All other developed separation techniques, however, have to exploit different physical phenomena besides boiling point differences. Thus a separation of an azeotropic mixture into the pure components is usually facilitated in a hybrid separation process.

Closest to pure distillation is (homogeneous) extractive distillation, where an entrainer is added to change the volatility of the azeotropic components. Suitable entrainer candidates can be found through Computer-Aided Molecular Design (CAMD), where components with appropriate mixture properties can be found based on group contribution methods [15]. The large number of possible entrainer candidates, however, requires reliable screening methods (see Section 3.2.1 and Ref. [16]).

The crossing of distillation boundaries using a heterogeneous entrainer is a technique widely used in industry to separate binary and multi-component azeotropic mixtures. In these processes, the immiscibility of two liquid phases is exploited in order to facilitate the separation. In typical designs, a heterogeneous stream is produced at the top of the column which is then split in a decanter into the entrainer-lean distillate product and the entrainer-rich reflux stream. The separation of a binary ethanol-water mixture using benzene or cyclohexane as an entrainer is a prototypical example [17–19]. Again, a large number of possible entrainer candidates require an efficient screening tool, which is presented in Section 3.2.2.

Other frequently employed unit operations to be

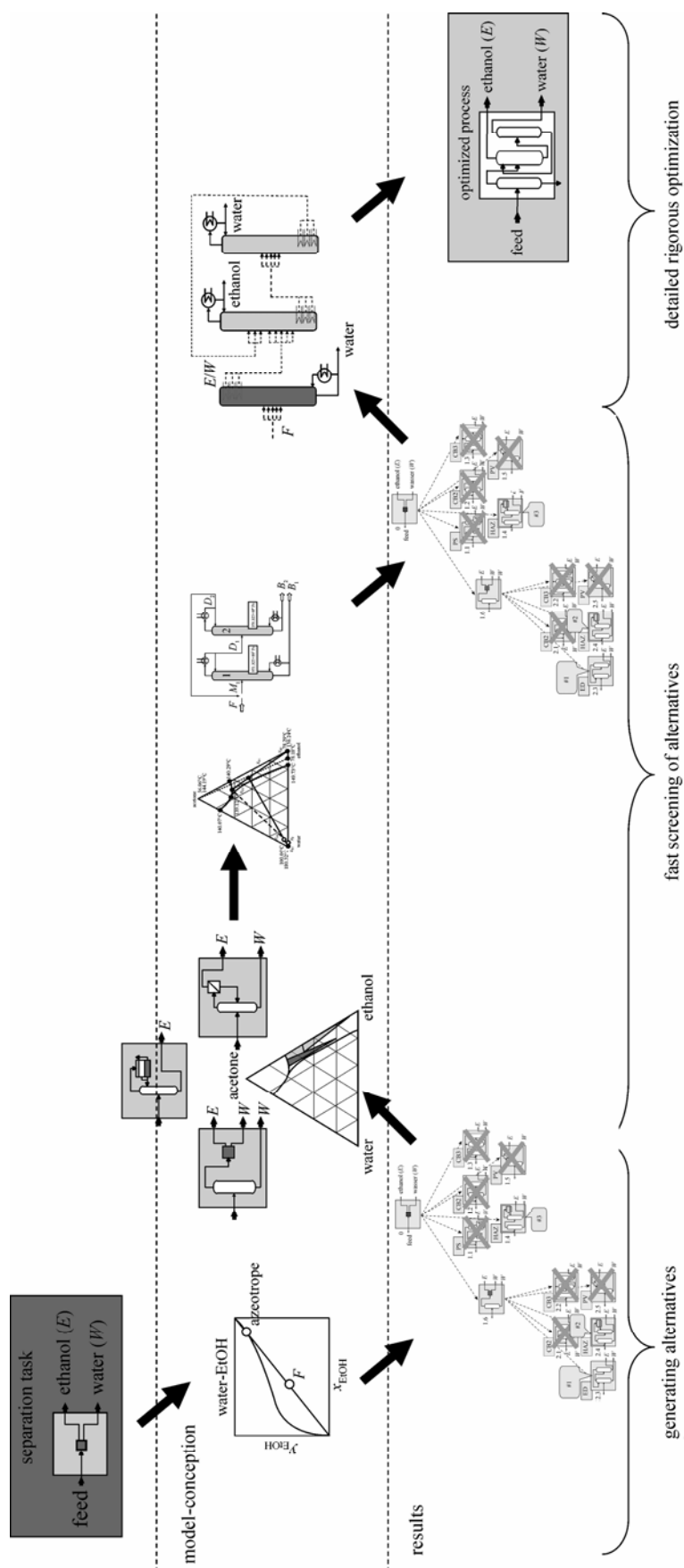


Figure 1 Systematic synthesis framework for separation processes (In the first step, different separation alternatives are designed. These are screened with shortcut methods in the second step. In the third step, the best remaining alternatives are then rigorously optimized using MINLP optimization)

considered in this step are membrane separation [20], extraction and crystallization [21] which often allow considerable energy savings. Shortcut tools for these process alternatives are described in Section 3.2.3.

3.2 Shortcut evaluation

Considering the large number of separation mechanisms and the even larger number of possible entrainer candidates for the separation of an azeotropic mixture, it is clear that not all envisioned alternatives generated in the previous step can be covered with simulation studies (see Section 2). The framework therefore relies on shortcut tools to calculate the minimum energy demand of each separation and to determine a few economically attractive flow sheet designs.

