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Global Optimization of Ideal Multi-component Distillation Columns

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This paper addresses the problem of determining cost-minimal process designs for ideal multi-component distillation columns. The special case of binary distillation was considered in former work [2]. Therein, a problem-specific bound-tightening strategy based on monotonic mole fraction profiles of single components was developed to solve the corresponding MINLPs, globally. In the multi-component setting, the mole fraction profiles of single components may not be monotonic, which is why the bound-tightening strategy from the binary case cannot be applied. In this follow-up paper, a model reformulation for ideal multi-component distillation columns is presented. The reformulation is achieved by suitable aggregations of the involved components. Proofs are given showing that mole fraction profiles of aggregated components are monotonic. This property is then used to adapt the bound-tightening strategy from the two-component case to the proposed model reformulation. Computational results are provided that indicate the usefulness of both the model reformulation and the adapted bound tightening technique for deterministic global optimization of ideal multi-component distillation column designs.

1. Introduction

The focus of this paper is on deterministic global mixed-integer non-linear optimization of distillation columns, often dominating the cost of chemical production processes. Despite recent progress in deterministic global optimization (e.g., see [5] and [7], for recent surveys), those problems are often very difficult to solve due to high computational effort, that is caused by non-convexities and high system order. Deterministic global optimization of distillation processes is, hence, a very challenging task.

In the literature, rigorous deterministic global optimization of distillation processes is not well-covered. In a recent publication [19], optimal sequencing of multi-component distillation columns at minimum reflux using so-called short-cut models is calculated with deterministic global optimization methods.

By dropping simplifying assumptions such as minimum reflux, tray-to-tray distillation models offer a wider range of validity compared to short-cut models. The increased computational effort is significantly reduced by applying problem-specific global optimization strategies as demonstrated for ideal binary mixtures in our previous work [2]. Therein, it has been shown that computational cost could be reduced by orders of magnitude using a specific bound tightening strategy, that is based on monotonicity of molar fractions throughout the column. The application was demonstrated for a hybrid distillation crystallization process for the separation of two closely boiling isomers. However, an extension to multi-component mixtures is non-trivial because molar fraction profiles associated with intermediate boiling components typically show non-monotonic behavior.

In this follow-up paper, a reformulation of a distillation column model is presented to overcome this problem. The reformulation is obtained by aggregation of single components, resulting in a linear transformation of the variables used for molar fractions. For ideal mixtures, we prove that the transformed variables show the desired monotonic behavior, which allows us to extend the bound tightening strategy from the binary case to the multi-component setting.

Bound tightening, also known as domain reduction or range reduction, is a common strategy in global optimization to reduce the initial domain of the problem variables without cutting off the optimal solutions. This results in two

benefits in view of deterministic global optimization. First of all, a reduction of the search space is achieved. But most importantly, available global optimization software often relies on the use of convex relaxations for non-linear mixed-integer optimization problems. In general, such convex relaxations can be tightened when the underlying domains are reduced.

In the literature, it is mainly distinguished between two basic types of domain reduction. Feasibility based bound tightening (FBBT) cuts off non-feasible solutions using the constraints of the underlying problem. Optimization based bound tightening (OBBT) applies optimization techniques in order to derive tighter variable bounds. Both types are integrated in many state-of-the-art global optimization software packages (e.g., see BARON [22], COUENNE [6], SCIP [26], and GloMIQO [18]).

For FBBT, standard methods are often based on interval arithmetic (e.g., see [21]) and the description of nonlinearities using expression trees (e.g., see [23] [25]). Bounds on the variables can be propagated onto the non-linear expressions via forward propagation. Also, the other way around, tighter bounds on the variables can be computed using the bounds on the nonlinearities (backward propagation). This procedure can be iterated until no further strengthening of the bounds is achieved. The iteration can be formally interpreted as an operator which is shown in [4] to have a limit point. For special problems, this point can be determined using polynomial time algorithms. In [3], the concept of FBBT is expanded on convex combinations of two linear constraints. In [9] additional results on constraint satisfaction problems with quadratic constraints are presented.

The key idea of OBBT is to consecutively minimize and maximize each variable appearing in the problem on the feasible set. This is in general as hard as finding the optimal solution of the problem itself, so a common approach is to only use (linear) relaxations of the feasible set. This procedure can be iterated multiple times in order to further tighten the bounds. OBBT can be more effective, but is often much more time-consuming. It is, hence, used very rarely or only at the root node of the branch-and-bound tree. For more details, we refer to work [11]. An early reference in which OBBT is applied in the context of heat exchanger networks is [20]. In [8], a so-called nonlinearities removal domain reduction is introduced by fixing the value of a variable whose domain is intended to be tightened. Under some assumptions, the equivalence of this approach to standard procedures is shown, and it is concluded that general domain reduction techniques are independent in the

ordering of the considered variables. In [11], Lagrangian variable bound constraints are described, making it easier to propagate bounds throughout the branching tree. Additionally, enhancements on the computation of OBBT are given.

According to this terminology, the bound tightening strategy that is developed in this paper for ideal multi-component distillation column models belongs to FBBT. We especially make use of interval arithmetics that we apply to two types of well-structured model constraints. Preliminary results of this work have already been presented in a conference paper [17].

The remainder of the paper is structured as follows. In Section 2, we present the ideal multi-component distillation column model we are working with. In Section 3, we derive an alternative model formulation by introducing suitable *aggregated components*. In Section 4, we prove that the transformed variables associated with each newly introduced aggregated component fulfill the desired property of monotonicity. This is exploited in Section 5 in order to extend the bound tightening strategy from the binary case [2] to the general ideal multi-component case. In Section 6, we solve several numerical test examples to global optimality and experimentally analyze the influence of the developed techniques on the running time.

2. Distillation Column Model

In this section, the model under consideration is presented. As in previous work [2, 15], we focus on a tray-by-tray model of a distillation column in steady state, and assume ideal liquid and gas phase, total condenser and total reboiler, single liquid feed flow at boiling temperature, and constant molar overflow. Notation and model description are basically taken from [2, 15] and adapted, if necessary. For a general introduction to the topic of thermal separation processes, we refer to [16].

We are given a mixture consisting of n single components labeled by $\{1, \dots, n\}$. The order of the components is defined with respect to the boiling point. Here, component 1 is the component with the lowest boiling point, and component n refers to the component with the highest boiling point. In the model, the composition of a mixture is given in terms of molar fractions. Thus, the sum of molar fractions over all components is equal to one at every position of the column, also known as the *summation conditions*.

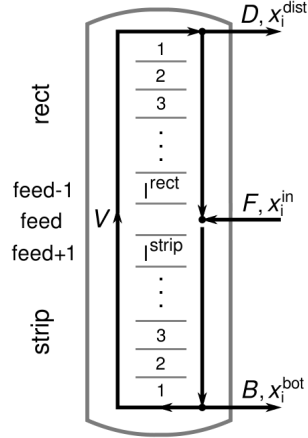


Figure 1: A fixed design of a distillation column. Numbers of trays in the rectifying and stripping sections are l^{rect} and l^{strip} . The total number of trays in the column is given by $l^{\text{col}} = l^{\text{rect}} + l^{\text{strip}} + 1$.

A sketch of a distillation column is shown in Figure 1. The mixture enters the column at the feed tray with molar feed flow F and initial composition x_i^{in} , $i = 1, \dots, n$. At the top tray (condenser), the distillate molar flow D leaves the column with composition x_i^{dist} , $i \in \{1, \dots, n\}$, and at the bottom tray (reboiler), the molar flow B leaves the column with composition x_i^{bot} , $i \in \{1, \dots, n\}$. V denotes the vapor flow that streams upwards through the column. The *overall mass balance equations*

$$Fx_i^{\text{in}} = Dx_i^{\text{dist}} + Bx_i^{\text{bot}}, \quad i \in \{1, \dots, n\} \quad (1)$$

ensure that the amount of component i entering the column coincides with the overall amount of component i leaving the column.

Rectifying section (above the feed tray) and stripping section (below the feed tray) can contain several trays. Trays of the rectifying section are numbered from the top to the bottom by $l_r = 1, \dots, l^{\text{rect}}$, and trays in the stripping section are numbered from the bottom to the top by $l_s = 1, \dots, l^{\text{strip}}$. Variables used for molar fractions of component i in liquid and in vapor phases are denoted by x_i and y_i , respectively. In order to specify the tray a variable is associated with, we introduce superscripts "feed", "feed-1", "feed+1", "rect" and "strip". Trays from the rectifying and stripping sections are additionally equipped with their associated index as subscript. The mass transfer in liquid and vapor phase through the column is then described by the *component mass balance*

equations

$$\begin{aligned}
y_{i,l_r+1}^{\text{rect}} &= v_r x_{i,l_r}^{\text{rect}} + (1 - v_r) y_{i,1}^{\text{rect}}, \\
v_s y_i^{\text{feed}} + x_i^{\text{feed}} &= v_s y_i^{\text{feed}+1} + v_r v_s x_i^{\text{feed}-1} + (1 - v_r v_s) x_i^{\text{in}}, \\
x_{i,l_s+1}^{\text{strip}} &= v_s y_{i,l_s}^{\text{strip}} + (1 - v_s) x_{i,1}^{\text{strip}},
\end{aligned} \tag{2}$$

for $i \in \{1, \dots, n\}$, $l_r \in \{1, \dots, u^{\text{rect}}\}$ and $l_s \in \{1, \dots, u^{\text{strip}}\}$, where u^{rect} and u^{strip} denote upper bounds imposed on l^{rect} and l^{strip} , respectively. We remark that in Equation (2) the subscripts indicating trays formally range to $u^{\text{rect}} + 1$ and $u^{\text{strip}} + 1$, respectively. This way, two artificial trays are introduced to the model. These two trays are later used to model the coupling of the feed tray with the rectifying and the stripping sections (see Equation (6)). The auxiliary variables $v_r, v_s \in [0, 1]$ defined as

$$v_r = \frac{V - D}{V} \quad \text{and} \quad v_s = \frac{V}{V + B} \tag{3}$$

describe the ratio of upward and downward molar flows in the rectifying and stripping section.

