Optimization-Based Methods for the Conceptual Design of Separation Processes for Azeotropic Mixtures

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1. Summary

The main objective of the Ph.D. thesis is the development of efficient and reliable methods for the design of distillation-based separation processes for azeotropic mixtures. In order to accomplish this objective several systematic numerical and optimization-based methods that take into account thermodynamically sound process models are developed. These methods significantly enhance the state-of-the art design capabilities of a process engineer and allow for a fast identification of energy-efficient and cost-effective distillation-based separation processes. At first the applicability of pinch-based shortcut methods to the separation of azeotropic multicomponent mixtures is analyzed. Taking into account the different definitions of distillation boundaries, it is demonstrated that highly accurate estimates of the minimum energy requirement for a specific separation can only be obtained by pinch-based-shortcut methods in case the product specifications represent the maximum feasible purity. Therefore, an accurate description of distillation boundaries at finite reflux ratios becomes mandatory. In order to identify such feasible products for multicomponent mixtures a novel test for split feasibility, based on a topological analysis of distillation regions and repeated residue and pinch curve computations, is developed. In that context also a novel approach for the computation of azeotropes in homogeneous and heterogeneous mixtures is introduced. Furthermore, an improved version of a pinch-based shortcut model is introduced that can directly be embedded in an equation-oriented optimization problem. In order to overcome the limitations of shortcut models and allow for a rigorous economic optimization, innovative solution approaches for rigorous equilibrium tray models based on superstructure formulations are presented. The developed design methods allow for a computationally efficient and robust optimization-based design of heterogeneous azeotropic distillation processes and membrane-assisted distillation processes by means of a sequentially relaxed mixed-integer nonlinear programming (MINLP) approach. In order to accurately determine phase stability for each equilibrium tray and to overcome the corresponding discontinuity problem when switching from a homogeneous to a heterogeneous state, the equilibrium computations are embedded in an implicit function, which furthermore performs a reformulation of the equilibrium solution. For the optimization of membrane-assisted distillation processes a membrane network superstructure with multiple stages and intermediate heat-exchangers for pervaporation-assisted processes are proposed. The separation performance of each membrane stage is determined based on an efficient one-dimensional integration of differential mass and energy balances based on a solution-diffusion type local flux model and orthogonal collocation on finite elements. While the developed sequential initialization and solution strategies allow for a computationally efficient and robust optimization, without requiring an initial feasible process design solution, the complexity of the optimization problems confines the applicable solvers to local optimization approaches. Finally, a new form of a hybrid evolutionary–deterministic optimization approach is presented, in order to reduce the necessary user input for the initialization and strengthen the confidence in the quality of the determined solution. For the first time a sophisticated deterministic MINLP approach and an evolutionary algorithm are combined. Handling all inequality constraints by means of the deterministic optimization approach and reducing the design degrees of freedom that are handled by the evolutionary algorithm to a minimum an exceptional performance is obtained.

2. Problem addressed

Conceptual process design is not only one of the most complex, but also one of the most important tasks in the development of a new chemical process. It comprises the determination of a general flowsheet structure, the selection of unit operations, their combination and interconnection as well as rough sizing and costing. The choices made in this early stage already set the course for a successful implementation, as they account for about 80% of the final cost of the entire process [1]. Consequently, significant research effort has been devoted to the development of systematic design methods, resulting in more than 2000 publications in the last 30 years [2]. Still, the majority of all fluid separation processes is conducted by means of distillation and the more than 40,000 distillation columns in the U.S. account for about half of the overall energy consumption of separation processes in the industrial sector [3,4]. The consideration of alternative separation processes and especially hybrid separation processes is an important factor to reduce this significant energy consumption and the corresponding greenhouse gas emissions. Especially distillation-based hybrid separations show a large potential for maintaining the benefits of distillation processes for high purity products and high capacities, while exploiting other separation techniques to overcome the limitations caused by distillation boundaries or other factors [5]. Such hybrid separation processes become increasingly important in view of the transition from the current fossil-based to a future bio-based production of chemicals, which requires innovative and energy-efficient separation processes for the processing of complex azeotropic mixtures resulting from new production routes using unconventional feedstocks. Consequently, there is an urgent need for suitable and efficient design methods for distillation-based and hybrid separation processes to consider new and innovative designs [6] and to overcome the limitations of heuristics [7].

3. State-of-the-art (*Chapter 2*)

The state-of-the-art in conceptual design methods for distillation-based hybrid separation processes for the separation of liquid mixtures is thoroughly reviewed [5] with respect to an extended process synthesis framework illustrated in Figure 1. The framework considers a separation into methods for process variant generation, shortcut methods for a rapid screening of alternatives, as well as optimization-based design methods based on conceptual models, e.g. rigorous equilibrium tray models for distillation, and rate-based engineering models. While a wide range of conceptual design tools for distillation processes is available, a large fraction of these tools is restricted by the underlying assumptions or simplified model formulations to ideal mixtures.