An overview of the developed shortcut methods for non-ideal multi-component mixtures is given in Table 1. The most important shortcut tools are described in the next few sections, starting with those for single units and later for coupled units where besides the minimum energy demand of the individual units an optimal operating point has to be found (see Section 3.3). Note that unless otherwise specified in the column "Limitation" in Table 1, the shortcut tools are suitable for an arbitrary number of components in the system, since they employ algebraic criteria for the calculations.

3.2.1 The rectification body method for homogeneous mixtures

The rectification body method (RBM) is used in the shortcut step to compute the minimum energy demand of the selected separation and to initialize the MINLP optimization. The main ideas of the RBM will be briefly reviewed below; a more detailed presentation is given by Bausa *et al.* [6] for simple distillation columns, by von Watzdorf *et al.* [22] and Brüggemann and Marquardt columns [23] for complex distillation columns and by Brüggemann and Marquardt [24] for extractive columns.

According to Levy *et al.* [7] the tray-to-tray profiles of the rectifying and stripping section need to intersect for a feasible column design. The point of intersection belongs to both column sections and is

located on the feed tray. Their boundary value method (BVM) calculates the respective profiles for an estimated energy demand by starting at the respective products. When the two profiles intersect, a feasible design has been found. This design method, however, is very sensitive towards trace impurities in the product compositions, therefore a number of tray-to-tray calculations are typically necessary to find the minimum energy demand of a separation. The BVM therefore cannot be automated and can only be used for ternary or quaternary mixtures, since the intersection of the profiles has to be checked visually. Based on the BVM, the zero-volume criterion (ZVC) [9], an algebraic criterion for minimum reflux based on the alignment of pinch points, has been proposed. Since the fulfillment of the criterion can be checked algebraically, it can be applied to any number of components. The method is, however, only applicable to direct and indirect cuts, since the topology of the split has to be known *a priori* [6].

As can be seen in Fig. 2, the RBM uses the pinch points to approximate the column profile. The locations of the pinch points are independent of the trace components and are mainly determined by the thermodynamic behavior of the mixture under consideration. After the pinch points have been calculated, the rectification bodies are determined by an automatic procedure. The resulting rectification bodies can be seen as a linear approximation of the envelope in the composition space of all possible column profiles. When the rectification bodies of the stripping and rectifying section intersect in a single point, the minimum energy of the separation has been found.