The separation behavior of component i is given by its volatility. Components with higher volatility accumulate in the vapor phase, while components with lower volatility accumulate in the liquid phase. We assume constant relative volatilities of the components, expressed by parameters $\alpha_i > 0$, for $i \in \{1, \dots, n\}$. Due to our assumption on the order of the components, we have that $\alpha_1 \geq \alpha_2 \geq \dots \geq \alpha_n$. At all trays, the interactions of the mole fractions in the vapor phase and in the liquid phase are given by the *phase equilibrium equations*

$$y_{i,l_r}^{\text{rect}} = \frac{\alpha_i x_{i,l_r}^{\text{rect}}}{\sum_{j=1}^n \alpha_j x_{j,l_r}^{\text{rect}}}, \quad y_i^{\text{feed}} = \frac{\alpha_i x_i^{\text{feed}}}{\sum_{j=1}^n \alpha_j x_j^{\text{feed}}}, \quad y_{i,l_s}^{\text{strip}} = \frac{\alpha_i x_{i,l_s}^{\text{strip}}}{\sum_{j=1}^n \alpha_j x_{j,l_s}^{\text{strip}}} \tag{4}$$

for $i \in \{1, \dots, n\}$, $l_r \in \{1, \dots, u^{\text{rect}}+1\}$ and $l_s \in \{1, \dots, u^{\text{strip}}+1\}$.

Total condenser and total reboiler are modeled by

$$x_i^{\text{dist}} = y_{i,1}^{\text{rect}} \quad \text{and} \quad x_i^{\text{bot}} = x_{i,1}^{\text{strip}}, \quad i = 1, \dots, n. \tag{5}$$

The total number l^{col} of trays used in a distillation column is given by the number of trays used in the rectifying section, the number of trays used in the

stripping section, and the feed tray. To specify l^{col} in our model, the following *coupling conditions* are imposed.

$$\begin{aligned} x_i^{\text{feed}-1} &= \sum_{l_r=1}^{u^{\text{rect}}} \beta_{l_r}^{\text{rect}} x_{i,l_r}^{\text{rect}}, & x_i^{\text{feed}} &= \sum_{l_r=1}^{u^{\text{rect}}} \beta_{l_r}^{\text{rect}} x_{i,l_r+1}^{\text{rect}}, & i &\in \{1, \dots, n\} \\ y_i^{\text{feed}+1} &= \sum_{l_s=1}^{u^{\text{strip}}} \beta_{l_s}^{\text{strip}} y_{i,l_s}^{\text{strip}}, & x_i^{\text{feed}} &= \sum_{l_s=1}^{u^{\text{strip}}} \beta_{l_s}^{\text{strip}} x_{i,l_s+1}^{\text{strip}}, & i &\in \{1, \dots, n\} \end{aligned} \quad (6a)$$

$$\begin{aligned} l^{\text{col}} &:= \sum_{l_r=1}^{u^{\text{rect}}} \beta_{l_r}^{\text{rect}} l_r + \sum_{l_s=1}^{u^{\text{strip}}} \beta_{l_s}^{\text{strip}} l_s + 1, \\ \sum_{l_r=1}^{u^{\text{rect}}} \beta_{l_r}^{\text{rect}} &= 1, & \beta_{l_r}^{\text{rect}} &\in \{0, 1\}, & l_r &= 1, \dots, u^{\text{rect}}, \\ \sum_{l_s=1}^{u^{\text{strip}}} \beta_{l_s}^{\text{strip}} &= 1, & \beta_{l_s}^{\text{strip}} &\in \{0, 1\}, & l_s &= 1, \dots, u^{\text{strip}}. \end{aligned} \quad (6b)$$

Note that the binary variables $\beta_{l_r}^{\text{rect}}$ and $\beta_{l_s}^{\text{strip}}$ attain value one if and only if tray l_r of rectifying section and tray l_s of stripping section are chosen to be the trays above and below the feed tray in the column.

The goal of the distillation column is to separate the more volatile components from the less volatile components under given purity constraints. Let the *split* $\sigma \in \{1, \dots, n-1\}$ be the index such that the components 1 to σ belong to the more volatile part and components $\sigma+1$ to n belong to the less volatile part of the mixture, and let $\pi^{\text{dist}}, \pi^{\text{bot}} \in [0, 1]$ denote the purity requirements imposed on the more volatile components at the condenser and on the less volatile components at the reboiler. Then, the *purity constraints* are given as follows.

$$\sum_{i=1}^{\sigma} x_i^{\text{dist}} \geq \pi^{\text{dist}} \quad \text{and} \quad \sum_{i=\sigma+1}^n x_i^{\text{bot}} \geq \pi^{\text{bot}}. \quad (7)$$

The objective function of our column model reflects the total annualized cost of the distillation process that needs to be minimized. In our work, we make use of the following cost function that is taken from previous work

[15].

$$\begin{aligned} \text{cost} = & 17544 V + 173.6 I^{\text{col}} + 2009.7 (0.2378 V + 0.0221 B) I^{\text{col}} \\ & + 2364.5 (0.2378 V + 0.0221 B)^{0.533} (0.2 I^{\text{col}} + 4)^{0.82} \\ & - 171.4 (0.2378 V + 0.0221 B)^{0.5} I^{\text{col}}. \end{aligned} \quad (8)$$

This objective function was originally developed for the distillation of dodecanal and 2-methylundecanal. However, its structure is typical for economical cost estimation and therefore suitable for the computational studies in our work.

3. Model Reformulation by Aggregating Components

As already mentioned in the introduction, the molar fractions of a single component may not behave monotonic in the multi-component setting. Such a typical situation is illustrated in Figure 2 (a) for component 2 (green curve) and component 3 (magenta curve). This fact makes it hard to generalize the

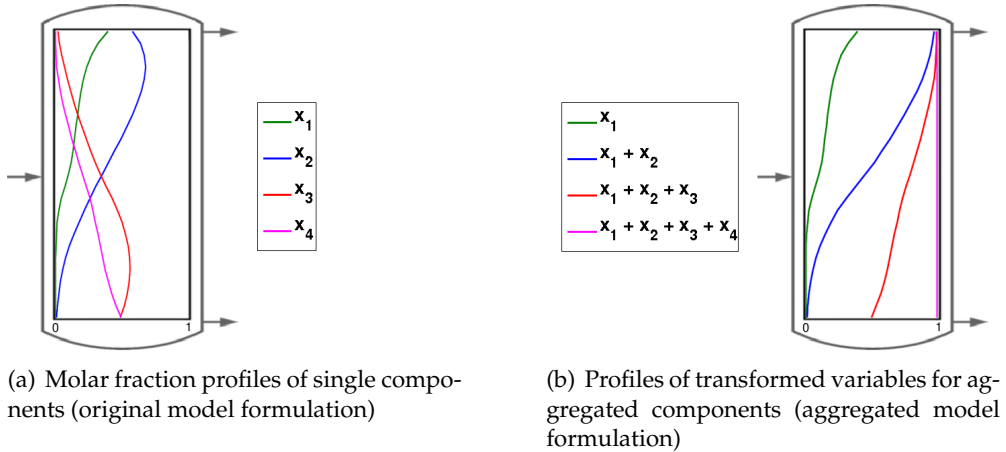


Figure 2: The figure shows molar fraction profiles and profiles of transformed variables in liquid phase for a four component mixture.

bound tightening strategy for the binary case [2] to the multi-component case, directly.

We overcome this problem by aggregating, for each $k \in \{1, \dots, n\}$, the first k components. This is achieved by summing up the corresponding variables used for molar fractions at every position of the distillation column.

To be more precise, let x_i and y_i (for $i \in \{1, \dots, n\}$) be the variables used for molar fractions of component i in the liquid and in the vapor phase at an arbitrary position. The associated sub- and superscripts indicating the specific position are omitted for a clean presentation. We label the *aggregated components* by $k \in \{1, \dots, n\}$ and introduce *aggregated concentration variables* X_k and Y_k for liquid and vapor phases. The original variables used for molar fractions and the new aggregated concentration variables are linearly linked to each other by the following bijective relations.

$$X_k = \sum_{i=1}^k x_i \quad \text{and} \quad Y_k = \sum_{i=1}^k y_i, \quad k = 1, \dots, n. \quad (9)$$

Next, we restate the distillation column model from Section 2 in terms of the aggregated components. For this, we introduce an (aggregated) *dummy component* 0 for which the liquid and vapor phase concentrations X_0 and Y_0 are zero at all positions. By definition and due to the summation conditions (i.e. $\sum_{i=1}^n x_i = \sum_{i=1}^n y_i = 1$), we have

$$0 = X_0 \leq X_1 \leq \dots \leq X_n = 1 \quad \text{and} \quad 0 = Y_0 \leq Y_1 \leq \dots \leq Y_n = 1. \quad (10)$$

Note that molar fractions do not appear in the Equations (3),(6b) or in the objective function (8). Hence, they remain unchanged in our aggregated model formulation. Observe further that the overall mass balance equations (1), the component mass balance equations (2), the coupling conditions (6a), total condenser and total reboiler conditions (5) and the purity constraints (7) are linear in the variables used for molar fractions. Therefore, we obtain the corresponding constraints for each aggregated component k by summing up the corresponding conditions associated with the first k single components. Only the phase equilibrium equations (4) are not linear in the original concentration variables and need to be adapted. The aggregated model formulation reads as

- The *aggregated overall mass balance equations*

$$FX_k^{\text{in}} = DX_k^{\text{dist}} + BX_k^{\text{bot}}, \quad k = 1, \dots, n. \quad (11)$$

- The aggregated component mass balance equations:

$$\begin{aligned} \gamma_{k,l_r+1}^{\text{rect}} &= v_r X_{k,l_r}^{\text{rect}} + (1 - v_r) \gamma_{k,1}^{\text{rect}}, \\ v_s \gamma_k^{\text{feed}} + X_k^{\text{feed}} &= v_s \gamma_k^{\text{feed}+1} + v_r v_s X_k^{\text{feed}-1} + (1 - v_r v_s) X_k^{\text{in}}, \\ X_{k,l_s+1}^{\text{strip}} &= v_s \gamma_{k,l_s}^{\text{strip}} + (1 - v_s) X_{k,1}^{\text{strip}}, \end{aligned} \quad (12)$$

for $k \in \{1, \dots, n\}$, $l_r \in \{1, \dots, u^{\text{rect}}\}$ and $l_s \in \{1, \dots, u^{\text{strip}}\}$.