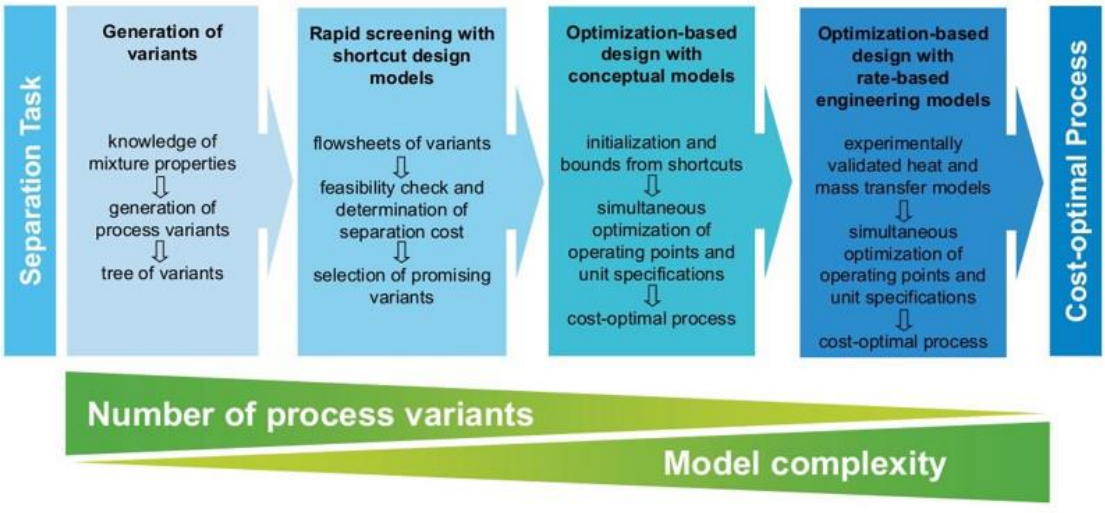

Figure 1: Extended process synthesis framework [5].

The identification of feasible splits is a mandatory prerequisite for variant generation. For distillation-based separations all azeotropes and distillation boundaries need to be determined. While azeotrope computation is available in most commercial simulators, the identification of feasible splits needs to be performed manually in most cases, oftentimes restricted to ternary mixtures, making use of residue curve maps or other graphical tools. Yet, only few publications propose a systematic algorithmic generation of process variants addressing multicomponent mixtures. While simple shortcut models, such as the Kremser method or Underwoods method are restricted to the separation of ideal mixtures, more sophisticated shortcut models, as e.g. based on the computation of characteristic pinch points have been proposed in literature [8]. These methods allow for a significant model reduction and are well suited for the screening of alternatives. However, the underlying assumption of a separation at vanishing driving force requires appropriate product specifications [8]. These have to be determined beforehand, taking into account split feasibility. However, this link has not been thoroughly established in the past. Rigorous equilibrium tray models and rate-based engineering models do not require an additional consideration of distillation boundaries and allow for an approximation of equipment size and capital cost investment in addition to utility requirements and operating costs. While superstructure-based optimization of distillation columns was introduced by Viswanathan and Grossmann [9] about 25 years ago, only few publications address the application considering non-ideal thermodynamic models. Activity coefficient models, such as the UNIQUAC or NRTL model, are highly nonlinear and add a vast number of equations and auxiliary variables to the problem, which not only increase the size and complexity of the model, but also complicate scaling and initialization. This complicates the application of a simultaneous equation-based solution approach tremendously and is probably a reason for the increasing interest in the application of metaheuristics, such as evolutionary or genetic algorithms, simulated annealing or swarm-based optimization methods, in combination with process simulators working with sequential modular simulation methods. Such an approach requires however a converged and feasible simulation model in the first place as well as an optimal choice of metaheuristic and parametrization to obtain an optimized solution, while providing no mathematical proof for optimality, not even local optimality. Consequently, deterministic optimization methods are seldom used in engineering practice and metaheuristics are applied only after a process design has been developed by means of a simulation-based approach beforehand. In order to apply superstructure-based optimization approaches to the separation of non-ideal mixtures, without the necessity of providing a feasible initial solution based on tedious simulation runs, a computational framework is required that especially addresses the solution of the complex equilibrium computations and allows for a systematic algorithmic initialization of the process models.

4. Key innovations

The key innovations in this thesis can be subdivided into three major sections. These comprise the evaluation of split feasibility and the applicability of pinch-based shortcut methods for distillation, the development of optimization models with embedded implicit functions and dedicated initialization procedures for distillation-based hybrid separation processes and the development of a new type of hybrid optimization algorithm based on an evolutionary algorithm and a sophisticated deterministic mixed-integer nonlinear programming approach.

