COMBINING SHORTCUT METHODS AND RIGOROUS MINLP OPTIMIZATION FOR THE DESIGN OF DISTILLATION PROCESSES FOR HOMOGENEOUS AZEOTROPIC MIXTURES

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For the separation of azeotropic mixtures with distillation usually a number of conceptual design alternatives are generated. Instead of evaluating the economic viability of the different alternatives by repetitive simulation studies, a combination of shortcut calculations and rigorous MINLP optimization is proposed. In this two step process the shortcut calculations are used to screen and rank many different alternatives. The most promising alternatives are then rigorously optimized with a detailed MINLP model. This methodology is demonstrated for a single column and then extended to a distillation flowsheet with two columns and a recycle stream. In the latter problem, an intermediate NLP optimization on the flowsheet level is employed to generate favorable initial values for the recycle stream. The combination of the two calculation levels increases the problem complexity incrementally. The availability of good initial values on each level improves reliability and solution times of the optimization problems.

KEYWORDS: distillation design, RBM, MINLP, conceptual design

INTRODUCTION

Large scale purification of reaction products in a chemical plant is typically accomplished through distillation. The costs associated with this purification are often a dominating factor in the total cost of a chemical process. The design of an efficient separation sequence is therefore important for a cost-effective process. In industrial practice this design is usually done by repetitive simulation studies, which are very time consuming. In addition the use of heuristics often leads to a non-systematic generation of flowsheets and the design of the most cost-effective process cannot be guaranteed.

Mathematical methods of mixed integer non-linear programming (MINLP) have therefore been applied for the design of distillation columns for nearly two decades. However, mostly columns and column sequences for zeotropic mixtures were optimized, since the initialization and bounding of a rigorous MINLP optimization is complicated even for these simple cases. In the azeotropic case the definition of a complex superstructure that includes every possible flowsheet alternative is required. In the most general form this superstructure also has to include different alternatives for the choice of an entrainer, different pressure levels or the combination of different unit operations (e.g. pervaporation combined with distillation) to a hybrid process. The definition of a superstructure and its mathematical representation is not trivial and very time consuming. The resulting optimization problems are large and characterized by many combinatorial degrees of freedom.

This further complicates the convergence of a numerical optimization algorithm even to a local optimum.

Shortcut methods, such as the Rectification Body Method (RBM) [1], allow the design engineer to test a design for feasibility, to target possible splits and to provide a rough economic estimate based on the minimum energy demand of the separation (assuming an infinitely long column). The basic RBM algorithm has been extended to complex column arrangements and to extractive columns. With these methods unfavourable processes can be excluded in an early design stage. The best possible solution cannot be determined at this stage, since no detailed column design information is known; however, the design alternatives can be ranked.

Recently an initialization strategy based on the theory of reversible distillation has been proposed [2], where a single column is characterized by exergetically optimized, non-sharp splits ("preferred separation"). The application of these ideas to the much more frequently used sharp splits, however, is not trivial. Additionally, mixtures that exhibit a tangent pinch cannot be handled consistently with this method. The RBM does not suffer from these limitations. It is therefore straightforward to use the results of the RBM calculations for the initialization and bounding of a rigorous optimization.

COMBINING SHORTCUT METHODS AND RIGOROUS MINLP OPTIMIZATION

This contribution proposes to split the synthesis problem for distillation columns and column sequences into several steps with increasing complexity. The definition of flowsheet alternatives and the generation of feasible splits is not covered in this contribution. The focus here is on the fast and reliable economic evaluation of the proposed conceptual alternatives. As can be seen in Figure 1, top, this is essentially a two step

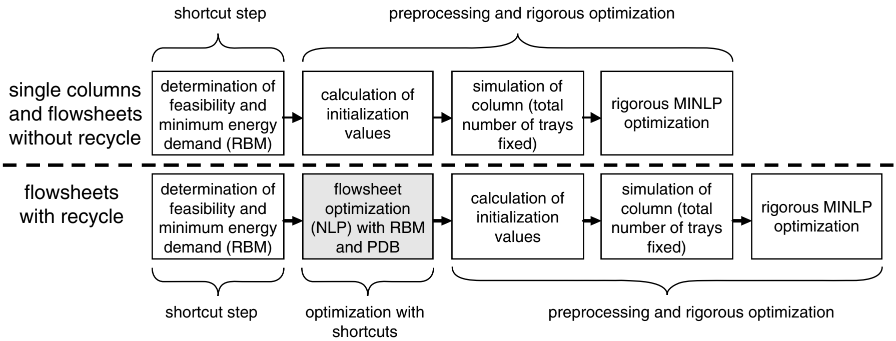

Figure 1. Initialization and optimization strategy for single columns and flowsheets without recycle (top) and for flowsheets with recycle (bottom)

procedure for a single column. In the first step a number of alternative splits for an azeotropic column or different techniques to split an azeotropic mixture into its pure components (e.g. different pressures or different entrainers) are screened using the rectification body method. Convergence of the RBM method can be used to test for feasibility of the specified split.