- The auxiliary variables constraints:

$$v_r = \frac{V - D}{V} \quad \text{and} \quad v_s = \frac{V}{V + B}. \quad (13)$$

- The aggregated phase equilibrium equations:

$$\begin{aligned} \gamma_{k,l_r}^{\text{rect}} &= \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s}^{\text{rect}} - X_{j-1,l_s}^{\text{rect}})}{\sum_{j=1}^n \alpha_j (X_{j,l_s}^{\text{rect}} - X_{j-1,l_s}^{\text{rect}})}, \\ \gamma_k^{\text{feed}} &= \frac{\sum_{j=1}^k \alpha_j (X_j^{\text{feed}} - X_{j-1}^{\text{feed}})}{\sum_{j=1}^n \alpha_j (X_j^{\text{feed}} - X_{j-1}^{\text{feed}})}, \\ \gamma_{k,l_s}^{\text{strip}} &= \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s}^{\text{strip}} - X_{j-1,l_s}^{\text{strip}})}{\sum_{j=1}^n \alpha_j (X_{j,l_s}^{\text{strip}} - X_{j-1,l_s}^{\text{strip}})}, \end{aligned} \quad (14)$$

for $k \in \{1, \dots, n\}$, $l_r \in \{1, \dots, u^{\text{rect}} + 1\}$ and $l_s \in \{1, \dots, u^{\text{strip}} + 1\}$.

- The aggregated constraints for the total condenser/reboiler:

$$X_k^{\text{dist}} = \gamma_{k,1}^{\text{rect}} \quad \text{and} \quad X_k^{\text{bot}} = X_{k,1}^{\text{strip}}, \quad k \in \{1, \dots, n\}. \quad (15)$$

- The aggregated coupling conditions:

$$\begin{aligned} X_k^{\text{feed}-1} &= \sum_{l_r=1}^{u^{\text{rect}}} \beta_{l_r}^{\text{rect}} X_{k,l_r}^{\text{rect}}, \quad X_k^{\text{feed}} = \sum_{l_r=1}^{u^{\text{rect}}} \beta_{l_r}^{\text{rect}} X_{k,l_r+1}^{\text{rect}}, \quad k \in \{1, \dots, n\} \\ \gamma_k^{\text{feed}+1} &= \sum_{l_s=1}^{u^{\text{strip}}} \beta_{l_s}^{\text{strip}} \gamma_{k,l_s}^{\text{strip}}, \quad X_k^{\text{feed}} = \sum_{l_s=1}^{u^{\text{strip}}} \beta_{l_s}^{\text{strip}} X_{k,l_s+1}^{\text{strip}}, \quad k \in \{1, \dots, n\} \end{aligned} \quad (16a)$$

$$\begin{aligned}
l^{\text{col}} &:= \sum_{l_r=1}^{u^{\text{rect}}} \beta_{l_r}^{\text{rect}} l_r + \sum_{l_s=1}^{u^{\text{strip}}} \beta_{l_s}^{\text{strip}} l_s + 1, \\
\sum_{l_r=1}^{u^{\text{rect}}} \beta_{l_r}^{\text{rect}} &= 1, \quad \beta_{l_r}^{\text{rect}} \in \{0, 1\}, \quad l_r = 1, \dots, u^{\text{rect}}, \\
\sum_{l_s=1}^{u^{\text{strip}}} \beta_{l_s}^{\text{strip}} &= 1, \quad \beta_{l_s}^{\text{strip}} \in \{0, 1\}, \quad l_s = 1, \dots, u^{\text{strip}}.
\end{aligned} \tag{16b}$$

- The *aggregated purity constraints*:

$$X_{\sigma}^{\text{dist}} \geq \pi^{\text{dist}} \quad \text{and} \quad (1 - X_{\sigma}^{\text{bot}}) \geq \pi^{\text{bot}}. \tag{17}$$

- The *objective function*:

$$\begin{aligned}
\text{cost} &= 17544 V + 173.6 l^{\text{col}} + 2009.7 (0.2378 V + 0.0221 B) l^{\text{col}} \\
&\quad + 2364.5 (0.2378 V + 0.0221 B)^{0.533} (0.2 l^{\text{col}} + 4)^{0.82} \\
&\quad - 171.4 (0.2378 V + 0.0221 B)^{0.5} l^{\text{col}}.
\end{aligned} \tag{18}$$

It turns out that the concentration variables of each aggregated component show the desired monotonic behavior, i.e. the overall molar fraction of all components above each possible split position $\sigma \in \{1, \dots, n-1\}$ change monotonically throughout the distillation column. This is illustrated in Figure 2 (b), and will be proven in Section 4.

4. Monotonicity of the Aggregated Concentration Profiles

In this section we prove that for each aggregated component, the corresponding concentration variables introduced in Section 3 behave monotonic through the distillation column. We refer to a sequence of liquid or vapor phase concentration values of an aggregated component as a (*concentration*) *profile*.

In what follows, we investigate the restrictions of each such profile to the stripping section and to the rectifying section, separately. Subsection 4.1 deals with the stripping section. We show that each profile is non-decreasing when

considered from the bottom to the top. For the rectifying section discussed in Subsection 4.2, we first apply a suitable transformation. That transformation traces the profiles restricted to the rectifying section back to the case of profiles restricted a stripping section. We then conclude that each profile also behaves non-decreasing in the rectifying section from bottom to the top.

As the coupling conditions in Equation (16) ensure that, for each profile, the parts restricted to the stripping section and restricted to the rectifying section must coincide at the feed tray, we finally obtain that each profile of an aggregated components runs monotonically through the distillation column.

4.1. Stripping Section

We omit superscript “strip” and denote by $X := (X_{k,l_s})_{k=0,\dots,n,l_s=1,\dots,u+1}$ and $Y := (Y_{k,l_s})_{k=0,\dots,n,l_s=1,\dots,u+1}$ the matrices consisting of all liquid and vapor phase concentration variables w.r.t. aggregated components (including the dummy one) and restricted to the stripping section.

With this notation and combining the phase equilibrium equations (14) with the component mass balance equations (12), we obtain the following subsystem that is satisfied by every feasible solution of our distillation column model from Section 3.

$$\begin{aligned}
X_{k,l_s+1} &= v_s \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s})} + (1 - v_s) X_{k,1}, & k &= 0, \dots, n, \\
& & l_s &= 1, \dots, u, \\
0 < X_{1,l_s} &\leq X_{2,l_s} \leq \dots \leq X_{n,l_s}, & l_s &= 1, \dots, u + 1, \\
X_{0,l_s} &= 0, X_{n,l_s} = 1, & l_s &= 1, \dots, u + 1, \\
X &\in \mathbb{R}^{(n+1) \times (u+1)}, \quad v_s \in [0, 1].
\end{aligned} \tag{19}$$

For our analysis, the following remarks are worth to mention.

- In System (19), we impose that all variables X_{k,l_s} , $k \geq 1$, are strictly positive. This assumption can be made with out loss of generality. Indeed, when $X_{k,l_s} = 0$ holds, for some $k \geq 1$ and some l_s , the recursive formula already implies that the concentration of component k is zero at every

position in the stripping section, and, hence, in the entire column. In that case we can exclude component k from our considerations.

- To keep the notation simple, we define the following expressions to denote the denominators appearing in (19).

$$N_{l_s}(X) := \sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}), \quad l_s = 1, \dots, u+1.$$

Note that $N_{l_s}(X) > 0$ holds for all X such that there is a $v_s \in [0, 1]$ with (X, v_s) being feasible to system (19).

- Finally, we observe the identities

$$\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s}) = \sum_{j=1}^{k-1} X_{j,l_s} (\alpha_j - \alpha_{j+1}) + X_{k,l_s} \alpha_k.$$

for $k = \{1, \dots, n\}$ and $l_s = \{1, \dots, u+1\}$, that we will frequently use throughout the proofs.

For a solution (X, v_s) feasible to system (19), we will next show that for each aggregated component $k \in \{1, \dots, n\}$, the sequence $\{X_{k,l_s}\}_{l_s=1}^{u+1}$ is non-decreasing. More precisely, we will prove a more general statement implying the desired property.

Theorem 1. *Let $X \in \mathbb{R}^{(n+1) \times (u+1)}$ and $v_s \in [0, 1]$ be feasible to system (19) for some $\alpha \in \mathbb{R}^n$ with $\alpha_1 \geq \alpha_2 \geq \dots \geq \alpha_n > 0$. Then,*

$$\frac{X_{k,l_s+1} - X_{k,l_s}}{X_{k,l_s}} \geq \frac{X_{k+1,l_s+1} - X_{k+1,l_s}}{X_{k+1,l_s}} \quad (20)$$

holds for each $k \in \{1, \dots, n-1\}$ and for each $l_s \in \{1, \dots, u\}$.

Proof. The statement is proven by induction on l_s . We first consider the case with $l_s = 1$. For an arbitrary $k \in \{1, \dots, n-1\}$, system (19) yields

$$\begin{aligned} X_{k,2} - X_{k,1} &= v_s X_{k,1} \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,1} - X_{j-1,1})}{N_1(X) X_{k,1}} - 1 \right) \quad \text{and} \\ X_{k+1,2} - X_{k+1,1} &= v_s X_{k+1,1} \left(\frac{\sum_{j=1}^{k+1} \alpha_j (X_{j,1} - X_{j-1,1})}{N_1(X) X_{k+1,1}} - 1 \right), \end{aligned}$$

or equivalently

$$\begin{aligned}\frac{X_{k,2} - X_{k,1}}{X_{k,1}} &= \frac{v_s}{N_1(X)} \cdot \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,1} - X_{j-1,1})}{X_{k,1}} \right) - v_s, \\ \frac{X_{k+1,2} - X_{k+1,1}}{X_{k+1,1}} &= \frac{v_s}{N_1(X)} \cdot \left(\frac{\sum_{j=1}^{k+1} \alpha_j (X_{j,1} - X_{j-1,1})}{X_{k+1,1}} \right) - v_s.\end{aligned}$$

Thus, in order to prove our statement for $l_s = 1$, we show that

$$\frac{\sum_{j=1}^k \alpha_j (X_{j,1} - X_{j-1,1})}{X_{k,1}} \geq \frac{\sum_{j=1}^{k+1} \alpha_j (X_{j,1} - X_{j-1,1})}{X_{k+1,1}}.$$

Observing that $X_{k+1,1} \geq X_{k,1}$ and $\sum_{j=1}^k \alpha_j (X_{j,1} - X_{j-1,1}) - \alpha_{k+1} X_{k,1} \geq 0$ hold, yields

$$\begin{aligned}\frac{\sum_{j=1}^{k+1} \alpha_j (X_{j,1} - X_{j-1,1})}{X_{k+1,1}} &= \frac{\sum_{j=1}^k \alpha_j (X_{j,1} - X_{j-1,1}) - \alpha_{k+1} X_{k,1}}{X_{k+1,1}} + \alpha_{k+1} \\ &\leq \frac{\sum_{j=1}^k \alpha_j (X_{j,1} - X_{j-1,1}) - \alpha_{k+1} X_{k,1}}{X_{k,1}} + \alpha_{k+1} \\ &= \frac{\sum_{j=1}^k \alpha_j (X_{j,1} - X_{j-1,1})}{X_{k,1}},\end{aligned}$$

i.e. for $l_s = 1$, the statement holds for each $k \in \{1, \dots, n\}$.