The algorithm is summarized as follows. For a given feed and given products the pinch lines are calculated. The locations of the pinch points on these pinch lines depend on the separation energy, which is varied automatically until the rectification bodies intersect in a single point.

Since the intersection of the rectification bodies is checked with an algebraic criterion, no visual inspection is necessary and the method can be used for *n*-component mixtures. The RBM can be used for the generation of feasible splits and for a quick economic evaluation of the separation. Furthermore, the occurrence of a tangent pinch can be detected and handled automatically.

Table 1 Overview on the available shortcut methods for different unit operations that were developed at Process Systems Engineering, RWTH Aachen University

Unit operation		Method	Cost parameter	Limitation	Automated
distillation	simple columns	RBM	$Q_{B,min}, Q_{C,min}$		
	complex columns	decomposition, RBM, bisection	$Q_{B,min}, Q_{C,min}, f$	none	completely
	sidestream columns	extended RBM	$Q_{B,min}, Q_{C,min}, S_{opt}, X_{S,opt}$		
distillation+decantation	heterogeneous distillation	nonlinear RBM	$Q_{B,min}, Q_{C,min}, f$	ternary	partly manual
distillation+absorption	extractive distillation	bifurcation analysis, RBM	$Q_{B,min}, Q_{C,min}, E_{min}$	none	completely
liquid-liquid extraction		pinch analysis	S_{min}	ternary quaternary	completely part. manually
pervaporation		integration of mass transfer law	A_{min}	mass transfer law known	completely
melt crystallization		Wintermantel rule, MINLP	$Q_{K,min}$	limited number of stages	completely

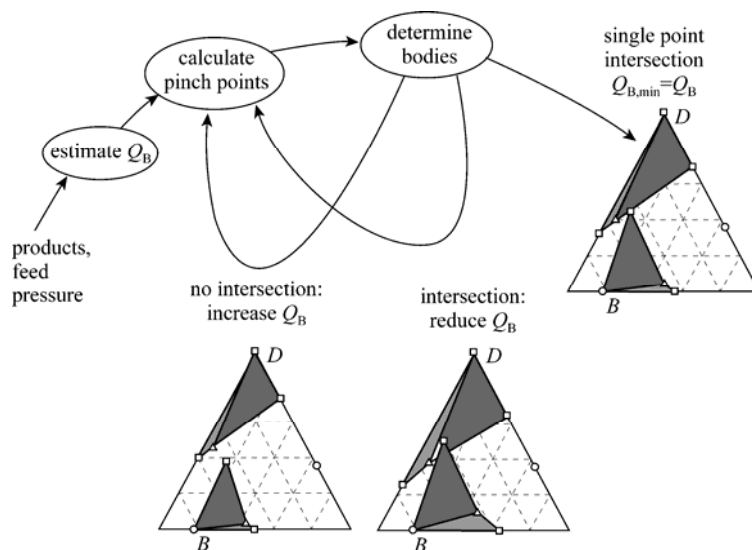


Figure 2 Algorithmic concept of the RBM (For a given feed, pressure and for given products the pinch points are calculated. From the pinch points the rectification bodies are calculated. Intersection of the bodies in a single point marks the condition for minimum energy)

3.2.2 The rectification body method for heterogeneous mixtures

A design method for ternary heterogeneous separations has been presented by Doherty and coworkers [18, 25, 26]. The determination of minimum energy demand and an assessment of the feasibility of the separation is based on the calculation of tray-by-tray profiles from given product compositions at different reflux ratios. However, these authors only consider processes with a heterogeneous liquid in the decanter at the top of the column and assume the trays in the column to be operated in the homogeneous region.

Starting from the geometrical analysis of tray-by-tray profiles suggested by Pham *et al.* [25], Urdaneta *et al.* [19] present an extension for multiple heterogeneous trays in both the rectifying and stripping sections of the column. These authors show that heterogeneous trays in the column complicate minimum energy demand analysis and conceptual column design, because of the resulting multi-parametric design problem formulation. The occurrence of phase splitting inside the column, however, might lead to significant energy savings.

