

New MINLP Model and Modified Outer Approximation Algorithm for Distillation Column Synthesis

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A new, *R*-graph based, superstructure and corresponding MINLP model for designing conventional distillation columns are presented. A GDP representation (GR) of the superstructure is first constructed, then it is transformed to MINLP representation to which, in turn, additional trivial improvements are added. The new model has been tested on binary mixture examples, and the obtained results are compared to the results of an MINLP model which developed according to the GDP model of Yeomans and Grossmann.⁹ The new model yields shorter computation time and provides better local optima. Additionally, the new model has been used for optimizing a complex multicomponent separation system consisting of several distillation columns. In order to handle such a complex system with a huge number of nonlinear equations, the outer approximation algorithm is modified to provide good initial values for the NLP subproblems.

1. Introduction

Distillation is one of the most widespread processes applied for separating multicomponent liquid mixtures. It is used for working up large volume or stream, and it requires high investment and operation outlays. The significance of the design of economically optimal distillation processes is of no question. Enormous interest has also been addressed to the area of designing optimal heat integrated distillation columns and distillation sequences. Minimizing the cost of a distillation process implies finding the optimal configuration of each individual column, as well. In the present article we consider staged column models only. The number of stages, and the stage numbers of the feed and side-stream points, are discrete decision variables. The total cost of a column may be modeled as the sum of the fix (capital) cost, depending on the number of stages and on the column diameter, and the variable (operation) cost related to the utility consumption. The objective of the design procedure is to find the optimal configuration of the column, which has the minimum total (annualized) cost. In order to model these processes, discrete decisions are required for calculating the number of stages.

Optimizing single columns is a well-known procedure; all the basic textbooks outline how to do it in an easy manner.¹ After approximately determining the minimum and the estimated optimal number of theoretical stages, optimizing over the continuous variables is performed at varied values of the discrete variables. This is a 2-dimension discrete array of continuous optimization tasks in the case of a single-feed, two-product column, because there are merely two column sections in this case. This task becomes much more difficult if several feeds and side-products are to be taken into account. The real problem, however, is synthesizing a distillation sequence, or a system of advanced distillation columns, or a complex flowsheet containing distillation units when the number of distillation columns and their connections are not known in advance.

In order to solve the complex synthesis problem outlined above, a proper superstructure for a single column, together with

a proper generalized disjunctive programming (GDP) model or a proper mixed-integer nonlinear programming (MINLP) model, is a minimum requirement. Once such a model works well for a single column, the problem of more complex flowsheets may also be addressed.

Mixed-integer nonlinear programming (MINLP) and generalized disjunctive programming (GDP) are the two exact methodologies commonly applied for solving process engineering problems with discrete decisions. The former includes algebraic equations describing the process, and binary variables related to discrete decisions. The latter method uses logic variables and expressions to represent the problem.² Both formulations have been successfully applied to rigorous models of distillation columns. Both methods apply a fixed maximum number of stages, and the actually used stages are selected from this set.

Mathematical formulations that represent rigorous models of distillation column configurations fall into two categories: (i) one task-one equipment (OTOE) representations and (ii) variable task-equipment (VTE) representations.³

In the OTOE representation, each stage has one task to work as an equilibrium stage. If a particular stage is not included in the structure, then that stage is bypassed.^{4–6} A boiler is located below the lowest stage of the column, and a condenser is located above the top stage. Binary variables represent the location of the feed stage, and the locations (i.e., stages) where the returning streams after condensation and boiling are led back to the column, i.e., the stage where the reflux stream is entered to, and where the reboiled vapor stream is entered to, respectively. Stages above the reflux stream location and below the reboiled vapor stream location do not exist in the solution; whereas all the other stages exist. Within this representation, there are three main different arrangements⁷ according to the specifications. (1) The sequence number of the feed stage is specified as parameter, whereas the stages where the reboil and reflux flows enter the column are variables. (2) The sequence number of the stage where the reboiled vapor enters the column is given, whereas the feed and the reflux inlet stage locations are variable. (3) The sequence number of the stage where the reflux stream enters the column is given, whereas the locations of the feed and the reboiled vapor streams are variables.

In the VTE representation, each stage has two alternative tasks. Each can behave as either an equilibrium stage or as an

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input-output operation in the stage with no mass transfer between the phases. Logic or binary variables assign which task of a stage is performed in the structure.^{8,9}

Ciric and Gu¹⁰ applied the OTOE approach to nonequilibrium reactive distillation processes. Smith and Pantelides¹¹ used the MINLP representation for designing reaction/separation networks. Bauer and Stilchmair¹² successfully applied this approach to separation of azeotropic mixtures. They chose the conception of denoting the location of the reboiler and the feed tray with binary variables. Dunneber and Pantelides¹³ also used the basic conception of the MINLP model for optimizing single columns; here the variables were the positions of the reflux and the feed streams. Bartfeld and co-workers⁷ provided a thorough comparison, and pointed out that the computationally most efficient arrangement involves variable reboiler and feed tray location.