The most promising alternatives of this step can then be optimized using the more rigorous but time consuming MINLP techniques. Here the results from the shortcut step can be used to approximate the column profiles and to derive tight bounds for a number of critical variables (e.g. temperatures or heat duties) [3]. The approximated column profile is also used to initialize the non-linear physical property calculations. The extension of the single column optimization to a flowsheet consisting of several columns without recycle streams is straightforward. Since the individual columns can be decoupled, the solution procedure shown in Figure 1 (top) is also applicable. The columns can be solved consecutively with the proposed procedure.

For a process with recycle streams, a decoupling of the columns is not possible. In this case, a flowsheet optimization where the objective function is determined by the sum of the reboiler energies as calculated by the RBM is used as an intermediate step, as shown in Figure 1, bottom. The optimal recycle stream and the minimal energy costs are determined in this step. Together with the PDB (pinch distillation boundaries, an analytical formulation of the distillation boundaries for minimum reflux [4]) a flowsheet of several columns can be optimized without detailed models. The optimized flowsheets can then be used to compare different processes at their optimal operating point. The detailed designs of the most promising alternatives of this step are obtained in a subsequent rigorous MINLP optimization. Here the results from the flowsheet optimization are used to provide a very good initial value for the recycle streams.

The design of distillation processes through a combination of the shortcut calculations with the flowsheet optimization and MINLP optimization exploits the strengths of these tools and avoids their weaknesses. The conceptual design of the columns is done in the shortcut step, where visualization and quick solution times help the design engineer to generate and rate alternatives. In a flowsheet optimization, these shortcut models are used to determine optimal recycle streams and operating points. The most promising alternatives from this step are rigorously optimized in a subsequent step. As in the case of single columns, the good initial values and bounds enhance the numerical stability and convergence speed. A large superstructure can therefore be avoided. The cost-optimal trade-off between stage numbers and energy costs for each individual column is determined by MINLP optimization.

The design of a single column as shown in Figure 1, top, and the design of a separation flowsheet, bottom of Figure 1, is illustrated with two case studies. In the first case study a distillation column for a homogeneous ternary azeotropic mixture is discussed. With this example the initialization and bounding is illustrated. In the second case study a pressure-swing process, consisting of two distillation columns with a recycle, is optimized to demonstrate the capabilities of this method.

Note that although only ternary mixtures are chosen in this paper to help the presentation, the RBM, the MINLP optimization and therefore this design methodology are applicable to homogeneous mixtures containing an arbitrary number of components.

ILLUSTRATIVE CASE STUDY

The azeotropic mixture of acetone, methanol and ethanol will be used in this illustrative example. The feed flow rate is 10 mol/s with a composition of 0.35/0.15/0.5. The feed is introduced into the column as saturated liquid. In this case study pure ethanol can be separated from the ternary feed, leaving a binary acetone-methanol mixture for further separation steps (the azeotrope can be broken by extractive distillation or a pressure swing process). It can be shown through the screening with the shortcut method that this split is economically very favourable. Here the initialization strategy proposed by Barttfeld et al. [2] is not applicable, since the initialization with products of the preferred split would result in a non-sharp separation where methanol is present in both column products.

The ternary diagram of this system together with the resulting rectification bodies at minimum reflux for the proposed split is shown in Figure 2 (left). The pinch points at the vertices of the rectification bodies are denoted by triangles for the saddle nodes and squares for the stable and unstable nodes. The column profile in a distillation column runs through the pinches in the order of increasing stability. As can be seen on the right of Figure 2, this information is used to approximate the column profile linearly by connecting the appropriate pinch points.