In this shortcut procedure, separation feasibility is checked by so-called continuous distillation regions (CDRs) which allow a more accurate analysis than the widely used simple distillation regions (SDRs). The CDRs can be seen as curved rectification bodies tailored to the heterogeneous case. Based on CDRs the minimum energy demand of heterogeneous distillation processes can also be calculated. The method is, however, still limited to three component mixtures, because intersection of the CDRs has to be done by visual inspection.

3.2.3 Shortcut methods for other unit operations

A number of other shortcut methods for a wide variety of unit operations have been developed in our research group. In the following a brief summary of shortcut methods for pervaporation membranes and melt crystallization is given.

Bausa and Marquardt [20] developed shortcut formulations for pervaporation membranes that can be transferred to other kind of membrane modules, too. Because the energy consumption of pervaporation is relatively small, its cost is mainly determined by the capital cost for the membrane units and for the replacement of worn-out membranes during operation. Thus, the installed membrane area can be used as a rough measure for total cost.

The minimum membrane area, a lower bound of the actual membrane area, can be used in analogy to the minimum energy demand of distillation to represent the target cost of the membrane unit. Similar to the assumption of the infinite number of stages for a distillation column, an infinite number of membrane modules and intermediate heat exchangers is assumed for the shortcut model of a staged pervaporation process. Consequently, isothermal operation at the maximum allowable temperature for the membrane can be assumed, which corresponds to a minimum membrane area. The minimum membrane area only depends on the properties of the membrane, the maximum allowable temperature, the permeate pressure, and the separation specifications. Thus, it is not necessary to decide on the strategy for reheating or the number and size of modules at the conceptual design stage.

In the literature on shortcut design procedures simple mass-transfer models are typically used. However, the highly non-ideal separation characteristic of pervaporation membranes cannot be described by these simple models. Instead, complex mass-transfer models based either on semi-empirical assumptions or on the detailed modeling of sorption equilibria and multi-component diffusion are required. In order to employ these accurate models for design, the shortcut model for membrane units in Ref. [20] does not rely on special largely simplistic mass-transfer models but makes use of the best models available. Further, there are no limitations on the number of components. These requirements can be seen in analogy to the shortcuts for distillation: in order to address non-ideal

systems, the shortcut procedure is capable of using general and appropriate thermodynamic models.

Wallert [21] presented a shortcut formulation for the design of melt crystallization processes, which allows for an estimation of the energy demand on the basis of feed and product specifications. In melt crystallization, a crystal melt is growing at a cooled surface. After a distinct crystallization time the solid-liquid separation is carried out by draining off the remaining liquid followed by re-melting of the crystal melt formed. Ideally, the gained product would be pure, but due to enclosed and adherent melt the crystal melt contains impurities. Therefore, more than one crystallization stage is needed to meet the required product purity. Since crystallization cascades usually contain only a few stages, the simplification of an infinite number of stages as in distillation and membrane separation does not hold here.

Consequently, Wallert [21] integrated the shortcut formulation for melt crystallization in an optimization problem to solve for the optimal number of crystallization stages and feed stage location while minimizing the energy demand of the process, which can be considered as a measure for assessing cost. The energy demand for the crystallization cascade is estimated by a methodology of Wellinshoff and Wintermantel [27], introducing the so-called crystallization effort, which is defined as the ratio of total amount of crystals produced to the amount of pure product. The shortcut optimization models for melt crystallization have also been integrated by Wallert into a hybrid separation process synthesis problem where crystallization is combined with distillation (modelled by the RBM, Section 3.2.1) for an economic separation process.

3.3 Flow sheet optimization

The extension of the shortcut procedures for a single separation unit to a flow sheet consisting of several separation units without recycle streams is straightforward. Since the individual units can be decoupled, the solution procedure presented by Kossack *et al.* [13] is also applicable.