The VTE approach was used for modeling distillation column by Yeomans and Grossmann.^{8,9} Here a GDP representation is used. The feed stage, the condenser, and the reboiler, are permanent units; the others are conditional. This approach was also applied successfully to reactive distillation column by Jackson and Grossmann.¹⁴ Here the feed location is also considered variable. Caballero and co-workers¹⁵ integrated their GDP models with a process simulator.

Bartfeld and co-workers⁷ provided an overview on the alternative representations invented for modeling distillation columns, and compared them on examples from computational point of view. They found that the most efficient formulation is the GDP representation since the MINLP formulations required longer computation time than the appropriate GDP representation, in all cases.

In order to improve the convergence properties of the solution algorithm, several straightforward methods have been constructed which use appropriate estimation of the bounding and initial values. Fletcher and Morton¹⁶ applied the approximation of infinite reflux ratio (i.e., total reflux) and minimum number of stages. The opposite version, with minimum reflux ratio and maximum allowed number of stages was used by Bartfeld and Aguirre,¹⁷ in order to find good initial values.

Although the problem of optimizing a process consisting of a single distillation column may be already considered as solved, the synthesis of complex distillation column systems is still a widely studied research area. In case of a larger problem, the strong nonlinearities and nonconvexities can cause problems in convergence even during the solution processes of single NLPs.

The most recent works in the topic are those of Bartfeld and co-workers¹⁸ and Grossmann et al.¹⁹ The latter reviewed the available superstructures for multicomponent distillation sequence and provided a numerical example with a superstructure containing several complex distillation columns. They successfully applied a decomposition strategy which first selects the column section and then optimizes the number of trays in it. However, they obviously had difficulties with solving NLPs (three NLPs required 54.7 min).

Considering these problems, it is still an interesting task to elaborate a model for a single column, keeping in mind the problem of finding a solution for complex systems. In the present paper, we first propose a new MINLP model for the synthesis of single conventional distillation columns with one feed and two products; the model is based on an *R*-graph representation of a superstructure.²⁰ Then using this model as a building block, we provide a modified MINLP algorithm for optimizing complex distillation systems. As the large number of nonlinear equations cause problems during the outer ap-

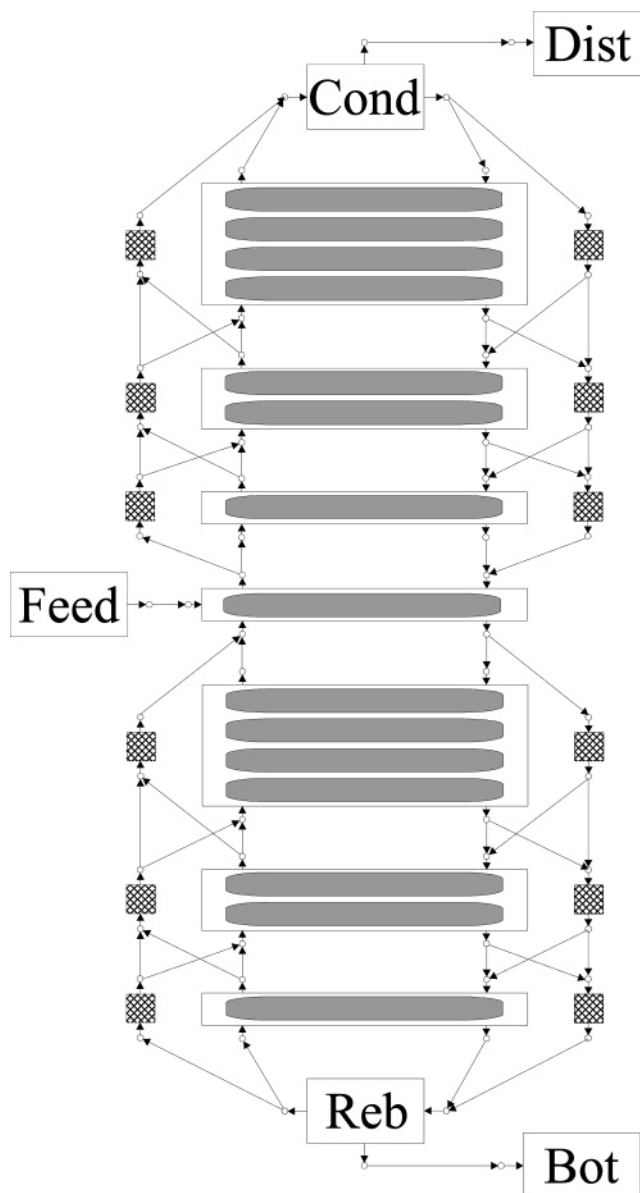


Figure 1. *R*-graph representation of the superstructure.

proximation algorithm, we insert an extra step before the NLP subproblems in each iteration.

The *R*-graph based new superstructure is presented as the basis of the GDP representation. The GDP representation derived from the superstructure, and then the MINLP representation obtained from the GDP, are detailed. Finally, numerical examples for testing the computational performance of the obtained model are discussed.