4.1. Split feasibility and pinch-based shortcut methods for distillation (*Chapter 3*)

Pinch-based shortcut methods provide an efficient means for model reduction without any simplifying assumptions concerning the thermodynamic behavior of a given mixture. However, they require the specification of feasible products with the highest possible purity, in order to match the assumption of a separation at vanishing driving force. While any feasible sharp split represents an appropriate product specification, it is more complex to determine appropriate product

specifications in the presence of distillation boundaries. Although the limiting residue curves are generally considered as a representation of distillation boundaries it is well known that composition profiles of distillation columns operated at finite reflux can in certain cases cross these so-called simple distillation boundaries (SDB) [10]. As has been shown e.g. by Krolikowski [11], the feasible product regions are limited by the SDB or the pitchfork distillation boundary (PDB), representing the limit for a reversible separation in a distillation column. Taking into account both concepts for the evaluation of distillation-boundaries, a general test for determining split feasibility is proposed in order to determine feasible products at maximum purity in multicomponent mixtures. Furthermore, the conditions under which pinch-based shortcut methods allow for an accurate determination of the minimum energy demand are critically evaluated in respect to the separation of azeotropic mixtures with inherent distillation boundaries.

4.1.1. A general test for split feasibility in multicomponent azeotropic systems

The general test for split feasibility is based on the computation of residue curves and the product pinch lines in combination with a pre-processing step for the analysis of the mixture topology. The latter defines the distillation regions and distillation boundaries in terms of the corresponding singular points (pure components and azeotropes), as well as their order, defined by the local stability information. Therefore a series of algorithms was implemented and embedded in a MATLAB tool. As a first step all azeotropes need to be determined and characterized. This is a particularly complex problem, as it requires a global search for all solutions to a strongly non-linear equation system. To this end a novel unifying approach for the computation of azeotropes and pinch points is proposed [12] (*Appendix A*), which builds on a combination of two previously introduced homotropy continuation approaches for the computation of all pinch lines and the evaluation of phase stability for heterogeneous systems [13,14]. Based on the knowledge of all azeotropes, including the local stability information, the topology of the composition space, including the distillation regions and distillation boundaries, are further evaluated by means of a computation of the adjacency and reachability matrices [15].

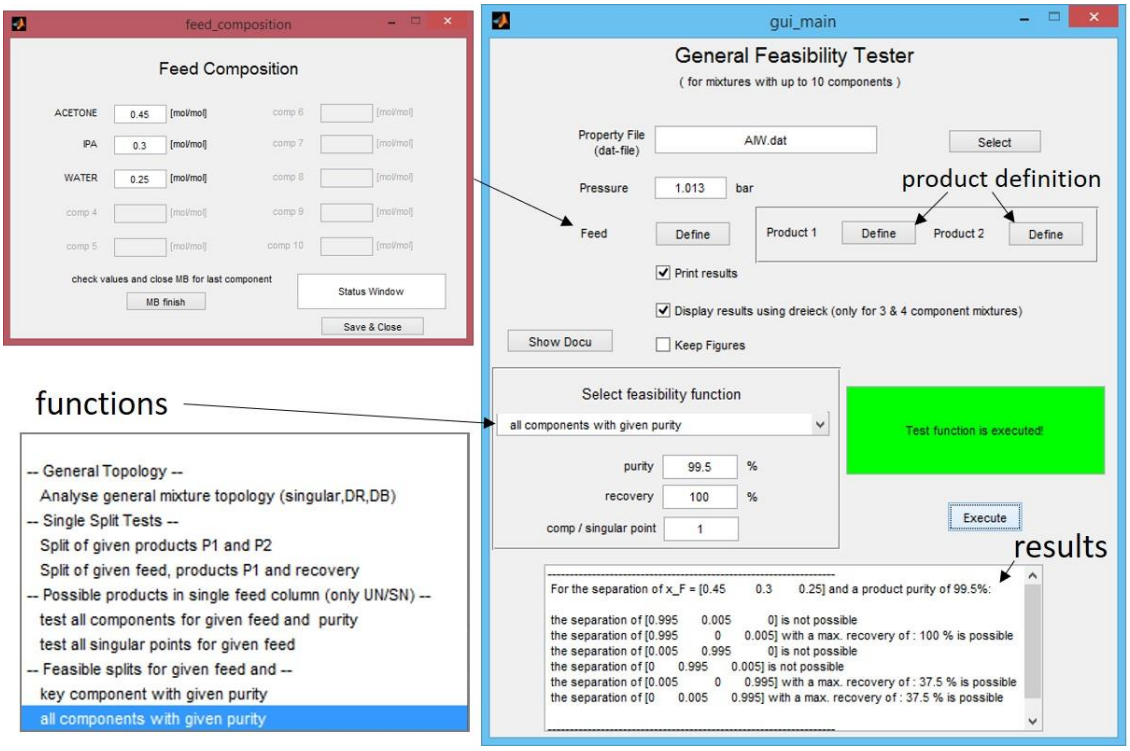

Figure 2: MATLAB tool for the evaluation of split feasibility and the identification of highest purity product specifications in multicomponent mixtures.