The rectification bodies and pinches are calculated by the RBM and exported to the software package GAMS, where the rigorous MINLP optimizations are run. In the next step the linearized column profiles for the composition as shown in Figure 2, right, and for the temperature are calculated. These initial values are then used to initialize a

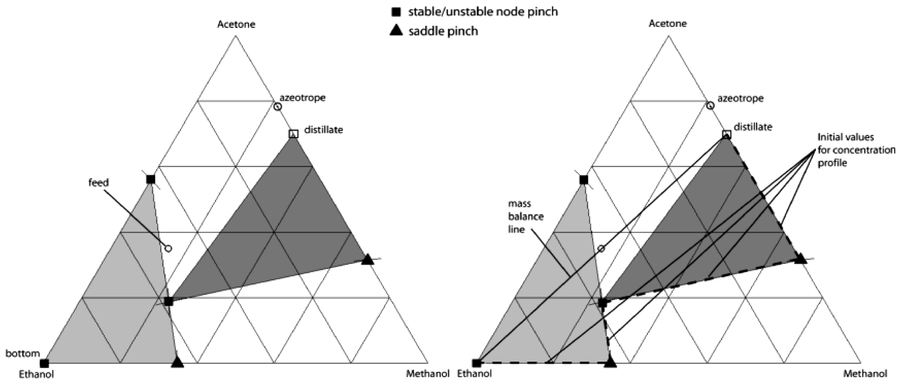

Figure 2. Specified products and rectification bodies at minimum reflux (left), mass balance line and linearized column profile for the initialization (right)

simulation calculation for a column with a large number of stages; in this case 60 stages are used initially. Although this simulation calculation is not needed theoretically, it enhances the stability of the following rigorous optimization. The objective function in the following rigorous MINLP optimization is the total annualized costs of the single column as given by

$$\min TAC = C_{inv,a} + \dot{C}_{op} \cdot t_A. \tag{1}$$

The optimization is constrained by a column model with a variable number of trays. The individual column trays are modelled as equilibrium trays, where the binary variables $b_{n,1}$ and $b_{n,2}$ denote the existence of a feed or the existence of a condenser on tray n, respectively:

$$y_{n,i} = K_{n,i} \cdot x_{n,i}, \tag{2}$$

$$L_{n-1}x_{i,n-1} + V_{n+1}y_{i,n+1} - (L_n + D_n)x_{i,n} - V_n y_{i,n} + b_{n,1}Fx_{i,f} = 0, \tag{3}$$

$$L_{n-1}h_{n-1}^L + V_{n+1}h_{n+1}^V - (L_n + D_n)h_n^L - V_n h_n^v + b_{n,1}Fh_F^L + b_{n,2}Q_C = 0, \tag{4}$$

$$\sum_{i=1}^{nc} y_{n,i} - 1 = 0 \tag{5}$$

$$\sum_{i=1}^{nc} x_{n,i} - 1 = 0 \tag{6}$$

$$\sum_{n=1}^{NT} b_{n,1} = 1 \tag{6}$$

$$\sum_{n=1}^{NT} b_{n,2} = 1 \tag{7}$$

where the index i denotes the individual component. Note that even though none of the trays above the condenser $b_{n,2} = 1$ exists in the column, the VLE equations (2) have to be evaluated even for these non-existing trays.

To prevent a feed above the condenser and to prevent the condenser on the same stage as the fixed reboiler, logical constraints are placed on the binary variables for a given tray N:

$$b_{N,1} + \sum_{n=N}^{N_{\max}} b_{n,2} \leq 1, \tag{8}$$

$$b_{n,2} = 0, \quad \text{for } n = NT. \tag{9}$$

The distribution coefficient $K_{n,i}$ in equation (2) is evaluated in an external procedure, which reduces the number of equations and variables in the optimization problem and therefore increases robustness. Furthermore the external function allows the choice of any G^E- or EOS-model without changing the column model. In this case the liquid phase behaviour was modelled by the Wilson model with parameters from ASPEN 12.1; the gas phase was modelled as an ideal gas.

The binary variable $b_{n,2}$ are connected with the product draw off on a tray D_n via

$$D_n \leq b_{n,2}MD \tag{10}$$

and

$$\sum_{n=1}^{N_{\max}} D_n = D, \tag{11}$$

where M is a sufficiently large Big-M value.

Furthermore a product purity needs to be set. In this case ethanol is drawn of in with high purity from the reboiler, $x_{n=NT,ethanol} = 0.999$.

The optimization of this case study is done with the local NLP solver SNOPT [5] and the branch and bound solver SBB [6]. The global optimum corresponds to a column with 51 stages and is found after 240s calculation time. Due to the non-convexity of the optimization problem these algorithms can only guarantee local optimality. In this case, however, the global optimum is found, as confirmed by enumeration.