The performance of our model is tested on three separate examples. Two of them are conventional distillation examples; the results with the new modified outer approximation algorithm are presented with the third example, a complex extractive distillation problem with four components and three possible columns.

2. *R*-Graph Representation of the Superstructure

The superstructure of a conventional distillation column consisting of maximum 15 equilibrium trays is represented by an *R*-supergraph shown in Figure 1. The equilibrium stages are represented by shaded ovals, and units of the superstructure are represented by rectangles. Some units contain shaded ovals;

these units represent so many equilibrium stages as shaded ovals. Some other units are hatched; these units represent the so-called vapor and liquid transport units; they have transmission roles only. The small circles represent input or output ports of the units. The edges departing from output ports, and arriving in input ports, represent streams. The edges departing from output ports, and arriving in input ports, represent streams. The edges pointing upward denote the heading direction of the vapor flows; the edges directed downward represent the liquid streams. Each unit containing one or more shaded ovals has a vapor and a liquid transport units on its each side; this triplet form a building block of the column. There is a source unit (Feed), and there are two sink units (Dist and Bot). These sink units represent the product destinations. The reboiler (Reb) and the condenser (Cond) units have two output ports each; in this way, the reflux ratio and the reboil ratio can be calculated with equations belonging to these particular units only.

In *R*-graph representation a unit is permanent, by definition, if all the sub-*R*-graphs contain it.²⁰ Feed, Dist, Bot, Cond, Reb, and the feed stage, are permanent units according to this definition; all the others are conditional.

The number of the equilibrium stages contained in the *k*th unit of a column section (calculated bottom up) is 2^{k-1} . This arrangement is applied in order to facilitate forming MINLP representation with minimum number of binary variables. The computational difficulty of solving an MILP/MINLP problem usually increases with the number of binary variables. Therefore, using as few binary variables as possible is preferable. This can be achieved by modifying the MINLP representation; but in some cases, like the one here, it can also be achieved by working out an appropriate superstructure, and supergraph.

An array of *n* binary variables, applied to distinguish structures, can take 2^n different values. This 2^n has to be at least as large as the number of different structures. If the superstructure includes *k* substructures then the minimum number of the binary variables needed to distinguish them is the lowest integer number which satisfies eq 1.²¹

$$n \geq \log_2 k \quad (1)$$

Consider a distillation column consisting of, for example, 15 equilibrium stages (7 stages above, 7 stages below, and the feed stage), shown in Figure 1. In the column section between the reboiler and the feed stage, selected for an example, eight different structure variants can be conceived of according to the number of equilibrium stages: 0, 1, 2, ..., or 7, in this particular case. It follows that $3 = \log_2 8$ binary variables are necessary to describe this column section.

The number of equilibrium stages contained in the *k*th unit (counted from bottom up) is 2^{k-1} in our superstructure. All the possible stage numbers can be generated with this configuration. For example, three stages can be assembled using the first and the second unit (Figure 2a), four stages are assigned by using the third unit (Figure 2b), five stages are assigned by using the first and the third units (Figure 2c), and so on. All the possible stage numbers are represented by only one graph, and structural redundancy is excluded already at the level of the superstructure in this way. Therefore, there is no need to introduce additional equations to exclude the abundant number of equivalent structures. When a unit is not used in a structure, then it is bypassed through the transport units.

The vapor stream starting, e.g., from the vapor output port of the first unit (containing one equilibrium stage) above the boiler can go to the vapor input port of the second unit, and/or to the input port of the vapor transfer unit shown left to the second unit above the boiler (this is the "second vapor transfer

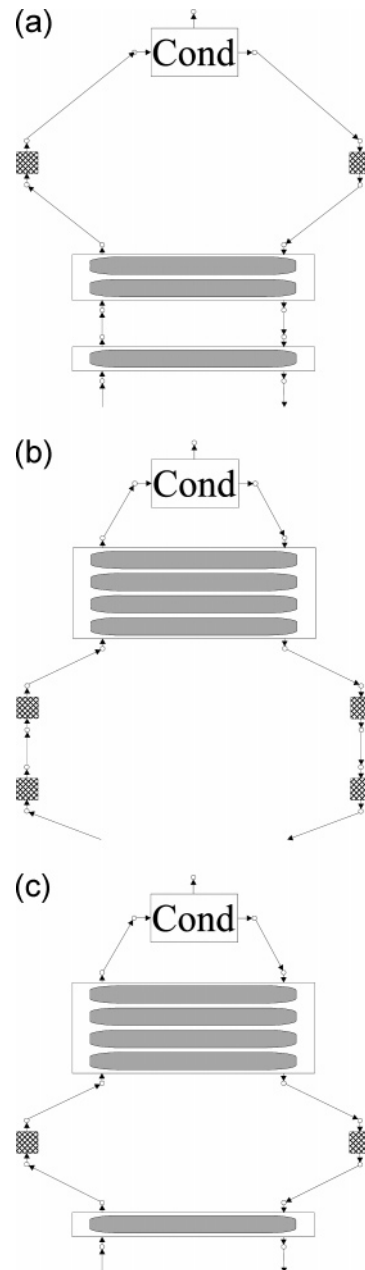


Figure 2. (a) Column section containing 3 equilibrium stages; (b) column section containing 4 equilibrium stages; and (c) column section containing 5 equilibrium stages.

unit"). The vapor input port of the third unit can receive vapor stream from the vapor output port of the second unit and/or from the output port of the second vapor transfer unit. Our intention with this arrangement is to provide a tool for bypassing the second unit and for bypassing any conditional unit in the column in this way. The final target is restricting the set of structures to enable only either the conditional unit in the column without the corresponding vapor and liquid transfer units, or both the corresponding transfer units without the conditional unit in the column. This restriction will be included in the MINLP model, but is not provided in the supergraph representation.