For a process with recycle streams, a decoupling of the separation units is not possible. In this case, a flow sheet optimization based on shortcut calculations is used as an intermediate step. The optimal recycle stream and the minimum energy demand for the entire flow sheet are determined in this step.

Using pinch distillation boundaries (PDB, an analytical formulation of the distillation boundaries for minimum reflux [28]) in combination with the RBM a flow sheet of several distillation columns can be optimized without detailed models [28]. The key advantage of the PDB over other formulations of distillation boundaries (such as simple distillation boundaries or continuous distillation boundaries (see Ref. [2, 28]) is that it can be determined from a nonlinear set of equations and is thus applicable to mixtures with an arbitrary number of components. The advantages of using shortcut methods rather than full models in this step are the very compact problem formulation and the shorter solution times as well as

the increased numerical robustness.

As mentioned above, during this flow sheet optimization the optimal recycle streams are determined. This allows the comparison of the flow sheet alternatives at their optimal operating point, which is crucial when a ranking of all possible alternatives is done.

3.4 MINLP optimization

With the RBM a detailed distillation column design is not possible. Similar to other pinch based methods it calculates the minimum energy demand for a column with an infinite number of trays. Therefore the optimal trade-off between investment costs—which mainly depend on the size and number of trays—and the operating costs—which are defined mainly by the cost of heating and cooling of the process streams—has to be found in a following MINLP optimization.

The optimal column design is typically computed through an optimization with an economic objective function [10, 11]. Since the number of trays and the feed tray location are discrete variables, a MINLP problem is solved in the design optimization. MINLP optimization of distillation columns using rigorous models has been introduced by Viswanathan and Grossmann [12]. Since then, a number of extensions to the models and algorithms have been presented; however, mostly ideal mixtures have been considered.

Reliability of the MINLP optimization and convergence to good local optima or even to the global optimum are still open issues. These issues have been addressed by our group with a novel solution approach, where a succession of relaxed MINLP problems with decreasing bounds is solved [13, 29].

The biggest advantage, however, comes from the integration of the MINLP optimization into the synthesis framework. This allows a very good initialization and bounding not only for single columns [13] but also for complex flow sheets, where the results from the flow-sheet optimization are used to provide very good initial values for the recycle streams [30]. Furthermore the formulation of a large superstructure can be avoided, because a number of alternatives can already be eliminated in the shortcut step.

The design of distillation processes through a combination of the shortcut calculations with the flow sheet optimization and MINLP optimization thus exploits the strengths of these tools and avoids their weaknesses. The good initial values and bounds enhance the numerical stability and the convergence rate. In addition, the cost-optimal trade-off between investment and operating costs for each individual column is determined by MINLP optimization with an economic objective function.

4 ILLUSTRATIVE EXAMPLE

The proposed separation example is illustrated in this section by a case study where the optimal separation of ethanol and water is developed. The chosen feed composition of 4% ethanol and 96% water closely

resembles that of a typical bioethanol fermenter effluent. In the search for an alternative fuel, bioethanol is increasingly popular and the purification of such a diluted ethanol/water mixture therefore becomes increasingly important. It should be noted, however, that the typical fermenter effluent will contain a number of impurities. We have to neglect these trace impurities in this case study to arrive at ternary separations which can still be calculated with the shortcut for heterogeneous mixtures (see Section 3.2.2), which is the preferred separation technique for this mixture in industrial practice [17–19]. Note that all other shortcuts are suitable for an arbitrary number of components. The results obtained here therefore can only have exemplary character for the purification of bioethanol.

4.1 Generating possible flow sheet alternatives

Following the procedures suggested in Section 3.1, the following alternatives can be found:

- (1) a pressure swing process where acetone is added as an entrainer to increase the separation performance of a pressure swing process [29, 31],
- (2) an extractive distillation process where glycol is added as an entrainer [24],
- (3) a heterogeneous distillation process which uses cyclohexane as an entrainer [17, 19],
- (4) a combination of a membrane separation and a homogeneous distillation column [20], and
- (5) processes that exploit a curved distillation boundary [32].