By evaluating the terminal points of the residue curves and the product pinch branches the according distillation region can be determined for any specific composition. By tracing the location at which the distillation region shifts along a mass balance line, the maximum purity specifications and the potential recovery of a specific component can be determined. Since no graphical interpretation is required, the method can be applied to multicomponent mixtures without a limit on the number of components. Figure 2 illustrates the developed MATLAB tool and indicates the different functions that have been developed.

4.1.2. Optimization-based design with pinch-based shortcut models

By definition, a pinch-based shortcut method approximates the performance of a distillation column close to a reversible operation, which mandates the existence of an infinite number of trays due to at least a single pinched zone in each section. This situation can only be warranted for sharp splits, for which at least one component present in the feed stream is absent in each product stream, or in case of a tangent pinch, which is usually not considered when specifying possible products. In case of a sharp split, the accuracy of pinch-based shortcut methods for the separation of zeotropic mixtures is only limited by the generally piecewise linear approximation of the composition profile. However, in case of azeotropic mixtures the highest product purity can be limited due to the presence of a distillation boundary, as discussed in the previous section. It is of imminent importance to provide an accurate estimation of the limiting distillation boundary when performing a process optimization by means of pinch-based shortcut methods. This is demonstrated for a complex entrainer-enhanced pressure-swing distillation process for the separation of ethanol and water, which has previously been the subject of different shortcut-based design methods. While the results obtained by Knapp and Doherty [16] and Brüggemann and Marquardt [17] resulted in deviations from a rigorous equilibrium-tray based optimization of 32 and 39% respectively, the applied pinch-based shortcut model in combination with a fitted Bezier curve, representing the limiting distillation boundary, results in an excellent approximation of the minimum energy duty. The applied pinch-based shortcut model is a reformulation of the previously introduced feed angle method [18], which provides significant numerical advantages and allows for a direct integration in an equation-based optimization problem formulation (*Appendix B*). Although this example demonstrates the capabilities of pinch-based shortcut models, it also illustrates the complexity in setting up the optimization problem appropriately, especially considering the representation of distillation boundaries. These methods should therefore be applied with caution.

4.2. Optimization-based design with rigorous thermodynamic models

In order to overcome the aforementioned problems rigorous equilibrium tray models can be applied in the optimization. These models are however more complex, especially in case of integrated processes with closed recycle streams. In order to facilitate a computationally efficient and robust optimization of such distillation-based processes, a decomposition of the optimization problem is proposed, whereas separable subsets of the equation system are defined as implicit functions and solved outside the main optimization algorithm, returning the necessary sensitivity information with appropriate accuracy. This allows for the application of dedicated solution-approaches for the implicit functions, including sequential solution strategies, such as inside-out algorithms for flash calculations or sophisticated homotopy-continuation approaches for the evaluation of phase stability [14]. The developed optimization-based design methods make use of such implicit functions via the external function facility of GAMS. To this end, pre-compiled dynamic link libraries (DLL) are accessed during the optimization by GAMS, forwarding the current information on variable values (z), while getting in return the evaluation of the implicit functions ($e(z)$) and sensitivity information ($\partial e(z)/\partial z$), as illustrated in Figure 3.

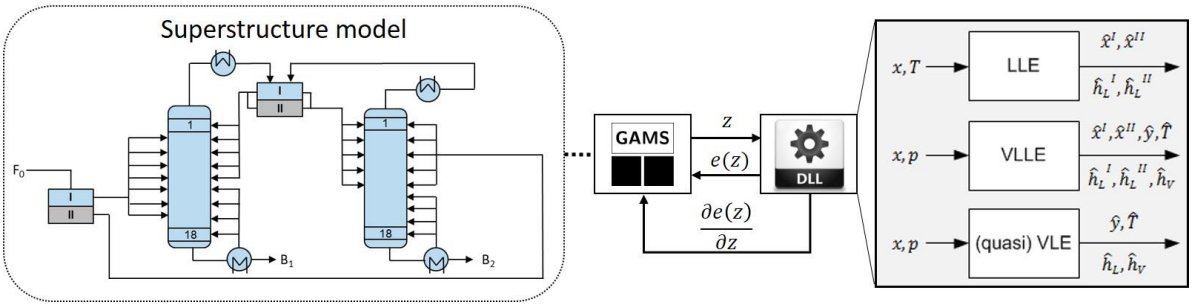

Figure 3: Illustration of the problem decomposition and the

In order to perform an automatic initialization of the resulting MINLP problems, such that no initial (feasible) simulation of the problem is required, dedicated solution strategies were developed. The MINLP problems are therefore solved as a series of relaxed NLP problems, making use of either nonlinear complementary constraints, as proposed by Kraemer et al. [19], or by means of additional penalty terms in the objective function. The developed optimization-based methods therefore do not only aim at the determination of a cost optimal process design, but utilize the underdeterminednes of the MINLP problem to facilitate the solution without providing a manually determined feasible solution beforehand.