3. GDP Representation (GR)

The basic GDP representation²² is generated according to the *R*-supergraph (*R*-graph of the superstructure). It contains the unit relations, the balances of the ports, logic constraints for

the existence of the units, and the objective function, and it uses distinct logic variables to each conditional units.

The unit relations of the source unit (Feed; eq 2) contain the calculation of the molar feed flows from the total feed flow and the feed compositions, and the calculation of the molar enthalpies of the feed from the feed temperature. The unit relations of the sink units (Bot, Dist; eqs 3 and 4) contain only the trivial positiveness constraints. The unit relations of the condenser (eq 5) and the reboiler (eq 6) include the heat and component balances. The equations given here are valid for total condenser and reboiler only, for the sake of simplicity. In this case, the vapor and liquid mole fractions are equal, and one of them may be omitted. This is why a liquid mole fraction is equal to the mole fraction computed from vapor component flow rates. For partial condenser and reboiler, additional equations are to be inserted to take into account the heat effects. The purity and recovery constraints are specified here, and the variable cost of the column is also calculated here. The unit relations of the fixed feed stage unit (eq 7) contain the MESH equations, and the fix cost of this stage. The column diameter is calculated in the reboiler, in the condenser and in the feed stage. The greatest among these diameters is the real column diameter.

$$F_i = Feed \cdot x_i^{Feed} \quad i \in I \quad (2a)$$

$$hF_i = \Phi_i^h(T^{Feed}) \quad i \in I \quad (2b)$$

$$Dis_i > 0 \quad i \in I \quad (3)$$

$$Bot_i > 0 \quad i \in I \quad (4)$$

$$V_i^{in,C} = L_i^{out,C,L} + L_i^{out,C,D} \quad i \in I \quad (5a)$$

$$QC = \sum_{i \in I} (V_i^{in,C} \cdot hV_i^{in,C} - (L_i^{out,C,L} + L_i^{out,C,D}) \cdot hL_i^{out,C}) \quad (5b)$$

$$hL_i^{out,C} = \Phi_i^h(T^C) \quad i \in I \quad (5c)$$

$$x_i^C = \frac{V_i^{in,C}}{\sum_{i \in I} V_i^{in,C}} \quad i \in I \quad (5d)$$

$$x_i^C = \frac{L_i^{out,C,L}}{\sum_{i \in I} L_i^{out,C,L}} \quad i \in I \quad (5e)$$

$$x_i^C = \frac{L_i^{out,C,D}}{\sum_{i \in I} L_i^{out,C,D}} \quad i \in I \quad (5f)$$

$$Ref = \frac{\sum_{i \in I} L_i^{out,C,L}}{\sum_{i \in I} L_i^{out,C,D}} \quad (5g)$$

$$x_i^C \geq \tau_i^D \quad i \in I \quad (5h)$$

$$x_i^C \leq \lambda_i^D \quad i \in I \quad (5i)$$

$$L_i^{out,C,D} \geq \xi_i^D \cdot F_i \quad i \in I \quad (5j)$$

$$c^C = \Phi^{cC}(QC) \quad (5k)$$

$$L_i^{in,R} = L_i^{out,R} + V_i^{out,R} \quad i \in I \quad (6a)$$

$$QR = \sum_{i \in I} (L_i^{in,R} \cdot hL_i^{in,R} - L_i^{out,R} \cdot hL_i^{out,R} - V_i^{out,R} \cdot hV_i^{out,R}) \quad (6b)$$

$$hL_i^{out,R} = \Phi_i^h(T^R) \quad i \in I \quad (6c)$$

$$hV_i^{out,R} = \Phi_i^H(T^R) \quad i \in I \quad (6d)$$

$$x_i^R = \frac{L_i^{in,R}}{\sum_{i \in I} L_i^{in,R}} \quad i \in I \quad (6e)$$

$$x_i^R = \frac{L_i^{out,R}}{\sum_{i \in I} L_i^{out,R}} \quad i \in I \quad (6f)$$

$$x_i^R = \frac{V_i^{out,R}}{\sum_{i \in I} V_i^{out,R}} \quad i \in I \quad (6g)$$