Now assume that, for some $l_s \geq 1$, the statement is true for each $k \in \{1, \dots, n-1\}$. We will show that for $l_s + 1$ the statement is then true for each $k \in \{1, \dots, n-1\}$, as well. For this, we define $m_k := \frac{X_{k,l_s}}{X_{k,l_s-1}}$ for each $k \in \{1, \dots, n\}$. By induction hypothesis, we have that $m_k \geq m_{k+1}$ holds for all $k \in \{1, \dots, n-1\}$.

Next, the values of the terms $X_{k,l_s+1} - X_{k,l_s}$ and $X_{k+1,l_s+1} - X_{k+1,l_s}$ are compared. Using the recursive formula and the definition of m_k , we obtain for $X_{k,l_s+1} - X_{k,l_s}$ that

$$\begin{aligned}v_s \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{N_{l_s}(X)} - \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s-1} - X_{j-1,l_s-1})}{N_{l_s-1}(X)} \right) &= \\ v_s \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{N_{l_s}(X)} - \frac{\sum_{j=1}^k \alpha_j \left(\frac{X_{j,l_s}}{m_j} - \frac{X_{j-1,l_s}}{m_{j-1}} \right)}{N_{l_s-1}(X)} \right) &.\end{aligned} \quad (21)$$

Moreover, we have that

$$\frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{m_1} \leq \sum_{j=1}^k \alpha_j \left(\frac{X_{j,l_s}}{m_j} - \frac{X_{j-1,l_s}}{m_{j-1}} \right) \leq \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{m_k}.$$

By the intermediate value theorem, there must exist some $\tilde{m} \in [m_k, m_1]$ with

$$\sum_{j=1}^k \alpha_j \left(\frac{X_{j,l_s}}{m_j} - \frac{X_{j-1,l_s}}{m_{j-1}} \right) = \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{\tilde{m}}. \quad (22)$$

Combining Formula (21) with Formula (22) gives rise to

$$\begin{aligned} X_{k,l_s+1} - X_{k,l_s} &= v_s \sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s}) \left(\frac{1}{N_{l_s}(X)} - \frac{1}{\tilde{m} N_{l_s-1}(X)} \right) \\ &= X_{k,l_s} v_s \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{X_{k,l_s}} \left(\frac{1}{N_{l_s}(X)} - \frac{1}{\tilde{m} N_{l_s-1}(X)} \right). \end{aligned} \quad (23)$$

Again, using the recursive formula and the definition of m_k , the second term can be rewritten as follows.

$$\begin{aligned} X_{k+1,l_s+1} - X_{k+1,l_s} &= v_s \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s}) + \alpha_{k+1} (X_{k+1,l_s} - X_{k,l_s})}{N_{l_s}(X)} \right. \\ &\quad \left. - \frac{\sum_{j=1}^k \alpha_j \left(\frac{X_{j,l_s}}{m_j} - \frac{X_{j-1,l_s}}{m_{j-1}} \right) + \alpha_{k+1} \left(\frac{X_{k+1,l_s}}{m_{k+1}} - \frac{X_{k,l_s}}{m_k} \right)}{N_{l_s-1}(X)} \right) \\ &= v_s \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{N_{l_s}(X)} - \frac{\sum_{j=1}^k \alpha_j \left(\frac{X_{j,l_s}}{m_j} - \frac{X_{j-1,l_s}}{m_{j-1}} \right)}{N_{l_s-1}(X)} \right) \\ &\quad + v_s \left(\frac{\alpha_{k+1} (X_{k+1,l_s} - X_{k,l_s})}{N_{l_s}(X)} - \frac{\alpha_{k+1} \left(\frac{X_{k+1,l_s}}{m_{k+1}} - \frac{X_{k,l_s}}{m_k} \right)}{N_{l_s-1}(X)} \right). \end{aligned}$$

Using Formula (22) and the fact that $m_{k+1} \leq m_k \leq \tilde{m}$ holds, we can further

estimate

$$\begin{aligned}
X_{k+1,l_s+1} - X_{k+1,l_s} &= v_s \sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s}) \left(\frac{1}{N_{l_s}(X)} - \frac{1}{\tilde{m} N_{l_s-1}(X)} \right) \\
&\quad + v_s \left(\frac{(\alpha_{k+1}(X_{k+1,l_s} - X_{k,l_s}))}{N_{l_s}(X)} - \frac{\alpha_{k+1} \left(\frac{X_{k+1,l_s}}{m_{k+1}} - \frac{X_{k,l_s}}{m_k} \right)}{N_{l_s-1}(X)} \right) \\
&\leq v_s \sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s}) \left(\frac{1}{N_{l_s}(X)} - \frac{1}{\tilde{m} N_{l_s-1}(X)} \right) \\
&\quad + v_s \left(\frac{(\alpha_{k+1}(X_{k+1,l_s} - X_{k,l_s}))}{N_{l_s}(X)} - \frac{\alpha_{k+1}(X_{k+1,l_s} - X_{k,l_s})}{\tilde{m} N_{l_s-1}(X)} \right) \\
&= v_s \sum_{j=1}^{k+1} \alpha_j (X_{j,l_s} - X_{j-1,l_s}) \left(\frac{1}{N_{l_s}(X)} - \frac{1}{\tilde{m} N_{l_s-1}(X)} \right).
\end{aligned}$$

Finally, we exploit that $X_{k+1,l_s} \geq X_{k,l_s}$ and that $\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s}) - \alpha_{k+1} X_{k,l_s} \geq 0$ holds. This yields

$$\begin{aligned}
&X_{k+1,l_s+1} - X_{k+1,l_s} \\
&\leq X_{k+1,l_s} v_s \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s}) - \alpha_{k+1} X_{k,l_s}}{X_{k+1,l_s}} + \alpha_{k+1} \right) \\
&\quad \cdot \left(\frac{1}{N_{l_s}(X)} - \frac{1}{\tilde{m} N_{l_s-1}(X)} \right) \\
&\leq X_{k+1,l_s} v_s \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s}) - \alpha_{k+1} X_{k,l_s}}{X_{k,l_s}} + \alpha_{k+1} \right) \\
&\quad \cdot \left(\frac{1}{N_{l_s}(X)} - \frac{1}{\tilde{m} N_{l_s-1}(X)} \right) \\
&= X_{k+1,l_s} v_s \left(\frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{X_{k,l_s}} \right) \left(\frac{1}{N_{l_s}(X)} - \frac{1}{\tilde{m} N_{l_s-1}(X)} \right).
\end{aligned} \tag{24}$$

From Formulas (23) and (24), we can deduce that

$$\frac{X_{k,l_s+1} - X_{k,l_s}}{X_{k,l_s}} \geq \frac{X_{k+1,l_s+1} - X_{k+1,l_s}}{X_{k+1,l_s}}$$

holds. □

We are now able to prove that the concentration profiles behave non-decreasing through the stripping section.

Corollary 2. Let (X, v_s) be a feasible solution to system (19) for some $\alpha \in \mathbb{R}^n$ with $\alpha_1 \geq \alpha_2 \geq \dots \geq \alpha_n > 0$. Let Y be the matrix consisting of all vapor phase concentration variables Y_{k,l_s} that are implied by X through the phase equilibrium equations (14). Then, for each aggregated component $k \in \{1, \dots, n\}$, both sequences $\{X_{k,l_s}\}_{l_s=1}^{u+1}$ and $\{Y_{k,l_s}\}_{l_s=1}^{u+1}$ are non-decreasing.

Proof. By definition, we have that $X_{n,l_s} = 1$ holds for $l_s = 1, \dots, u+1$. Thus, the statement holds for $k = n$. For each fixed $l_s \in \{1, \dots, u\}$, we obtain from Theorem 1 that

$$\frac{X_{1,l_s+1} - X_{1,l_s}}{X_{1,l_s}} \geq \frac{X_{2,l_s+1} - X_{2,l_s}}{X_{2,l_s}} \geq \dots \geq \frac{X_{n,l_s+1} - X_{n,l_s}}{X_{n,l_s}} = 0.$$

By assumption $X_{k,l_s} > 0$, for all $k \in \{1, \dots, n\}$ and $l_s \in \{1, \dots, u+1\}$, it follows that $X_{k,l_s+1} - X_{k,l_s} \geq 0$, for all $k = 1, \dots, n$. This proves the statement for sequence $\{X_{k,l_s}\}_{l_s=1}^{u+1}$.

Using Equation (12), and $X_{k,l_s+2} \geq X_{k,l_s+1}$, for all k and l_s , we can further derive, for all $k = 1, \dots, n$ and $l_s = 1, \dots, u^{\text{strip}}$, that

$$v_s Y_{k,l_s+1} + (1 - v_s) X_{k,1} \geq v_s Y_{k,l_s} + (1 - v_s) X_{k,1} \Leftrightarrow v_s (Y_{k,l_s+1} - Y_{k,l_s}) \geq 0.$$

This implies that $Y_{k,l_s+1} - Y_{k,l_s} \geq 0$ holds for $v_s > 0$. Moreover, if $v_s = 0$, then we can deduce from equation (12) that $X_{k,1} = X_{k,2} = \dots = X_{k,u+1}$. By phase equilibrium equations (14), it follows that $Y_{k,1} = Y_{k,2} = \dots = Y_{k,u+1}$. \square

4.2. Rectifying Section

Next, we prove monotonicity for the profiles when restricted to the rectifying section. We omit superscript “rect” and denote the matrices consisting of all liquid and vapor phase concentration variables of aggregated components (including the dummy one) and restricted to the rectifying section by $X := (X_{k,l_r})_{k=0,\dots,n, l_r=1,\dots,u+1}$ and $Y := (Y_{k,l_r})_{k=0,\dots,n, l_r=1,\dots,u+1}$.