Since ethanol is very diluted in the feed, either a

two-column process or a three-column process that includes a preconcentrator column should be considered for the heterogeneous distillation [alternative (3)], the combination of a membrane separation and a homogeneous distillation (4) and the curved boundary processes (5). On the other hand, extractive distillation (2) is only useful for a more concentrated feed while the pressure swing process (1) works only for the diluted process feed.

All mentioned process alternatives are depicted in the scenario tree shown in Fig. 3. The alternatives numbered 1.1–1.5 depict the processes without a preconcentrator, which is shown as unit 1.6. The processes 2.1–2.5 therefore include the preconcentrator. It can be seen that even for such a simple process a large number of alternatives can be found. The number of alternatives is even larger when more than one choice of an entrainer would have been included for the extractive and the heterogeneous processes.

4.2 Shortcut evaluation

While the curved boundary processes (1.2, 1.3, 2.1 and 2.2 in Fig. 3) developed in the previous step offer potential energy savings, this process class is difficult to control and operate under industrial conditions [32]. These processes are only useful as a theoretical concept, but no industrial application is known. We exclude these four alternatives therefore from further considerations.

For the remaining two column processes the minimum energy demand is now determined using the

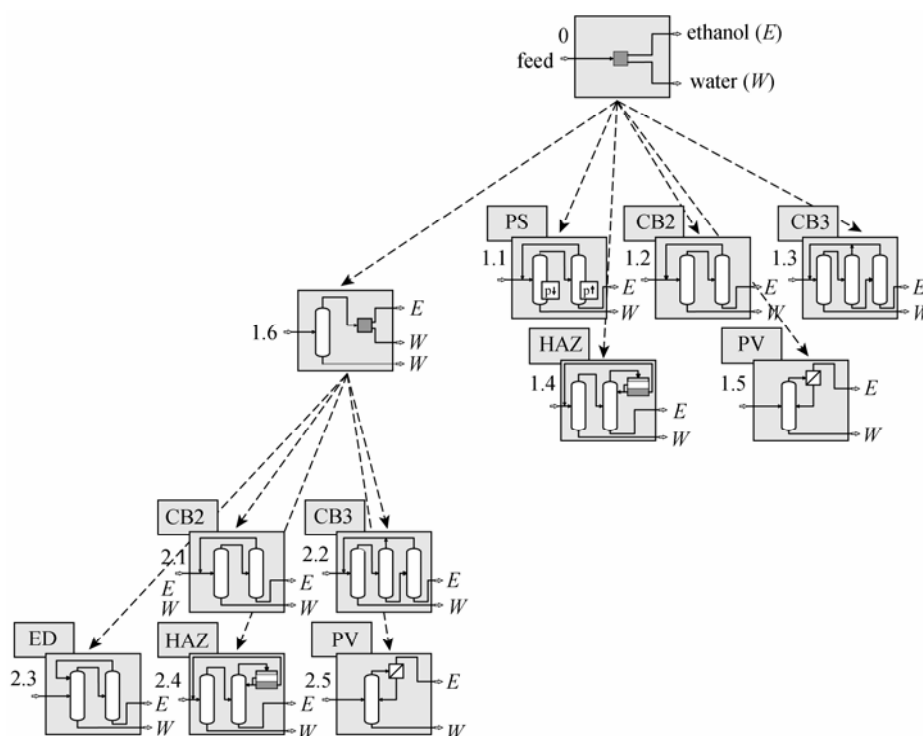


Figure 3 Process alternatives for the separation of a diluted ethanol/water mixture (The alternatives numbered 1.1–1.5 depict the processes without a preconcentrator, which is shown as unit 1.6. The processes 2.1–2.5 therefore include the preconcentrator)

PS—pressure swing distillation; CB—curved distillation boundary process; ED—extractive distillation; HAZ—heteroazeotropic distillation; PV—distillation/pervaporation

shortcut methods described in the previous section. The heteroazeotropic distillation (alternative 1.4) can be directly evaluated using the method described by Urdaneta *et al.* [19]. For the distillation/pervaporation process (alternative 1.5) the shortcut developed by Bausa and Marquardt [20] can be used directly.