$$x_i^R \geq \tau_i^R \quad i \in I \quad (6h)$$

$$x_i^R \leq \lambda_i^R \quad i \in I \quad (6i)$$

$$L_i^{out,R} \geq \xi_i^R \cdot F_i \quad i \in I \quad (6j)$$

$$V_s^{crit} \geq \sum_i V_i^{out,R} \quad s = 1 \quad (6k)$$

$$c^R = \Phi^{cR}(QR) \quad (6l)$$

$$V_i^{in,F} + L_i^{in,F} + F_i^{in,F} = V_i^F + L_i^F \quad i \in I \quad (7a)$$

$$L_i^{out,F} = L_i^F \quad i \in I \quad (7b)$$

$$V_i^{out,F} = V_i^F \quad i \in I \quad (7c)$$

$$L_i^F = LIQ^F \cdot x_i^F \quad i \in I \quad (7d)$$

$$V_i^F = VAP^F \cdot y_i^F \quad i \in I \quad (7e)$$

$$\sum_{i \in I} (V_i^{in,F} \cdot hV_i^{in,F} + L_i^{in,F} \cdot hL_i^{in,F} + F_i^{in,F} \cdot hF_i^{in,F}) = \sum_{i \in I} (V_i^F \cdot hV_i^F + L_i^F \cdot hL_i^F) \quad (7f)$$

$$hV_i^F = \Phi_i^H(T^F) \quad i \in I \quad (7g)$$

$$hL_i^F = \Phi_i^h(T^F) \quad i \in I \quad (7h)$$

$$\sum_{i \in I} x_i^F = 1 \quad (7i)$$

$$\sum_{i \in I} y_i^F = 1 \quad (7j)$$

$$K_i^F \cdot x_i^F = y_i^F \quad i \in I \quad (7k)$$

$$K_i^F = \frac{\gamma_i^F \cdot P_i^{0F}}{P^F} \quad i \in I \quad (7l)$$

$$\gamma_i^F = \Phi_i^{\gamma}(x_i^F, T^F, P^F) \quad i \in I \quad (7m)$$

$$P_i^{0F} = \Phi_i^P(x_i^F) \quad i \in I \quad (7n)$$

$$V_s^{crit} \geq VAP^F \quad s = 2 \quad (7o)$$

$$c^F = \Phi^c(V_s^{crit}) \quad (7p)$$

The unit relations of the conditional units contain two sets of equations with logic “OR” (\vee) relation between them. The first set of equations are taken into consideration when the unit exists in a particular structure; the logic variable of the unit is true (Z) in this case. If the unit does not exist in a structure then the other set of equations has to be satisfied; the logic variable of the unit is false ($\neg Z$) in this case.

As a particular example, the unit relations of the third unit in a column section (containing four equilibrium stages) are shown in eq 8. When the unit exists, the MESH equations of all the included equilibrium stages and the calculation of the

fix cost related to this unit are taken into consideration. The component material and enthalpy balances are different for the first (lowest), the last (uppest) and the inner equilibrium stages, because the inlet vapor/liquid stream of the unit ($V_i^{in,s,k}/L_i^{in,s,k}$) goes directly to the first/last equilibrium stage of the unit, and the outlet liquid/vapor stream ($L_i^{out,s,k}/V_i^{out,s,k}$) leaves from the first/last equilibrium stage of the unit.

If the unit does not exist in a structure then all the component flowrate, enthalpy, and cost variables related to the unit, take zero value. It means that there is neither inlet nor outlet. The inner variables of the unit (e.g., mole fractions and fugacities) can take any value; they do not have any effect to the solution because all the inlet and outlet variables take zero.

The unit relations of units containing more than four equilibrium stages are similar to eq 8. The only difference is that the set of equilibrium stages is not $J4$ but Jn , where n is the number of stages in the unit.

The unit relations of the second unit in a column section containing two equilibrium stages have two differences from eq 8. The first is that the set of equilibrium stages is $J2$ instead of $J4$. The second difference is that there are only two stages (a first and a last) in that unit; therefore, the component material balance and the enthalpy balance of the inner stages are missing.

The unit relations of the first unit in a column section containing only one equilibrium stage are shown in eq 9. There are merely one component material balance and one enthalpy balance for the single stage in this unit. The set of equilibrium