Recap that in our model description the trays in the rectifying section are labeled from top to bottom. For this labeling, we show that the sequences $\{X_{k,l_r}\}_{l_r=1}^{u+1}$ and $\{Y_{k,l_r}\}_{l_r=1}^{u+1}$ are non-increasing for every $k \in \{1, \dots, n\}$. Therefore, the profiles considered from the bottom to the top are non-decreasing.

In order to derive a system for the rectifying section that corresponds to system (19) of the stripping section, we need the well-known *inverses* of the phase

holds when $\alpha_1 \geq \alpha_2 \geq \dots \geq \alpha_n > 0$ in the original order. This means that system (28) satisfies all conditions of Theorem 1 and Corollary 2. We can, hence, conclude that, for every $k \in \{1, \dots, n\}$, both sequences $\{\hat{X}_{k,l}\}_{l=1}^{i+1}$ and $\{\hat{Y}_{k,l}\}_{l=1}^{i+1}$ are non-decreasing. Using the transformations rules (27), again, we can draw the following conclusion.

Corollary 3. *Let (Y, v_r) be a feasible solution to system (26) for some $\alpha \in \mathbb{R}^n$ with $\alpha_1 \geq \alpha_2 \geq \dots \geq \alpha_n > 0$. Let X be the matrix consisting of all liquid phase concentrations variables X_{k,l_r} , that are implied by Y through the phase equilibrium equations (25). Then, for each aggregated component $k \in \{1, \dots, n\}$, both sequences $\{Y_{k,l_r}\}_{l_r=1}^{u+1}$ and $\{X_{k,l_r}\}_{l_r=1}^{u+1}$ are non-increasing.*

5. Domain Reduction Techniques

In this section, we use the results from Section 4 to derive a problem-specific bound tightening strategy for our distillation column model associated with the aggregated components (Subsection 5.1). For this, we adapt the arguments used in previous work [2] for binary mixtures to the multi-component case with aggregated components. In Subsection 5.2, we moreover restate a method to derive additional bounds on the aggregated concentration variables by computing the fixed points of the concentration profiles. This method has already been applied in [15] to the binary distillation case. Both techniques are implemented in global optimization software and their impact is computationally evaluated in Section 6.

5.1. Bound Tightening Strategy

The monotonic behavior of the aggregated concentration profiles together with the aggregated component mass balance equations allow us to propagate given bounds on the aggregated concentration variables at a certain tray to the aggregated concentration variables associated with an adjacent tray.

For this, recap that, for every $k \in \{1, \dots, n\}$, the aggregated component mass balance equations (12)

$$\begin{aligned} Y_{k,l_r+1}^{\text{rect}} &= v_r X_{k,l_r}^{\text{rect}} + (1 - v_r) Y_{k,1}^{\text{rect}}, & l_r &= 1, \dots, u^{\text{rect}}, \\ X_{k,l_s+1}^{\text{strip}} &= v_s Y_{k,l_s}^{\text{strip}} + (1 - v_s) X_{k,1}^{\text{strip}}, & l_s &= 1, \dots, u^{\text{strip}} \end{aligned}$$

associated with the trays in the rectifying and stripping sections form two families of recursive functions (one for each section). By analyzing the partial derivatives, one can show that in both cases the recursive functions behave monotonic in each of their arguments (see also [2] for the binary case). The analysis is mainly straightforward. Only the partial derivatives

$$\frac{\partial Y_{k,l_r+1}^{\text{rect}}}{\partial v_r} = X_{k,l_r}^{\text{rect}} - Y_{k,1}^{\text{rect}} \quad \text{and} \quad \frac{\partial X_{k,l_s+1}^{\text{strip}}}{\partial v_s} = Y_{k,l_s}^{\text{strip}} - X_{k,1}^{\text{strip}}$$

need special attention. For these, we remark that the monotonicity of the concentration profiles ensures for each aggregated component $k \in \{1, \dots, n\}$ that

$$X_{k,l_r}^{\text{rect}} \leq X_{k,1}^{\text{rect}}, \quad l_r = 1, \dots, u^{\text{rect}} \quad \text{and} \quad Y_{k,l_s}^{\text{strip}} \geq Y_{k,1}^{\text{strip}}, \quad l_s = 1, \dots, u^{\text{strip}} \quad (29)$$

hold. As $X_{k,l_s} > 0$, we moreover observe that the phase equilibrium equations can be restated as follows.

$$Y_{k,l_r}^{\text{rect}} = X_{k,l_r}^{\text{rect}} \frac{\sum_{j=1}^k \alpha_j \left(\frac{X_{j,l_r}^{\text{rect}}}{X_{k,l_r}^{\text{rect}}} - \frac{X_{j-1,l_r}^{\text{rect}}}{X_{k,l_r}^{\text{rect}}} \right)}{X_{k,l_r}^{\text{rect}} \sum_{j=1}^k \alpha_j \left(\frac{X_{j,l_r}^{\text{rect}}}{X_{k,l_r}^{\text{rect}}} - \frac{X_{j-1,l_r}^{\text{rect}}}{X_{k,l_r}^{\text{rect}}} \right) + \sum_{j=k+1}^n \alpha_j (X_{j,l_r}^{\text{rect}} - X_{j-1,l_r}^{\text{rect}})}. \quad (30)$$

Note further that the numerator in Equation (30) is a convex combination of parameters $\alpha_1, \dots, \alpha_k$. From $\alpha_k \leq \alpha_{k-1} \leq \dots \leq \alpha_1$, it follows that the numerator is greater or equal to α_k . The denominator is a convex combination of the numerator and parameters $\alpha_{k+1}, \dots, \alpha_n$. As $\alpha_n \leq \dots \leq \alpha_{k+1} \leq \alpha_k$, we can conclude that the fractional term in the right-hand-side of Equation (30) is greater or equal to one. This implies that $Y_{k,l_r}^{\text{rect}} \geq X_{k,l_r}^{\text{rect}}$. In a similar way, we can verify that $Y_{k,l_s}^{\text{strip}} \geq X_{k,l_s}^{\text{strip}}$ holds. Combining these results shows that $\partial Y_{k,l_r+1}^{\text{rect}} / \partial v_r \leq 0$ and $\partial X_{k,l_s+1}^{\text{strip}} / \partial v_s \geq 0$.

Thus, given bounds on the arguments in (12) can be used to compute bounds on the aggregated concentration variables associated with the consecutive tray via standard interval arithmetic (e.g., see also [12]). The resulting formulas are stated in the following two lemmas, where Lemma 4 addresses the stripping section and Lemma 5 deals with the rectifying section. In both lemmas, superscripts “strip” and “rect” are neglected for keeping the notation simple.

Lemma 4. (*Stripping Section*)

Consider any $l_s \in \{1, \dots, u\}$ and $k \in \{1, \dots, n\}$. Assume further that v_s ranges on

$[v_s^{lo}, v_s^{up}]$, Y_{k,l_s} ranges on $[Y_{k,l_s}^{lo}, Y_{k,l_s}^{up}]$ and that $X_{k,1}$ ranges on $[X_{k,1}^{lo}, X_{k,1}^{up}]$. Then, lower and upper bounds X_{k,l_s+1}^{lo} , X_{k,l_s+1}^{up} on X_{k,l_s+1} are given by

$$X_{k,l_s+1}^{lo} = v_s^{lo} Y_{k,l_s}^{lo} + (1 - v_s^{lo}) X_{k,1}^{lo}, \quad X_{k,l_s+1}^{up} = v_s^{up} Y_{k,l_s}^{up} + (1 - v_s^{up}) X_{k,1}^{up}.$$

Lemma 5. (Rectifying Section)

Consider any $l_r \in \{1, \dots, u\}$ and $k \in \{1, \dots, n\}$. Assume further that v_r ranges on $[v_r^{lo}, v_r^{up}]$, X_{k,l_r} ranges on $[X_{k,l_r}^{lo}, X_{k,l_r}^{up}]$ and that $Y_{k,1}$ ranges on $[Y_{k,1}^{lo}, Y_{k,1}^{up}]$. Then, lower and upper bounds Y_{k,l_r+1}^{lo} , Y_{k,l_r+1}^{up} on Y_{k,l_r+1} are given by

$$Y_{k,l_r+1}^{lo} = v_r^{up} X_{k,l_r}^{lo} + (1 - v_r^{up}) Y_{k,1}^{lo}, \quad Y_{k,l_r+1}^{up} = v_r^{lo} X_{k,l_r}^{up} + (1 - v_r^{lo}) Y_{k,1}^{up}.$$

It is worth to mention that Equation (29) does not hold for the variables used for the molar fractions in the original model formulation from Section 2, e.g., see molar fraction profile of second component (green curve) in Figure 2 (a). Thus, Lemma 4 and Lemma 5 are not applicable in that case.

The purity constraints (17) already provide (strong) valid bounds on the concentration variables at the condenser and, hence, at the first tray of the rectifying section as well as on the concentration variables at the reboiler and the first tray (in our ordering) of the stripping section. Starting with these bounds, our next goal is to propagate bounds on the concentration variables tray by tray through each section by repeatedly applying the formulas for bound calculations from Lemma 4 and Lemma 5. This procedure defines the bound tightening strategy.

However, a re-use of the formulas from Lemma 4 and Lemma 5 will make it necessary to translate bounds on the aggregated concentration variables associated with the vapor or the liquid phase into valid bounds on the aggregated concentration variables in the other phase. This is achieved by exploiting the phase equilibrium equations (14) and their inverses (25), respectively, and leads to the formulas as given in Lemma 6 (for the stripping section) and in Lemma 7 (for the rectifying section). Again, superscripts “strip” and “rect” are omitted to keep the statements easy to read. The proofs are postponed to Appendix B.