COMPLEX EXAMPLE WITH RECYCLE: PRESSURE SWING PROCESS FOR ETHANOL-WATER SEPARATION

The improved robustness and solution speed gained from the combination of the shortcut calculations and the rigorous optimization is suited especially well for the optimization of flowsheets consisting of more than one distillation column.

As a second case study, the purification of ethanol from a water-ethanol mixture in a two column pressure swing process with the entrainer acetone, as proposed by Knapp and Doherty [7], is investigated. These authors propose to separate water from the feed mixture of $x_{f,water} = 0.958$ and $x_{f,ethanol} = 0.042$ as the bottom product in the first column and ethanol as the bottom product in a high pressure column (10atm). To further enhance the pressure swing area of the binary azeotrope, acetone is used as an entrainer in this process. The flowsheet of the process is shown in Figure 3, left.

The total recycle flow rate and the amount of acetone in the process are additional degrees of freedom in the optimization problem, which further complicate convergence. It is therefore suggested that after the shortcut calculations for the two columns a flowsheet optimization to determine the optimal recycle stream (see Figure 1, bottom) is run before the entire flowsheet is optimized as a MINLP problem. The following assumptions were made in the NLP as well as the MINLP optimization:

- pressure change equipment is not modelled
- all products are drawn of as saturated liquid
- all feed streams are supplied to the column as saturated liquid.

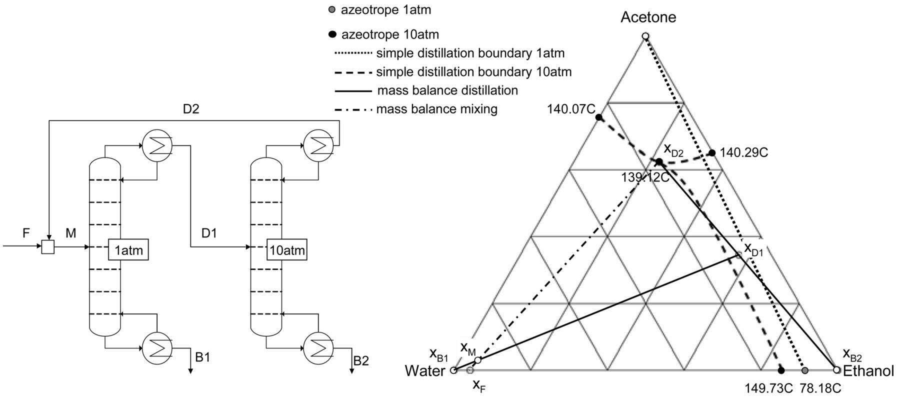

Figure 3. Pressure swing process: Flowsheet (left), and optimized mass balances in a ternary diagram (right) with simple distillation boundaries for 1atm (chain dotted line) and 10 atm (dashed lines)

As noted by Brüggemann [8], the third assumption violates the energy balance around the mixer and the pump. However since no phase change is required in heating the streams to their boiling point, the resulting heating energies are several orders of magnitude lower than the energy needed in the column and do not need to be considered when a conceptual design of the process is envisioned.

After the conceptual design, a flowsheet optimization as shown in the grey box in Figure 1, bottom, follows. Here the objective function is defined as the sum of the reboiler energies as determined by the RBM for the two columns. These reboiler energies are minimized to find the optimal recycle stream. The feasibility of the flowsheet is ensured by using the pinch distillation boundaries (PDBs) as defined by Brüggemann and Marquardt [4]. The PDBs represent the distillation boundaries at minimum reflux and are especially well suited in this context since any column calculated with the RBM will operate at minimum energy. The PDBs can be evaluated analytically using a homotopy algorithm. The model for the flowsheet optimization is then given by:

$$\min \phi_{En}(u_j) = Q_{B_1,\min}(u) + Q_{B_2,\min}(u) \tag{12}$$

$$\text{s.t.} \quad m_{1,i} - d_{1,i} = b_{1,i}, \tag{13}$$

$$d_{1,i} - d_{2,i} = b_{2,i}, \tag{14}$$

$$m_1(u_j) \geq 1, \tag{15}$$

$$m_2(u_j) \geq 1, \tag{16}$$

$$u_j \geq 0, \quad j = 1, \ldots, 3C \tag{17}$$

Table 1. Resulting flow rates for the optimized pressure swing flowsheet

Flow rate (mol/s)	Fresh feed	Mixed feed	Distillate column 1	Bottom column 1	Distillate column 2	Bottom column 2
Acetone	0	0.62	0.62	0	0.62	0
Ethanol	0.42	0.7	0.7	0	0.28	0.42
Water	9.58	9.67	0.09	9.58	0.09	0

where u_j represent the unknown flow rates of the process, which are the component flows of the mixed inlet stream m_i and the distillate streams ($d_{1,i}$, $d_{2,i}$). The feasibility of the process is ensured through the constraints given by equations (15) and (16). Every evaluation of these constraints triggers a homotopy continuation which evaluates the pinch distillation boundaries and returns the according values based on the input variables u.