Chart 1. Equation 8

$Z_{s,k}$ \wedge $V_{i,s,k}^{in} + L_{i,j-1,s,k} = V_{i,j,s,k} + L_{i,j,s,k} \quad j \in J4^{first} \quad (8-1)$ $V_{i,j-1,s,k} + L_{i,j+1,s,k} = V_{i,j,s,k} + L_{i,j,s,k} \quad j \in J4^{inner} \quad (8-2)$ $V_{i,j-1,s,k} + L_{i,s,k}^{in} = V_{i,j,s,k} + L_{i,j,s,k} \quad j \in J4^{last} \quad (8-3)$ $L_{i,s,k}^{out} = L_{i,j,s,k} \quad j \in J4^{first} \quad (8-4)$ $V_{i,s,k}^{out} = V_{i,j,s,k} \quad j \in J4^{last} \quad (8-5)$ $L_{i,j,s,k} = LIQ_{j,s,k} \cdot x_{i,j,s,k} \quad j \in J4 \quad (8-6)$ $V_{i,j,s,k} = VAP_{j,s,k} \cdot y_{i,j,s,k} \quad j \in J4 \quad (8-7)$ $\sum_{i \in I} (V_{i,s,k}^{in} \cdot hV_{i,s,k}^{in} + L_{i,j+1,s,k} \cdot hL_{i,j+1,s,k}) = \sum_{i \in I} (V_{i,j,s,k} \cdot hV_{i,j,s,k} + L_{i,j,s,k} \cdot hL_{i,j,s,k}) \quad j \in J4^{first} \quad (8-8)$ $\sum_{i \in I} (V_{i,j-1,s,k} \cdot hV_{i,j-1,s,k} + L_{i,j+1,s,k} \cdot hL_{i,j+1,s,k}) = \sum_{i \in I} (V_{i,j,s,k} \cdot hV_{i,j,s,k} + L_{i,j,s,k} \cdot hL_{i,j,s,k}) \quad j \in J4^{inner} \quad (8-9)$ $\sum_{i \in I} (V_{i,j-1,s,k} \cdot hV_{i,j-1,s,k} + L_{i,s,k}^{in} \cdot hL_{i,s,k}^{in}) = \sum_{i \in I} (V_{i,j,s,k} \cdot hV_{i,j,s,k} + L_{i,j,s,k} \cdot hL_{i,j,s,k}) \quad j \in J4^{last} \quad (8-10)$ $hL_{i,j,s,k} = \Phi_i^h(T_{j,s,k}) \quad j \in J4 \quad (8-11)$ $hV_{i,j,s,k} = \Phi_i^h(T_{j,s,k}) \quad j \in J4 \quad (8-12)$ $hL_{i,s,k}^{out} = hL_{i,j,s,k} \quad j \in J4^{first} \quad (8-13)$ $hV_{i,s,k}^{out} = hV_{i,j,s,k} \quad j \in J4^{last} \quad (8-14)$ $\sum_{i \in I} x_{i,j,s,k} = 1 \quad j \in J4 \quad (8-15)$ $\sum_{i \in I} y_{i,j,s,k} = 1 \quad j \in J4 \quad (8-16)$ $K_{i,j,s,k} \cdot x_{i,j,s,k} = y_{i,j,s,k} \quad j \in J4 \quad (8-17)$ $K_{i,j,s,k} = \frac{\gamma_{i,j,s,k} \cdot P_{i,j,s,k}^0}{P_{j,s,k}} \quad j \in J4 \quad (8-18)$ $\gamma_{i,j,s,k} = \Phi_i^{\gamma}(x_{j,s,k}, T_{j,s,k}, P_{j,s,k}) \quad j \in J4 \quad (8-19)$ $P_{i,j,s,k}^0 = \Phi_i^P(x_{i,j,s,k}) \quad j \in J4 \quad (8-20)$ $V_s^{crit} \geq VAP_{j,s,k} \quad j \in J4 \quad (8-21)$ $c_{s,k} = \Phi^c(V_s^{crit}) \quad j \in J4 \quad (8-22)$	$\neg Z_{s,k}$ \wedge $L_{i,s,k}^{in} = 0 \quad (8-23)$ $V_{i,s,k}^{in} = 0 \quad (8-24)$ $L_{i,s,k}^{out} = 0 \quad (8-25)$ $V_{i,s,k}^{out} = 0 \quad (8-26)$ $L_{i,j,s,k} = 0 \quad j \in J4 \quad (8-27)$ $V_{i,j,s,k} = 0 \quad j \in J4 \quad (8-28)$ $hL_{i,s,k}^{in} = 0 \quad (8-29)$ $hV_{i,s,k}^{in} = 0 \quad (8-30)$ $hL_{i,s,k}^{out} = 0 \quad (8-31)$ $hV_{i,s,k}^{out} = 0 \quad (8-32)$ $hL_{i,j,s,k} = 0 \quad j \in J4 \quad (8-33)$ $hV_{i,j,s,k} = 0 \quad j \in J4 \quad (8-34)$ $c_{s,k} = 0 \quad (8-35)$
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$$i \in I, s \in S, k \in \{k \in K \mid k = 3\} \quad (8)$$