Lemma 6. (Stripping Section)

Let $l_s \in \{1, \dots, u + 1\}$ be fixed. Assume further that, for every $k \in \{1, \dots, n\}$, lower and upper bounds X_{k,l_s}^{lo} , X_{k,l_s}^{up} on X_{k,l_s} are given, where

$$X_{k,l_s}^{lo} \leq X_{k+1,l_s}^{lo} \quad \text{and} \quad X_{k,l_s}^{up} \leq X_{k+1,l_s}^{up}, \quad \text{hold for } k = 1, \dots, n.$$

Then, for each k , lower and upper bounds Y_{k,l_s}^{lo} , Y_{k,l_s}^{up} on Y_{k,l_s} are given by

$$Y_{k,l_s}^{lo} = \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s}^{a_k} - X_{j-1,l_s}^{a_k})}{\sum_{j=1}^n \alpha_j (X_{j,l_s}^{a_k} - X_{j-1,l_s}^{a_k})} \quad \text{and} \quad Y_{k,l_s}^{up} = \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s}^{b_k} - X_{j-1,l_s}^{b_k})}{\sum_{j=1}^n \alpha_j (X_{j,l_s}^{b_k} - X_{j-1,l_s}^{b_k})},$$

where we define for $j = 1, \dots, n$

$$X_{j,l_s}^{a_k} := \begin{cases} X_{j,l_s}^{lo}, & \text{if } j \leq k, \\ X_{j,l_s}^{up}, & \text{if } j > k, \end{cases} \quad \text{and} \quad X_{j,l_s}^{b_k} := \begin{cases} X_{j,l_s}^{up}, & \text{if } j \leq k, \\ \max\{X_{k,l_s}^{up}, X_{j,l_s}^{lo}\}, & \text{if } j > k. \end{cases}$$

Lemma 7. (Rectifying Section)

Let $l_r \in \{1, \dots, u+1\}$ be fixed. Assume further that, for every $k \in \{1, \dots, n\}$, lower and upper bounds Y_{k,l_r}^{lo} , Y_{k,l_r}^{up} on Y_{k,l_r} are given, where

$$Y_{k,l_r}^{lo} \leq Y_{k+1,l_r}^{lo} \quad \text{and} \quad Y_{k,l_r}^{up} \leq Y_{k+1,l_r}^{up}, \quad \text{hold for } k = 1, \dots, n.$$

Then, for each k , lower and upper bounds X_{k,l_r}^{lo} , X_{k,l_r}^{up} on X_{k,l_r} are given by

$$X_{k,l_r}^{lo} = \frac{\sum_{j=1}^k \alpha_j^{-1} (Y_{j,l_r}^{a_k} - Y_{j-1,l_r}^{a_k})}{\sum_{j=1}^n \alpha_j^{-1} (Y_{j,l_r}^{a_k} - Y_{j-1,l_r}^{a_k})} \quad \text{and} \quad X_{k,l_r}^{up} = \frac{\sum_{j=1}^k \alpha_j^{-1} (Y_{j,l_r}^{b_k} - Y_{j-1,l_r}^{b_k})}{\sum_{j=1}^n \alpha_j^{-1} (Y_{j,l_r}^{b_k} - Y_{j-1,l_r}^{b_k})},$$

where we define for $j = 1, \dots, n$

$$Y_{j,l_r}^{a_k} := \begin{cases} \min\{Y_{j,l_r}^{up}, Y_{k,l_r}^{lo}\}, & \text{if } j < k, \\ Y_{j,l_r}^{up}, & \text{if } j \geq k, \end{cases} \quad \text{and} \quad Y_{j,l_r}^{b_k} := \begin{cases} Y_{j,l_r}^{lo}, & \text{if } j < k, \\ Y_{j,l_r}^{up}, & \text{if } j \geq k. \end{cases}$$

5.2. Fixed Points

A further way to tighten the model formulation from Section 3 is to determine the fixed points from the recursive functions given by the component mass balance equations (12) and the phase equilibrium equations (14). Corollaries 2 and 3 imply that, for each aggregated component k , the four infinite sequences

$$\{X_{k,l_s}^{\text{strip}}\}_{l_s \in \mathbb{Z}_{\geq 1}}, \{Y_{k,l_s}^{\text{strip}}\}_{l_s \in \mathbb{Z}_{\geq 1}} \quad \text{and} \quad \{X_{k,l_r}^{\text{rect}}\}_{l_r \in \mathbb{Z}_{\geq 1}}, \{Y_{k,l_r}^{\text{rect}}\}_{l_r \in \mathbb{Z}_{\geq 1}}$$

must converge since they are monotonic and range on the bounded interval $[0, 1]$. Due to the monotonic behavior, the limit of each sequence further

provides either a lower or an upper bound valid for each element of the sequence. As done in [15] for the binary case, we can exploit that property by incorporating, for each $k \in \{1, \dots, n\}$, the following (redundant) non-linear constraints to the aggregated model formulation.

$$\begin{aligned}
X_k^{\text{strip},\star} &= v_s Y_k^{\text{strip},\star} + (1 - v_s) X_{k,1}^{\text{strip}}, \\
Y_k^{\text{strip},\star} &= \frac{\sum_{j=1}^k \alpha_j (X_j^{\text{strip},\star} - X_{j-1}^{\text{strip},\star})}{\sum_{j=1}^n \alpha_j (X_j^{\text{strip},\star} - X_{j-1}^{\text{strip},\star})}, \\
X_k^{\text{strip},\star} &\geq X_{k,l_s}^{\text{strip}}, \quad Y_k^{\text{strip},\star} \geq Y_{k,l_s}^{\text{strip}}, \quad l_s = 1, \dots, u^{\text{strip}} + 1, \\
Y_k^{\text{rect},\star} &= v_r X_k^{\text{rect},\star} + (1 - v_r) Y_{k,1}^{\text{rect}}, \\
X_k^{\text{rect},\star} &= \frac{\sum_{j=1}^k \alpha_j^{-1} (Y_j^{\text{rect},\star} - Y_{j-1}^{\text{rect},\star})}{\sum_{j=1}^n \alpha_j^{-1} (Y_j^{\text{rect},\star} - Y_{j-1}^{\text{rect},\star})}, \\
X_k^{\text{rect},\star} &\leq X_{k,l_r}^{\text{rect}}, \quad Y_k^{\text{rect},\star} \leq Y_{k,l_r}^{\text{rect}}, \quad l_r = 1, \dots, u^{\text{rect}} + 1.
\end{aligned} \tag{31}$$

We however remark that, in general, the fixed points lead to weaker bounds than the bounds that can be obtained by the bound tightening strategy.

6. Computational Studies

In this section, we computationally evaluate the impact of the presented techniques on the performance of global optimization software. For this, we consider several numerical test instances dealing with ideal multi-component distillation processes. The objective of all instances is to find an optimal column design w.r.t. cost function (18) that separates the more volatile components from the less volatile components.

6.1. Test Setting

We consider 16 test instances.

The reference test instance *ex-ref* consists of a mixture of $n = 4$ components with initial composition $x_i^{\text{in}} = \frac{1}{4}$, $i \in \{1, 2, 3, 4\}$, and with the constant relative volatilities $(\alpha_1, \alpha_2, \alpha_3, \alpha_4) = (6, 4, 1.2, 1)$. The number l^{col} of trays that can be used in the entire distillation column is bounded by 25. Every section

consists of at least one tray, so that the upper bound on the number of trays used for the rectifying as well as for the stripping section is given by $u^{\text{rect}} = u^{\text{strip}} = 23$. Molar flows F , B , D and V are given in terms of mols^{-1} . The feed molar flow F is fixed to 1, while the remaining molar flows are variable and may range as follows. $0 \leq V \leq 20$, $0 \leq B, D \leq 1$. We choose the split σ to be 2. Recap from Section 3 that σ defines the more volatile single components $(1, \dots, \sigma)$ withdrawn from the condenser and the less volatile single components $(\sigma + 1, \dots, n)$ withdrawn from the reboiler. With respect to split σ , we call the components σ and $\sigma + 1$ *key* components, while the others are called *non-key* components. The purity requirements are given by $\pi^{\text{dist}} = \pi^{\text{bot}} = 0.99$.

The remaining test instances are defined by changing the values of several parameters, resulting in five groups of further test instances that are briefly explained, next.

The first group is defined by varying the constant relative volatilities for the *non-key* components from the reference instance. The specifications are given in Table 1.

Instance	<i>ex-adis1</i>	<i>ex-adis2</i>	<i>ex-adis3</i>
$(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$	(12, 4, 1.2, 1)	(12, 8, 2.4, 1)	(24, 8, 2.4, 1)

Table 1: Specification of test instances with change in the distribution of volatilities

The second group consists of two further instances for that the split σ is changed. Moreover, the constant relative volatilities are adapted in such a way that the ratios between the volatilities of the key components are the same as in the reference setting. Table 2 shows the concrete specifications.

Instance	<i>ex-apos1</i>	<i>ex-apos2</i>
σ	1	3
$(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$	(6.67, 2, 1.5, 1)	(8, 5, 3.33, 1)

Table 2: Specification of test instances with changing σ

In the third group, we change the initial composition of the mixture as given in Table 3.

Instance	<i>ex-con1</i>	<i>ex-con2</i>	<i>ex-con3</i>
$(x_1^{\text{in}}, x_2^{\text{in}}, x_3^{\text{in}}, x_4^{\text{in}})$	$(\frac{1}{10}, \frac{2}{5}, \frac{2}{5}, \frac{1}{10})$	$(\frac{1}{4}, \frac{2}{5}, \frac{1}{10}, \frac{1}{4})$	$(\frac{1}{4}, \frac{1}{10}, \frac{2}{5}, \frac{1}{4})$

Table 3: Specification of test instances by varying the initial composition of the mixture

Group four consists of the test instances, for that we vary the purity requirements on condenser and reboiler. In addition, we adapt the constant relative volatilities in order to keep the separation processes approximately as difficult as the separation process of the reference instance. Table 4 provides the specific setting for the changed parameters.

Instance	<i>ex-pur1</i>	<i>ex-pur2</i>	<i>ex-pur3</i>
$(\pi^{\text{dist}}, \pi^{\text{bot}})$	(0.95, 0.95)	(0.99, 0.95)	(0.95, 0.99)
$(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$	(3.64, 2.42, 1.2, 1)	(4.62, 3.08, 1.2, 1)	(4.62, 3.08, 1.2, 1)

Table 4: Specification of test instances with different purity requirements

Finally, we define a fifth group of test instances where different numbers of components are considered. For each such instance, we adapt split σ , initial composition and relative volatilities accordingly, as summarized in Table 5.