The minimum energy demand of the pressure swing process (alternative 1.1) is strongly dependent on the operating point. To facilitate a fair comparison, this optimal operating point is determined in a flow sheet optimization as described in Section 3.3 using shortcut methods [28, 30].

The three-column processes can be analyzed the same way. For the extractive separation the shortcut method developed by Brüggemann and Marquardt is used [24]. For the sake of brevity we restrict ourselves here to a single entrainer choice (ethylene glycol), which is the most commonly used entrainer for extractive distillation.

The results from the shortcut step are summarized in Table 2. The different process alternatives are compared with respect to their minimum energy demand. The shortcut for the pervaporation modules calculates a minimum membrane area, which has to be converted into minimum energy demand to allow a comparison. Obviously, the exact choice on the conversion parameters has a big influence on the final energy demand of these processes, here a cost of US\$5350 per square meter of membrane is assumed [20].

From the calculations given in Table 2, the following ranking for the flow sheet alternatives can be determined based on minimum energy demand:

- (1) extractive distillation in a three-column process (2.3),
- (2) heterogeneous distillation in a three-column process (2.4),
- (3) heterogeneous distillation in a two-column process (1.4).

Table 2 Summary of the minimum energy demands for the different process alternatives as determined in the shortcut step (The minimum membrane area calculated for the distillation/pervaporation process was converted into minimum energy demand to allow for an easier comparison. Obviously the exact choice on the conversion parameters has a big influence on the final energy demand of these processes)

Process alternative		Energy demand/MW·kmol ⁻¹			
		1st column	2nd column	3rd column	Total
two-column processes	pressure swing process (1.1)	18.9	13.41	–	32.31
	heteroazeotropic distillation (1.4)	5.26	9.34	–	14.6
	distillation/pervaporation (1.5)	6.77	15.5	–	22.27
three-column processes	extractive distillation (2.3)	6.77	3.2	0.685	10.66
	heteroazeotropic distillation (2.4)	4.7	8.2	0.24	13.14
	distillation/pervaporation (2.5)	6.54	4.25	14.3	25.09