4.2.1. Design of heterogeneous azeotropic distillation processes (*Chapter 4*)

The design of heteroazeotropic distillation processes is particularly interesting for the separation of azeotropic mixtures, in case miscibility gaps are presented in the given mixture, or can be introduced by an additional solvent and exploited by combining distillation with decantation. The mathematical optimization of such processes is tremendously complicated because of the strongly nonlinear thermodynamic models, required to appropriate describe the potential vapor-liquid-liquid phase equilibrium (VLLE), but even more so due to the necessity to correctly identify phase stability. Even if the correct thermodynamic equilibrium solution is determined, another problem results from the erratic change in one of the single liquid phase compositions in case a tray composition is shifted across the boundary of a miscibility gap during the optimization. This discontinuity of the equation system impedes the direct application of a deterministic gradient-based optimization approach. In order to overcome these limitations a dedicated phase stability test is incorporated in the external function, which furthermore preforms a reformulation of the equilibrium solution in order to “hide” the discontinuity and render the problem continuous and continuously differentiable [20].

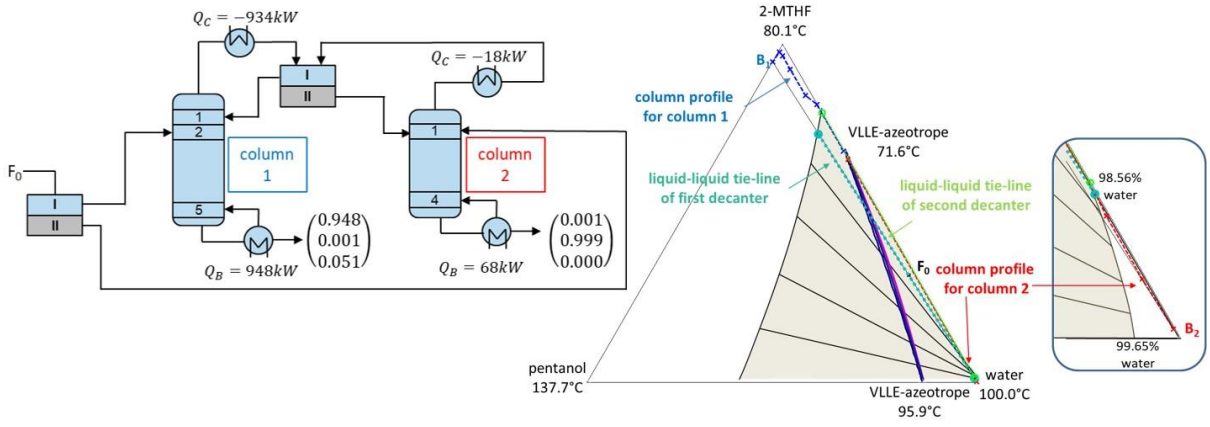

Figure 4: Resulting process for the purification of 2-MTHF based on an integrated hybrid process using two distillation columns and two decanters.

The external function does not only allow for the correct identification of phase stability, using the homotopy-continuation approach of Bausa and Marquardt [14], but also comprises all thermodynamic models and related auxiliary variables, required to solve the thermodynamic equilibrium problem and the computation of specific enthalpies. Therefore, only the connectivity model of the superstructure and the related mass and energy balances are directly implemented in the optimization model in GAMS, significantly reducing the size and the complexity of the equations system handled by the solver in GAMS. The developed optimization-based design method is demonstrated for several case studies, including classical process configurations for heteroazeotropic distillation, closed-loop configurations with a solvent recovery column, as well as a dedicated process flowsheet for the purification of 2-Methyltetrahydrofuran (2-MTHF), which was previously identified as promising oxygenated biofuel candidate [21]. The resulting process, which was determined based on the superstructure indicated in Figure 3, is illustrated in Figure 4. Since design problems such as the 2-MTHF purification can be solved in few minutes of computational time, including the initialization of the flowsheet model, the approach provides the basis for more complex applications, such as the determination of promising solvents in an integrated solvent and process design approach.