Instance	<i>ex-comp1</i>	<i>ex-comp2</i>	<i>ex-comp3</i>	<i>ex-comp4</i>
n	2	3	5	5
σ	1	1	2	1
$(x_1^{\text{in}}, \dots, x_n^{\text{in}})$	$(\frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{8}, \frac{1}{8})$	$(\frac{1}{2}, \frac{1}{4}, \frac{1}{10}, \frac{3}{40}, \frac{3}{40})$
$(\alpha_1, \dots, \alpha_n)$	(3.33, 1)	(4, 1.2, 1)	(6, 4, 1.2, 1.1, 1)	(6.67, 2, 1.5, 1.2, 1)

Table 5: Test instances where the number of components is changed

6.2. Results

For each instance, two MINLP formulations are derived. The first formulation, called *MINLP-orig*, is based on the original distillation column model

as presented in Section 2. The second formulation makes use of the model formulation with aggregated concentration variables introduced in Section 3 and is called *MINLP-ref*. Both formulations have been implemented using the following standard reformulation techniques. Due to their redundancy, all variables that are associated with the (corresponding) last component n as well as the variables $x_i^{\text{dist}}, x_i^{\text{bot}}, i = 1, \dots, n$, and $X_k^{\text{dist}}, X_k^{\text{bot}}, k = 1, \dots, n$, are eliminated. Moreover, each rational function appearing in one of the model constraints is expanded by its denominator and restated by polynomial constraints.

All MINLPs are implemented and solved within a SCIP 3.2 framework [1] using CPLEX 12.6.0 [14] as LP-sub-solver and IPOPT 3.12.4 [27] (incl. HSL-routines [13]) as NLP-sub-solver.

Additionally, we apply several different solution strategies to *MINLP-ref*. The first strategy, indicated by *w/ Mo*, adds the (redundant) conditions on monotonicity from Corollaries 2 and 3. The second strategy takes the fixed-point equations (31) into account and is labeled by *w/ Fix*. In the third strategy, the bound tightening procedure as described in Section 5 is used at every node in the branch and bound tree. This is achieved by implementing a domain propagation routine as an own `constraint_handler` in SCIP. The label *w/ BT* indicates that the bound tightening strategy is switch on.

All computations are carried out on a 3.00GHz Intel Xeon E5450 Processor with a limit of 30 GB memory space for each run. Moreover, running time is limited to 24 hours and the relative optimality gap is chosen to be 10^{-4} . Symbol `time` indicates that the corresponding instance is not solved within the given time limit.

Our computational results are summarized in Table 6. Using the original formulation *MINLP-orig*, most instances are not solved to global optimality within the time limit (see Column 2 of Table 6). For some instances, this is also the case when formulation *MINLP-ref* is used (see Column 3 of Table 6). Using *MINLP-ref* we, however, observe less running times for those instances that are solved within the time limit.

Adding the (redundant) monotonicity conditions and the fixed point equations (*w/ Mo* and *w/ Mo, Fix*) has a mixed influence on the running time (see Columns 3,4 of Table 6). On the one hand, some instances are solved faster or can only be solved in the time limit with the additional strategies. On the other hand, there are instances that need more running time or even exceed the time limit.

Ex.	MINLP -orig	MINLP -ref	MINLP-ref w/ Mo	MINLP-ref w/ Mo, Fix	MINLP-ref w/ BT	MINLP-ref w/ Mo, BT
<i>ref</i>	time	7151	time	67801	2419	11948
<i>adis1</i>	42117	16564	2715	9783	327	2134
<i>adis2</i>	time	84832	2827	5273	1009	541
<i>adis3</i>	time	time	3817	1865	1536	483
<i>apos1</i>	71870	6530	49186	3592	8014	2976
<i>apos2</i>	time	time	9911	5494	312	181
<i>con1</i>	31080	8056	1311	27391	1102	352
<i>con2</i>	time	time	66749	3178	332	1186
<i>con3</i>	time	9566	20944	28785	1958	789
<i>pur1</i>	time	72917	70301	12230	26859	2815
<i>pur2</i>	time	23620	38988	70112	1961	593
<i>pur3</i>	time	26157	time	time	1126	395
<i>comp1</i>	136	62	74	27	12	11
<i>comp2</i>	3254	464	281	1066	239	234
<i>comp3</i>	time	time	6534	time	871	562
<i>comp4</i>	time	time	15914	8291	2130	3658

Table 6: Running time in CPU seconds using the SCIP framework. Label time means that the time limit of 24 hours of computation time is exceeded.

When applying the bounding tightening strategy *w/ BT*, we first notice that all instances are globally solved within the time limit (see Column 5 of Table 6). Our results further show that the use of that strategy has a positive influence on the running time for all but instance *apos1*. When the bound tightening strategy is combined with the strategy that adds the redundant conditions on the monotonicity (*w/ Mo, BT*), similar observations can be made (see Column 6 of Table 6).

Comparing our results for *MINLP-orig* either with the results for *MINLP-ref w/ BT* or with the results for *MINLP-ref w/ BT, Mo*, it turns out that on average the running times are reduced to less than 5% in the latter cases. In these calculations, the running time is set to the time limit of 24 hours of computation time for those instances exceeding it.

6.3. Optimization using Gams

For sake of completeness, we finally investigate the computational behavior of non-opensource software packages on our MINLP formulations. For this, we chose the global optimization solvers BARON 16.3.4 [24] and SCIP 3.2 as provided within the modeling system GAMS 24.7.1[10]. We remark that our focus is on the question how the solvers work on the different model formulations rather than on comparing the performances of the solvers against each other.

Again, the computations are carried out on a 3.00GHz Intel Xeon E5450 Processor with a limit of 30 GB memory space, a time limit of 24 hours of computation time and relative optimality gap of 10^{-4} , for each run. Both solvers are used with default settings, CPLEX as LP-subsolver and CONOPT (for BARON) and IPOPT (for SCIP) as NLP-subsolver.

In the following, we consider the model formulations *MINLP-orig*, *MINLP-ref* and *MINLP-ref w/ Mo, Fix* as defined in Subsection 6.2. We are not able to implement the bound-tightening strategy in the non-open-source environment GAMS, so that this strategy is excluded from further considerations.

As most of the test instances from Subsection 6.1 could not be solved within the time limit of 24 hours computation time, we derive from our reference test instance *ex-ref* a new test set consisting of four simpler separation tasks. The specifications of the parameters differing from *ex-ref* are given in Table 7.

Instance	<i>exg-ref</i>	<i>exg-adis</i>	<i>exg-apos</i>	<i>exg-fcon</i>
σ	2	2	1	2
$u^{\text{col}}/u^{\text{rect}}/u^{\text{strip}}$	10/8/8	10/8/8	10/8/8	10/8/8
$(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$	(24, 16, 1.2, 1)	(48, 16, 1.2, 1)	(26.67, 2, 1.5, 1)	(24, 15, 1.2, 1)
$(x_1^{\text{in}}, x_2^{\text{in}}, x_3^{\text{in}}, x_4^{\text{in}})$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$(\frac{1}{10}, \frac{2}{5}, \frac{2}{5}, \frac{1}{10})$

Table 7: Specification of the test setting used for the computations with GAMS

The computational results obtained by applying the solvers BARON and SCIP are displayed in Tables 8 and 9, respectively. The results indicate that the proposed formulation in terms of the aggregated components as well as the

redundant monotonicity conditions and fixed point constraints can have a quite positive influence on the running time, even though this does not hold for every test instance.

Instance	<i>MINLP-orig</i>	<i>MINLP-ref</i>	<i>MINLP-ref</i> <i>w/ Mo, Fix</i>
<i>exg-ref</i>	4649	894	61
<i>exg-adis</i>	183	321	66
<i>exg-apos</i>	140	1612	147
<i>exg-con</i>	1886	2770	141

Table 8: Running time in seconds using the GAMS software, solver: BARON.

Instance	<i>MINLP-orig</i>	<i>MINLP-ref</i>	<i>MINLP-ref</i> <i>w/ Mo, Fix</i>
<i>exg-ref</i>	529	31	72
<i>exg-adis</i>	391	80	57
<i>exg-apos</i>	44	66	88
<i>exg-con</i>	116	28	36

Table 9: Running time in seconds using the GAMS software, solver: SCIP.

7. Conclusion

This article introduced a reformulation of the variables used for mole fractions of ideal multi-component distillation column models. The reformulated variables turned out to be monotonic, which allowed us to design a bound tightening strategy and to apply it onto deterministic global optimization software. It was shown that a significant reduction in running time is already given by using the reformulated model. Further significant reduction was achieved with the proposed problem-specific bound tightening strategy. Focus in the present paper was on simple column configurations and ideal thermodynamics. Future work will focus on global optimization of more complex column configurations, including hybrid separation processes as well as non-ideal thermodynamics.

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A. Proof of Corollary 3

Consider system (26) with parameters $\alpha_1 \geq \alpha_2 \geq \dots \geq \alpha_n > 0$ and variables (Y, v_r) . We show that applying the transformation rules (27) to (Y, v_r) and $\alpha_1, \dots, \alpha_n$ leads to system (28) with parameters $\hat{\alpha}_1 \geq \hat{\alpha}_2 \geq \dots \geq \hat{\alpha}_n > 0$ and with variables \hat{X}, \hat{v}_s whose feasible solutions satisfy the conditions of Theorem 1 (and Corollary 2). Note that feasible solutions to system (26) are in one-to-one correspondence to solutions feasible to (28) via the transformation rules (27). As we obtain from Corollary 2 that, for every feasible solution (\hat{X}, \hat{v}_s) , the sequences $\{\hat{X}_{k,l_s}\}_{l_s=1}^{\hat{u}+1}$ with $k = 1, \dots, n$ are non-decreasing, the corresponding sequences $\{Y_{k,l_r}\}_{l_r=1}^{u+1}$, $k = 1, \dots, n$ are non-increasing.

The first part of system (26) is given as a combination of the mass balance equations (12) and the inverted phase equilibrium equations (25).

$$Y_{k,l_r+1} = v_r X_{k,l_r} + (1 - v_r) Y_{k,1} \quad \text{and} \quad X_{k,l_r} = \frac{\sum_{j=1}^k \alpha_j^{-1} (Y_{j,l_r} - Y_{j-1,l_r})}{\sum_{j=1}^n \alpha_j^{-1} (Y_{j,l_r} - Y_{j-1,l_r})},$$

for $k \in \{1, \dots, n\}$ and $l_r \in \{1, \dots, u\}$. We apply the transformation rules (27) to each constraint, separately. Recap that after the transformation, the components appear in reverse order. To indicate that, we introduce a new index $m := n - k$.