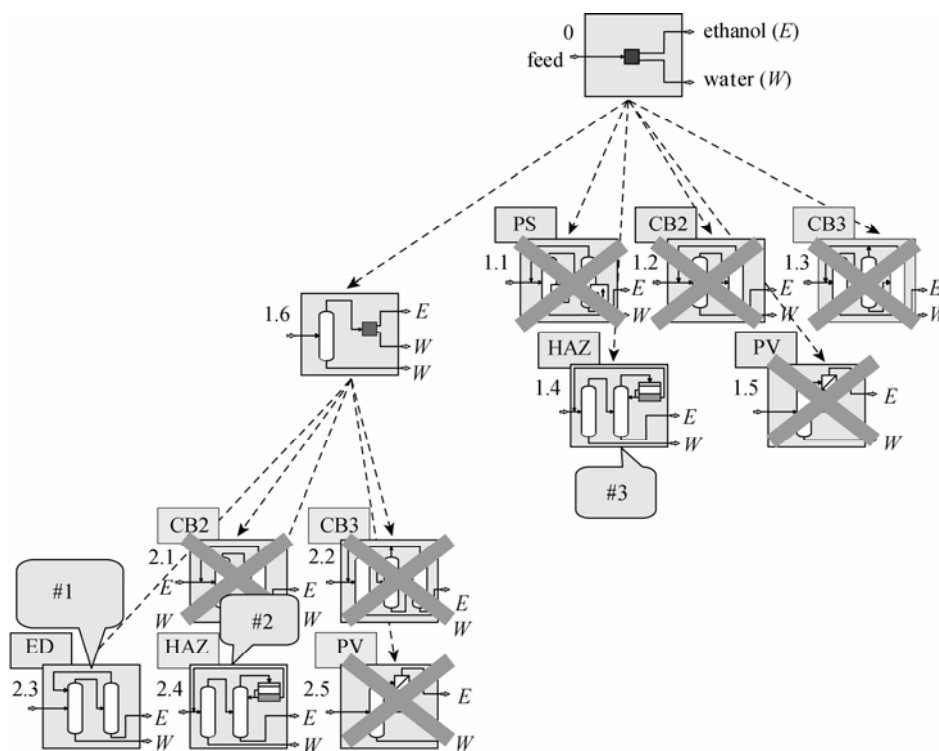


Figure 4 Process alternatives for the separation of a diluted ethanol/water mixture (The alternatives numbered 1.1–1.5 depict the processes without a preconcentrator, which is shown as unit 1.6. The processes 2.1–2.5 therefore include the preconcentrator)

Table 3 Detailed column configurations for the extractive distillation process

Column	Investment cost /US\$	Operating cost /US\$	Reboiler duty /MW	Number of trays	Feed tray	Extractive feed tray	Diameter /m
preconcentrator column	6.24×10^5	9.5×10^5	6.8	52	42	–	1.92
extractive column	3.37624×10^8	5.29×10^5	3.75	28	23	5	1.58
entrainer recovery column	1.15624×10^8	2.77×10^5	0.908	18	7	–	0.44

The heterogeneous distillation in a two-column process offers potential investment savings, albeit at a slightly higher energy consumption over the three-column processes. All other alternatives can be discarded after this step, since they require too much energy and will never be cost effective. This is illustrated in Fig. 4, where the discarded alternatives are crossed out. For the remaining alternatives the number obtained from a ranking according to Table 2 is shown.

There is nevertheless a bigger margin between the extractive distillation and the two heterogeneous processes and we can conclude that this process alternative is the best choice. This result is supported by Blass [33] who reports that extractive distillation is usually the most energy efficient separation technique, although sometimes purity constraints cannot be met.

4.3 MINLP optimization

As mentioned in Section 3.4 the results computed in the shortcut step can be used to initialize this computation. Furthermore an efficient solution algorithm allows the robust solution of this challenging optimization problem.

The goal of this synthesis step is to determine the optimal column design. Therefore very detailed specifications of the entire column, such as number of trays, tray diameter and heat exchanger area, are determined in this step. The most important column parameters are shown in Table 3 for the extractive distillation setup. With the developed successive relaxed MINLP solution algorithm (SR-MINLP, [13, 29]) an optimization run for this large problem takes only about 5 minutes.

5 SUMMARY AND CONCLUSIONS

When reviewing the classical synthesis methods for a conceptual design of separation process, no single synthesis method solves the problems associated with this design task alone. Therefore a synthesis framework which combines shortcut models and MINLP optimization is proposed. In this framework the synthesis task separated into three distinctive steps. In the first step different flow sheets are generated. In the second step these alternative flow sheet structures are evaluated with shortcut methods. After this step usually a large number of alternatives can be discarded, since their minimum energy demand is much larger than that of the best alternatives. The remaining process alternatives are then optimized in the third step to calculate detailed information. Since a number of alternative flow sheets have already been elimi-

nated, only a few optimization runs are necessary in this final step. The optimization is further improved through an excellent initialization with the results from the shortcut step and through a novel solution technique.

To make the developed shortcut algorithms usable in an industrial environment, an ASPEN plug-in based on the CAPE-OPEN interface has been developed by AixCAPE (<http://www.aixcape.org>). We are working to extend this plug-in to cover all our developed shortcut methods and eventually the entire synthesis framework.

Future research will focus on the algorithmic support to generate separation process flow sheets, the inclusion of reactors and heat integration into the framework. In new projects the shortcuts for membrane separation and heteroazeotropic distillation will be improved. Furthermore, the extension of the framework to batch processes is planned.

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