4.2.2. Design of hybrid membrane-assisted distillation processes (*Chapter 5*)

In order to enable the assessment of hybrid membrane-assisted distillation processes the developed optimization-based design method is extended by additional membrane process models and dedicated initialization procedures. Since the separation performance of membrane processes is generally kinetically controlled, a rate-based model is mandatory. In order to enable an efficient and robust optimization of membrane processes with multiple subsequent stages and inter-stage heating, as well as integrated hybrid separation processes, the model implementation is tailored in several ways. First a flexible membrane network model is introduced, which not only allows for the existence of a permeate or retentate recycle, as well as pressurization of the feed stream and inter-stage heating, but also potential bypassing of each available stage (st), such that the number of stages is a design degree of freedom in the optimization. The resulting superstructure is illustrated in Figure 4.

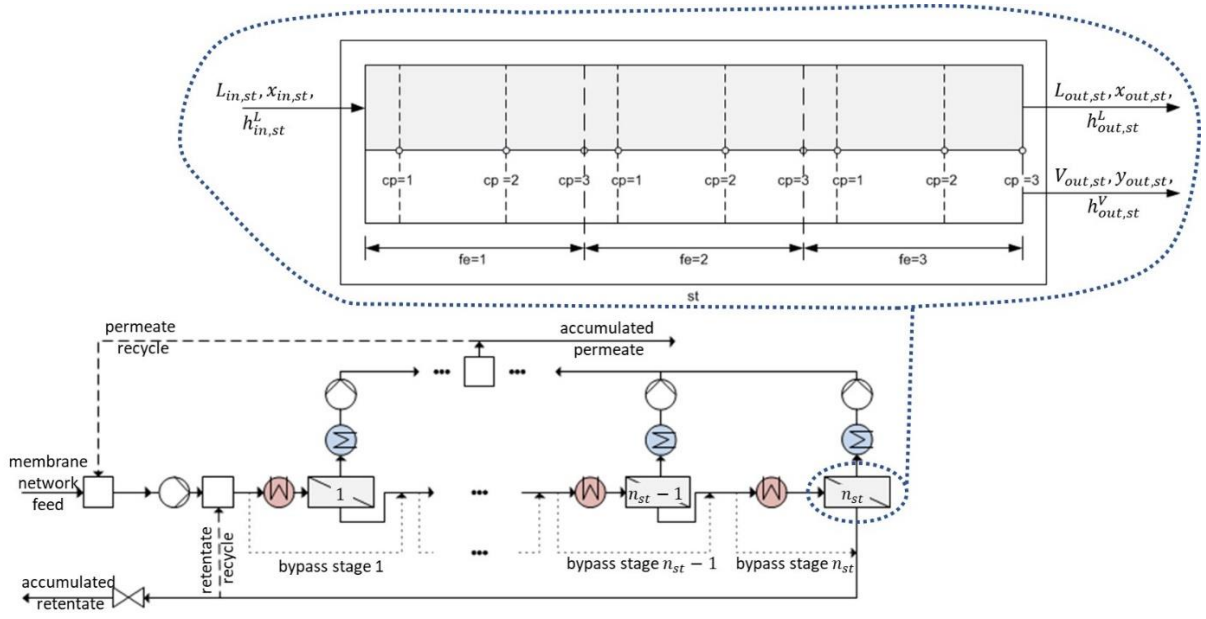

Figure 4: Illustration of the membrane network superstructure and the discretization along the axial length of a membrane stage (st), by means of three equidistant finite elements (fe), each subdivided by three collocation points (cp) according to the Radau II collocation method.

In order to determine an accurate solution of the differential mass and energy balances along the axial length of each membrane stage an efficient model reduction by means of an orthogonal collocation on finite elements is utilized. By application of a Radau II collocation method [22] with three finite elements (fe) and three collocation points (cp), an accuracy equivalent to that obtained by a finite discrete approach with 100 equidistant grid points is reached. The local mass transfer rates at each collocation point are determined by a semi-empirical solution-diffusion type correlation for the membrane permeance. All thermodynamic property computations for the evaluation of the driving force, e.g. the difference in chemical potential, are computed as implicit functions in terms of external equations. An automatic initialization of the membrane cascade and membrane-assisted distillation processes is further performed by means of a structured solution approach.

The optimization-based design method is demonstrated for several case studies; including the separation of a ternary mixture of methyl tert-butyl ether (MTBE), n-butene, and methanol (MeOH) by means of an integrated hybrid process [23]. The optimization-based design approach is first used to validate the results of a previously applied shortcut-based optimization [24]. It is further shown that a relocating of the side stream of the distillation column and an increase in permeate pressure from 50 to 60 mbar allows to satisfy a temperature limitation for the membrane material, while the overall cost can be reduced by 17%, using just one of four available membrane stages. The according superstructure model and the final process design are illustrated in Figure 5.