Since the RBM only computes reasonable values for a sensible choice of the input variables (sensible meaning in this case that equations (13)–(17) are fulfilled), a feasible path optimizer has to be used for the optimization of this NLP model. In this case CFSQP [9] has been used to compute the optimal solution for the recycle stream, which are scaled values taken from Brüggemann [8] and given in Table 1.

The resulting reboiler energies of $Q_{B1,\min} = 189\,\text{kW}$ and $Q_{B2,\min} = 134\,\text{kW}$ differ by about 5% from the values obtained by Knapp and Doherty. The difference in the overall minimum energy demand can be attributed to the different definitions of the feasibility boundaries [4,8]. It should be noted here that the first column exhibits a tangent pinch. This tangent pinch cannot be handled consistently by the initialization procedure proposed by Barttfeld and Aguirre [2]. The RBM has additional checks to detect this situation and calculates the correct minimum energy demand even in this situation [8]. The initialization procedure thus remains the same for each column.

After the flowsheet optimization, the optimal recycle stream is known. The results of this optimization as well as the rectification bodies are passed to the detailed column optimization. Here each column is modelled by the equations (2)–(11) as presented in the last section. The cost correlations for the high pressure column are adjusted to account for the higher costs of the column shell and heating utility. The distillate effluent is defined by mass balances around each column, while the bottom flows are fixed to obey the overall mass balance of the flowsheet.

In the first step of the solution algorithm the columns are decoupled. Each column is optimized individually as a relaxed MINLP with the solver CONOPT [10]. After each column optimization is finished, the entire flowsheet is optimized as a regular MINLP with the solvers SBB/CONOPT. The recycle streams at the optimal solution of the MINLP problem are in the vicinity of the values that were determined by the flowsheet optimization.

The resulting separation energies for the columns are determined as $Q_{B1} = 133\,\text{kW}$ and $Q_{B2} = 144\,\text{kW}$, where the energy reduction in column 1 can be attributed to a further optimized recycle stream. The final mass balances are shown in Figure 3, right. It has been found that the intermediate flowsheet optimization for the optimal recycle stream greatly helped convergence of the rigorous MINLP optimization.

SUMMARY AND CONCLUSION

A new design methodology for azeotropic distillation and azeotropic column sequences has been presented. Instead of repetitive and time consuming simulation studies or MINLP optimization of large superstructures to determine the cost-optimal process to separate azeotropic mixtures, the design process is split into several steps with increasing complexity. The initial screening of different alternatives to separate an azeotropic mixture into its pure components can be done with shortcut calculations via the Rectification Body Method (RBM). In the case of a single column the results from the calculation with the RBM can be used directly to initialize and bound variables for a rigorous MINLP optimization. These good initial values and tight bounds have been found to decrease the required solution time and to greatly increase the robustness of the optimization step.

When a flowsheet with a recycle stream is considered, a flowsheet optimization is used to determine the optimal recycle stream. In this flowsheet optimization the columns can be represented by the RBM model. This intermediate optimization is used to initialize the recycle streams in the MINLP optimization. For the individual columns in the flowsheet the results from the RBM are used analogously to the single column case to initialize and bound the rigorous column models. In this case the robustness and convergence properties of the complex MINLP optimization were significantly increased by using the tight bounds available through the shortcut step. Furthermore the initialization of the recycle stream with the values found in the flowsheet optimization greatly helped the convergence of the rigorous optimization.

The optimization procedure can be automated and works nearly without user intervention after the shortcut calculations have been completed. The case studies demonstrate the robustness and reliability of this methodology for the synthesis of distillation columns or column sequences.

The obtained optimal values in the second case study can be further reduced by heat integration of the two columns. Furthermore the operating pressures of the columns can be treated as a degree of freedom. This leads to more complicated and detailed cost functions which are not easy to set up [8]. The energy integration, however, can be worked into the design methodology at the different levels and will be studied in further research. Future research will also focus on the improvement of the MINLP algorithms and on the extension of this methodology to heterogeneous mixtures.

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