For all $k \in \{0, \dots, n\}$ and all $l \in \{1, \dots, u\}$, we obtain

$$\begin{aligned} Y_{k,l+1} = v_r X_{k,l} + (1 - v_r) Y_{k,1} &\Leftrightarrow (1 - Y_{k,l+1}) = 1 - (v_r X_{k,l} + (1 - v_r) Y_{k,1}) \\ &\Leftrightarrow (1 - Y_{k,l+1}) = v_r (1 - X_{k,l}) + (1 - v_r) (1 - Y_{k,1}). \end{aligned}$$

Thus, the transformation rules (27) yield

$$\hat{X}_{k,l+1} = \hat{v}_s \hat{Y}_{k,l} + (1 - \hat{v}_s) \hat{X}_{k,1}, \quad m = 0, \dots, n, \quad l = 1, \dots, u. \quad (32)$$

For the inverted phase equilibrium equations, we further derive that

$$\begin{aligned}
\hat{Y}_{n-k,l} &= 1 - X_{k,l} = \left(1 - \frac{\sum_{j=1}^k \alpha_j^{-1}(Y_{j,l} - Y_{j-1,l})}{\sum_{j=1}^n \alpha_j^{-1}(Y_{j,l} - Y_{j-1,l})}\right) = \frac{\sum_{j=k+1}^n \alpha_j^{-1}(Y_{j,l} - Y_{j-1,l})}{\sum_{j=1}^n \alpha_j^{-1}(Y_{j,l} - Y_{j-1,l})} \\
&= \frac{\sum_{j=k+1}^n \alpha_j^{-1}((1 - \hat{X}_{n-j,l} - (1 - \hat{X}_{n-(j-1),l}))}{\sum_{j=1}^n \alpha_j^{-1}((1 - \hat{X}_{n-j,l} - (1 - \hat{X}_{n-(j-1),l}))} \\
&= \frac{\sum_{j=k+1}^n \alpha_j^{-1}(\hat{X}_{n-(j-1),l} - \hat{X}_{n-j,l})}{\sum_{j=1}^n \alpha_j^{-1}(\hat{X}_{n-(j-1),l} - \hat{X}_{n-j,l})} = \frac{\sum_{j=k+1}^n \hat{\alpha}_{n+1-j}(\hat{X}_{n+1-j,l} - \hat{X}_{n-j,l})}{\sum_{j=1}^n \hat{\alpha}_{n+1-j}(\hat{X}_{n+1-j,l} - \hat{X}_{n-j,l})}
\end{aligned}$$

holds for every $k \in \{1, \dots, n\}$ and for every $l \in \{1, \dots, u+1\}$. By an index shift $p := n+1-j$, we derive the equivalence to the non-inverted phase equilibrium equation (14).

$$\begin{aligned}
\hat{Y}_{n-k,l} &= \frac{\sum_{p=1}^{n-k} \beta_p(\hat{X}_{p,l} - \hat{X}_{p-1,l})}{\sum_{p=1}^n \beta_p(\hat{X}_{p,l} - \hat{X}_{p-1,l})}, & n &= 0, \dots, n \\
& & l &= 1, \dots, u+1 \\
\Leftrightarrow \hat{Y}_{m,l} &= \frac{\sum_{p=1}^m \beta_p(\hat{X}_{p,l} - \hat{X}_{p-1,l})}{\sum_{p=1}^{n+1} \beta_p(\hat{X}_{p,l} - \hat{X}_{p-1,l})}, & m &= 0, \dots, n \\
& & l &= 1, \dots, u+1
\end{aligned} \tag{33}$$

Combining equation (32) and (33), we obtain the first line from system (28).

The second line of system (28) results from the following relation.

$$Y_{k+1,l} \geq Y_{k,l}, \quad k = 0, \dots, n-1 \quad \Leftrightarrow \quad \hat{X}_{m-1,l} \leq \hat{X}_{m,l}, \quad m = 1, \dots, n.$$

The third line of system (28) trivially holds.

It remains to argue that the transformed constant relative volatilities $\hat{\alpha}_m = \alpha_{(n+1)-m}^{-1}$, $m = 1, \dots, n$, are strictly positive and monotonically non-decreasing in the new ordering of the components. This, however, holds as $\alpha_1 \geq \dots \geq \alpha_n > 0$ implies that

$$0 < \alpha_1^{-1} \equiv \hat{\alpha}_n \leq \dots \leq \alpha_n^{-1} \equiv \hat{\alpha}_1.$$

Now, we can conclude that any feasible solution to system (28) satisfies the conditions of Theorem 1 and Corollary 2. \square

B. Proof of Lemma 6 and Lemma 7

We only give a proof for Lemma 6 dealing with the stripping section. The correctness of Lemma 7 can be shown in a similar way.

In what follows, superscript “strip” is omitted, again.

Proof. (Lemma 6)

We interpret the aggregated phase equilibrium equations (14)

$$Y_{k,l_s}(X) = \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s})}$$

as functions in the liquid phase concentration variables. For all $k, q \in \{1, \dots, n\}$ and for all $l_s \in \{1, \dots, u + 1\}$, we consider the partial derivatives $\partial Y_{k,l_s}(X) / \partial X_{q,l_s}$ where we distinguish the three cases $q \leq k - 1$, $q = k$ and $q \geq k + 1$. To keep notation short, we introduce constant $\alpha_{n+1} := 0$.

For $q \leq k - 1$, we obtain

$$\begin{aligned} \frac{\partial Y_{k,l_s}(X)}{\partial X_{q,l_s}} &= \frac{(\alpha_q - \alpha_{q+1}) \sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{(\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}))^2} - \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})(\alpha_q - \alpha_{q+1})}{(\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}))^2} \\ &= \frac{(\alpha_q - \alpha_{q+1}) \sum_{j=k+1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{(\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}))^2}. \end{aligned}$$

As $(\alpha_q - \alpha_{q+1}) \geq 0$ holds, this derivative is non-negative for all $k \in \{1, \dots, n\}$ and all $l_s \in \{1, \dots, u + 1\}$.

For $q = k$ we obtain

$$\begin{aligned} \frac{\partial Y_{q,l_s}(X)}{\partial X_{q,l_s}} &= \frac{\alpha_q \sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}) - \sum_{j=1}^q \alpha_j (X_{j,l_s} - X_{j-1,l_s})(\alpha_q - \alpha_{q+1})}{(\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}))^2} \\ &= \frac{\alpha_q \sum_{j=q+1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}) + \alpha_{q+1} \sum_{j=1}^q \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{(\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}))^2}, \end{aligned} \quad (34)$$

which is also non-negative for all $q \in \{1, \dots, n\}$ and all $l_s \in \{1, \dots, u + 1\}$.

For $q \geq k + 1$ we obtain

$$\frac{\partial Y_{k,l_s}(X)}{\partial X_{q,l_s}} = \frac{-\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})(\alpha_q - \alpha_{q+1})}{(\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s}))^2}, \quad (35)$$

which is non-positive for all $k \in \{1, \dots, n\}$ and all $l_s \in \{1, \dots, u + 1\}$ due to $(\alpha_q - \alpha_{q+1}) \geq 0$.

This shows that the phase equilibrium equations are component-wise monotonic. Therefore, we can apply simple interval arithmetic, again, leading to following lower and upper bounds on the vapor phase concentration variables Y_{k,l_s+1} .

$$Y_{k,l_s}^{\text{lo}} = \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s}^{a_k} - X_{j-1,l_s}^{a_k})}{\sum_{j=1}^n \alpha_j (X_{j,l_s}^{a_k} - X_{j-1,l_s}^{a_k})} \quad \text{and} \quad Y_{k,l_s}^{\text{up}} = \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s}^{b_k} - X_{j-1,l_s}^{b_k})}{\sum_{j=1}^n \alpha_j (X_{j,l_s}^{b_k} - X_{j-1,l_s}^{b_k})},$$

where for $j = 1, \dots, n$

$$X_{j,l_s}^{a_k} := \begin{cases} X_{j,l_s}^{\text{lo}}, & \text{if } j \leq k, \\ X_{j,l_s}^{\text{up}}, & \text{if } j > k, \end{cases} \quad \text{and} \quad X_{j,l_s}^{b_k} = \begin{cases} X_{j,l_s}^{\text{up}}, & \text{if } j \leq k, \\ X_{j,l_s}^{\text{lo}}, & \text{if } j > k, \end{cases} \quad (36)$$

We remark that the upper bound Y_{k,l_s}^{up} on Y_{k,l_s} is not tight when $X_{k,l_s}^{\text{up}} > X_{k',l_s}^{\text{lo}}$ holds for some $k' > k$. In those cases, we can compute an improved upper bound on Y_{k,l_s} by finding the maximum of

$$Y_{k,l_s}(X) = \frac{\sum_{j=1}^k \alpha_j (X_{j,l_s} - X_{j-1,l_s})}{\sum_{j=1}^n \alpha_j (X_{j,l_s} - X_{j-1,l_s})}$$

restricted to $X_{k',l_s}^{\text{lo}} \leq X_{k,l_s} \leq X_{k',l_s} \leq X_{k,l_s}^{\text{up}}$. As $\partial Y_{k,l_s}(X)/\partial X_{k,l_s} \geq 0$ and $\partial Y_{k,l_s}(X)/\partial X_{k',l_s} \leq 0$, it follows that $X_{k,l_s} = X_{k',l_s}$ must hold for a solution on that the maximum is attained. A comparison of Equations (34) and (35) gives rise to the relation

$$\frac{\partial Y_{k,l_s}(X)}{\partial X_{k,l_s}} + \sum_{j=k+1}^n \frac{\partial Y_{k,l_s}(X)}{\partial X_{j,l_s}} \geq 0.$$

This shows that the maximum is attained when $X_{k,l_s} = X_{k',l_s} = X_{k,l_s}^{\text{up}}$. Hence, we can replace the definition of $X_{j,l_s}^{b_k}$ in Equation (36) by

$$X_{j,l_s}^{b_k} = \begin{cases} X_{j,l_s}^{\text{up}}, & \text{if } j \leq k, \\ \max\{X_{k,l_s}^{\text{up}}, X_{j,l_s}^{\text{lo}}\}, & \text{if } j > k. \end{cases}$$

This completes the proof. \square