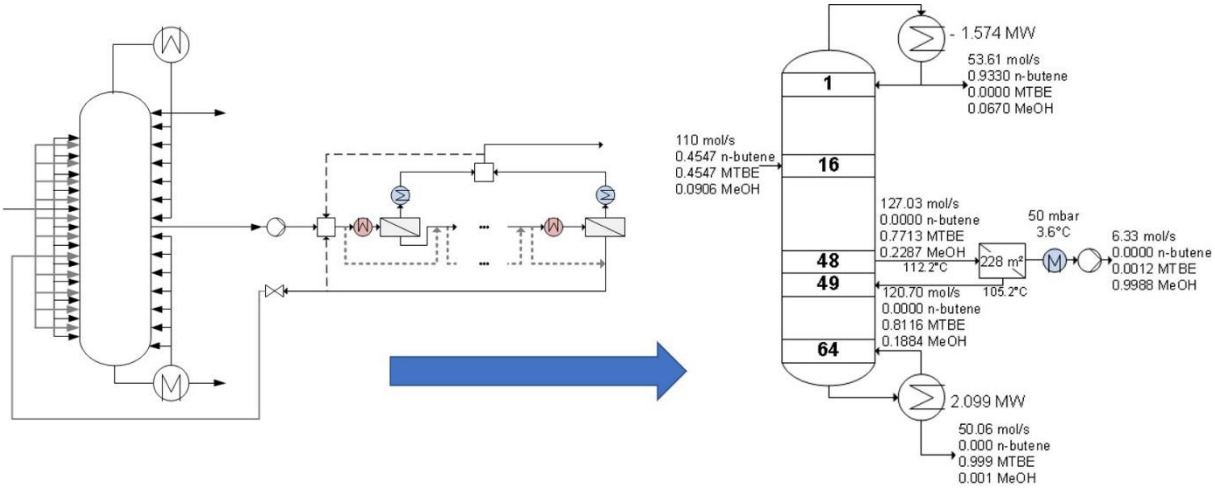

Figure 5: Illustration of the superstructure of the integrated hybrid separation process and the final design obtained for the MTBE case study.

4.3. A novel and sophisticated hybrid optimization approach (Chapter 6)

While the developed optimization-based design methods allow for a computational efficient and robust assessment of complex separation processes considering rigorous thermodynamic models, the highly nonlinear MINLP problems are only solved to local optimality. In order to increase the confidence in the quality of the final result a novel hybrid optimization approach was developed, which embeds the developed optimization-based design methods into the inner loop of a larger framework that employs an evolutionary algorithm (EA) on the outer loop. The different steps of this hybrid optimization approach, which was published in [25], are illustrated in Figure 6. As an important difference to other hybrid, or so-called memetic, optimization approaches, the developed algorithm addresses both continuous and discrete design decisions inside the inner loop. This bears the important advantage that the design space of the evolutionary algorithm can be reduced significantly.

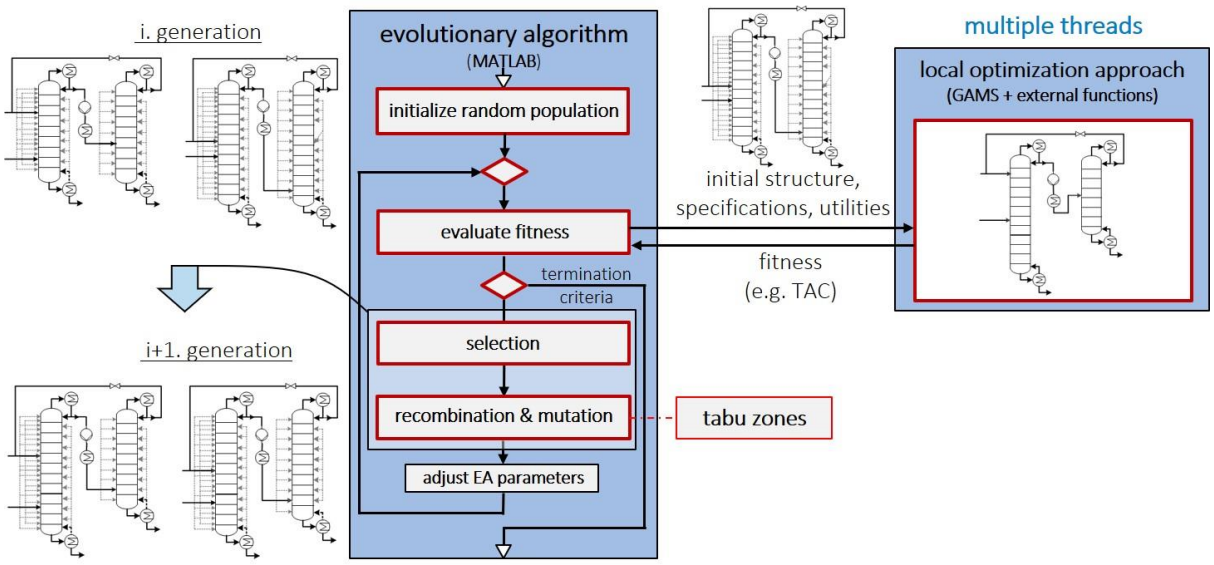

Figure 6: Illustration of the developed hybrid optimization approach, building on a combination of an evolutionary algorithm and a sophisticated local optimization approach that solves full MINLP problems.