Chart 2. Equation 9

$$\left[\begin{array}{l}
 Z_{s,k} \\
 \wedge \\
 V_{i,s,k}^{in} + L_{i,s,k}^{in} = V_{i,j,s,k} + L_{i,j,s,k} \\
 L_{i,s,k}^{out} = L_{i,j,s,k} \\
 V_{i,s,k}^{out} = V_{i,j,s,k} \\
 L_{i,j,s,k} = LIQ_{j,s,k} \cdot x_{i,j,s,k} \\
 V_{i,j,s,k} = VAP_{j,s,k} \cdot y_{i,j,s,k} \\
 \sum_{i \in I} (V_{i,s,k}^{in} \cdot hV_{i,s,k}^{in} + L_{i,s,k}^{in} \cdot hL_{i,s,k}^{in}) = \sum_{i \in I} (V_{i,j,s,k} \cdot hV_{i,j,s,k} + L_{i,j,s,k} \cdot hL_{i,j,s,k}) \\
 hL_{i,j,s,k} = \Phi_i^h(T_{j,s,k}) \\
 hV_{i,j,s,k} = \Phi_i^h(T_{j,s,k}) \\
 hL_{i,s,k}^{out} = hL_{i,j,s,k} \\
 hV_{i,s,k}^{out} = hV_{i,j,s,k} \\
 \sum_{i \in I} x_{i,j,s,k} = 1 \\
 \sum_{i \in I} y_{i,j,s,k} = 1 \\
 K_{i,j,s,k} \cdot x_{i,j,s,k} = y_{i,j,s,k} \\
 K_{i,j,s,k} = \frac{\gamma_{i,j,s,k} \cdot P_{j,s,k}^0}{P_{j,s,k}} \\
 \gamma_{i,j,s,k} = \Phi_i^{\gamma}(x_{j,s,k}, T_{j,s,k}, P_{j,s,k}) \\
 P_{i,j,s,k}^0 = \Phi_i^P(x_{i,j,s,k}) \\
 V_s^{crit} \geq VAP_{j,s,k} \\
 c_{s,k} = \Phi^{c1}(V_s^{crit})
 \end{array} \right] \vee \left[\begin{array}{l}
 -Z_{s,k} \\
 \wedge \\
 L_{i,s,k}^{in} = 0 \\
 V_{i,s,k}^{in} = 0 \\
 L_{i,s,k}^{out} = 0 \\
 V_{i,s,k}^{out} = 0 \\
 L_{i,j,s,k} = 0 \\
 V_{i,j,s,k} = 0 \\
 hL_{i,j,s,k} = 0 \\
 hV_{i,j,s,k} = 0 \\
 hL_{i,s,k}^{in} = 0 \\
 hV_{i,s,k}^{in} = 0 \\
 hL_{i,s,k}^{out} = 0 \\
 hV_{i,s,k}^{out} = 0 \\
 c_{s,k} = 0
 \end{array} \right]$$

$$i \in I, j \in J1, s \in S, k \in \{k \in K \mid k = 1\} \tag{9}$$

stages in the unit, $J1$, contains a single element only, but the set notation is used for the sake of analogy with other units containing more equilibrium stages.

The unit relations of the liquid (eq 10) and vapor (eq 11) transport units also contain two sets of equations with a logic “OR” between them. When a transport unit exists ($Z_{s,k}^V$ or $Z_{s,k}^L$ is true), the inlet stream goes through the unit without any change

in concentration or enthalpy. When a transport unit does not exist ($-Z_{s,k}^V$ or $-Z_{s,k}^L$), all the inlet and outlet variables take zero value; i.e., there is neither inlet nor outlet stream in that case. Charts 1–4 show eqs 8–11.

Two variable arrays belong to each stream between units: component flowrates (dL or dV) and component molar enthalpies (hdL or hdV). These variables are shown in Figure 3a. The first

Chart 3. Equation 10

$$\left[\begin{array}{l}
 Z_{s,k}^L \\
 \wedge \\
 tL_{i,s,k}^{in} = tL_{i,s,k}^{out} \tag{10-1} \\
 htL_{i,s,k}^{in} = htL_{i,s,k}^{out} \tag{10-2}
 \end{array} \right] \vee \left[\begin{array}{l}
 -Z_{s,k}^L \\
 \wedge \\
 tL_{i,s,k}^{in} = 0 \tag{10-3} \\
 tL_{i,s,k}^{out} = 0 \tag{10-4} \\
 htL_{i,s,k}^{in} = 0 \tag{10-5} \\
 htL_{i,s,k}^{out} = 0 \tag{10-6}
 \end{array} \right]$$

$$i \in I, s \in S, k \in K \tag{10}$$

Chart 4. Equation 11

$$\left[\begin{array}{l}
 Z_{s,k}^V \\
 \wedge \\
 tV_{i,s,k}^{in} = tV_{i,s,k}^{out} \\
 htV_{i,s,k}^{in} = htV_{i,s,k}^{out}
 \end{array} \right] \vee \left[\begin{array}{l}
 -Z_{s,k}^V \\
 \wedge \\
 tV_{i,s,k}^{in} = 0 \\
 tV_{i,s,k}^{out} = 0 \\
 htV_{i,s,k}^{in} = 0 \\
 htV_{i,s,k}^{out} = 0
 \end{array} \right]$$