All continuous design degree of freedom are optimized solely by the deterministic optimization approach in the inner loop. The evolutionary algorithm covers only the initialization of structural design degree of freedom, as well as the optimization of discrete design choices, which result in distinct discontinuities of the optimization problem. The latter include e.g. the choice of a utility, entailing different costs and valid operating pressure ranges, or more pronounced the choice of different mass separating agents (MSA), which require a modification of the thermodynamic model. By outsourcing this decision to the EA, the deterministic optimization has to consider only the selected MSA and the according thermodynamic model, as in a disjunctive programming problem. Solving the problem as a single MINLP problem would require the simultaneous integration of all thermodynamic models for the different MSA candidates, resulting in a severely larger and more complex optimization problem.

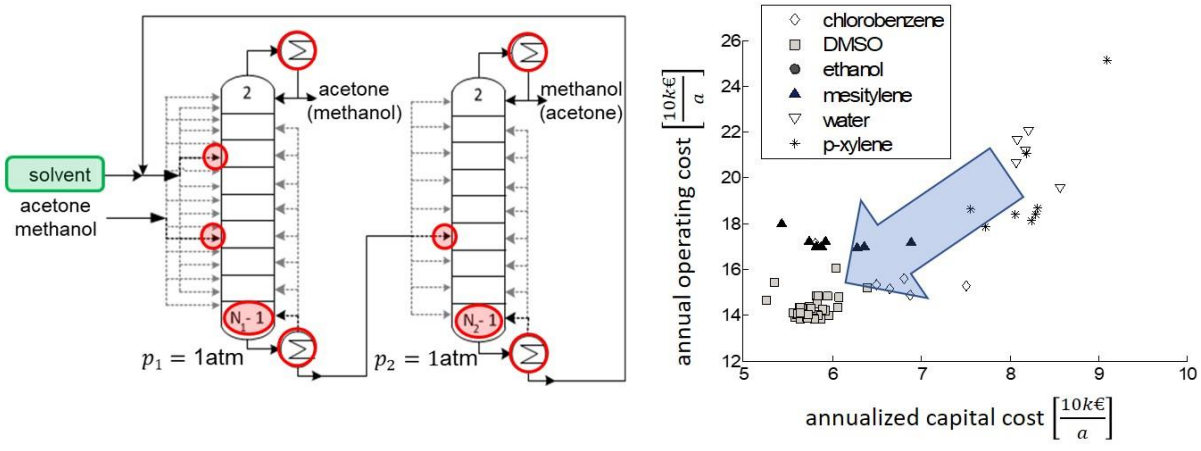

Figure 7: Illustration of the superstructure model for the extractive distillation of an acetone-methanol mixture using different solvents, as well as the results obtained by a single run of the hybrid optimization approach.

The hybrid optimization approach is further accelerated by the use of tabu zones, as well as a parallelization of the evaluation of different individuals in each generation. The latter is easily

realized by means of a multi-threading approach. The efficiency of the optimization approach is demonstrated in detail for several case studies, including an extractive distillation process, considering a set of six different entrainer candidates [25]. The superstructure and the results of this case study for one run of the hybrid optimization approach are illustrated in Figure 7. The deterministic local optimization approach determines the number of equilibrium trays, the feed tray locations and the required heat duties (red). Only the choice of a solvent is exclusively handled by the evolutionary algorithm (green), while the initial number of equilibrium trays and the feed positions for each local optimization are set by the evolutionary algorithm as well. The illustration of the costs indicates the capability of the hybrid optimization approach to identify potential tradeoffs between operational and capital costs, providing an approximation of a pareto front. The reliability of the optimization approach is verified by repeated evaluations, showing a deviation of less than 1% in the TAC of the best design of each run. None of the runs required more than 3h of CPU time and in each run between 86-98% of all individuals resulted in feasible and locally optimized solutions of the inner MINLP problem. This is one of the significant benefits of the proposed hybrid approach, which handles all inequality constraints by the deterministic optimization approach in the inner loop.

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* Highlighted publications by ***M. Skiborowski*** relate to work commenced and reported on in the thesis.