$$i \in I, s \in S, k \in K \tag{11}$$

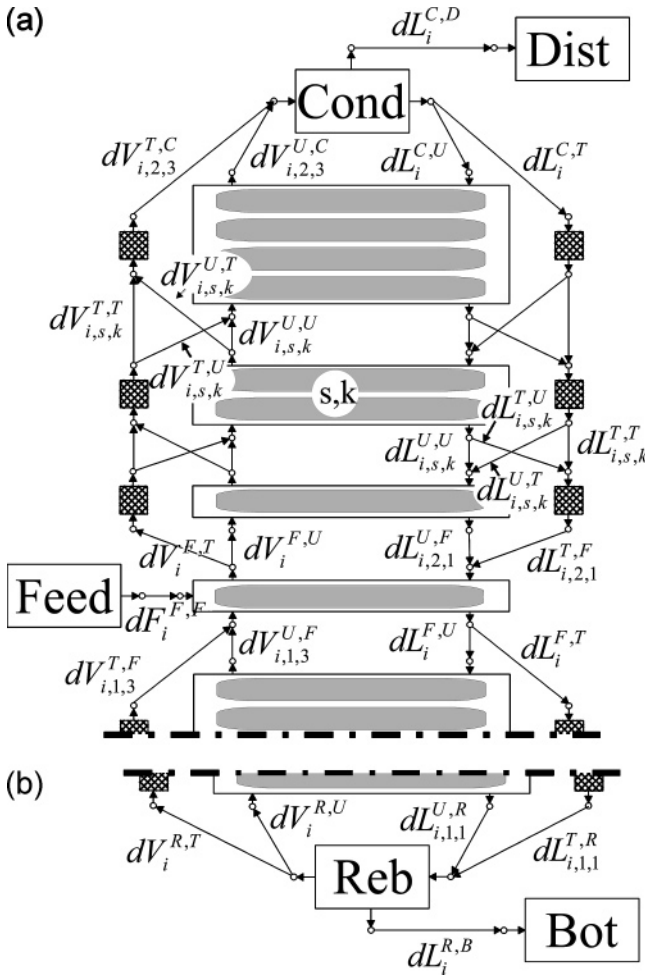


Figure 3. (a) Component material flowrate variables of the edges between units and (b) component material flowrate variables of the edges between reboiler and unit with $k = 1$.

superscript of these variables denotes the type of the unit from which the edge starts, the second superscript denotes the type of the unit at which the edge ends (U = unit containing equilibrium stages; T = transport unit; F = feed stage or feed source unit; C = condenser; R = reboiler; D = distillate sink unit; and B = bottom product sink unit). These variables either have three subscripts or merely one, depending on if the edge starts from an output port of a conditional unit or from a permanent one, respectively. The first subscript denotes the component ($i \in I$). The second subscript (if exists) denotes the column section ($s \in S$), and the third one (if exists) denotes the ordinal number of the unit where the stream comes from in the column section ($k \in K$).

The material balances of the input and output ports are expressed by summing up the inlet and outlet flowrate variables. For example, the material balances of the input and output vapor ports of the k th unit containing equilibrium stages in the s th column section are as follow:

$$dV_{i,s,k-1}^{U,U} + dV_{i,s,k-1}^{T,U} = V_{i,s,k}^{in} \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{first}\} \quad (12)$$

$$V_{i,s,k}^{out} = dV_{i,s,k}^{U,U} + dV_{i,s,k}^{U,T} \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{last}\} \quad (13)$$

Similarly, eqs 14 and 15 express the material balances of the input and output port, respectively, of the k th vapor transport unit in the s th column section.

$$dV_{i,s,k-1}^{U,T} + dV_{i,s,k-1}^{T,T} = tV_{i,s,k}^{in} \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{first}\} \quad (14)$$

$$tV_{i,s,k}^{out} = dV_{i,s,k}^{T,U} + dV_{i,s,k}^{T,T} \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{last}\} \quad (15)$$

The enthalpy balances of the output ports are simple equalities, as they are expressed for the output vapor port of the k th unit containing equilibrium stages in the s th column section (eqs 16 and 17) and for the output port of the vapor transport unit next to it (eqs 18 and 19).

$$hdV_{i,s,k}^{U,U} = hV_{i,s,k}^{out} \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{first}\} \quad (16)$$

$$hdV_{i,s,k}^{U,T} = hV_{i,s,k}^{out} \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{first}\} \quad (17)$$

$$hdV_{i,s,k}^{T,U} = htV_{i,s,k}^{out} \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{last}\} \quad (18)$$

$$hdV_{i,s,k}^{T,T} = htV_{i,s,k}^{out} \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{last}\} \quad (19)$$

The molar enthalpy of the inlet streams, in the input ports, of a unit is calculated from the molar enthalpy of the streams ending in the input port:

$$hV_{i,s,k}^{in} = \Phi_i^{hdV}(hdV_{i,s,k-1}^{U,U}, hdV_{i,s,k-1}^{T,U}) \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{first}\} \quad (20)$$

$$htV_{i,s,k}^{in} = \Phi_i^{hdV}(hdV_{i,s,k-1}^{U,T}, hdV_{i,s,k-1}^{T,T}) \quad i \in I, s \in S, k \in \{k | k \in K, k \neq \text{first}\} \quad (21)$$

These equations may be highly nonconvex. In the MINLP representation discussed later, however, a unit containing equilibrium stages and the corresponding transport units cannot exist simultaneously. In that case, the molar enthalpy of the inlet stream of a unit can be simply calculated as the sum of the molar enthalpies carried along the edges from the previous transport unit and the previous unit containing equilibrium stages. Such a technique can be applied because only one of them can be positive; the other one is constrained to be zero. The material and enthalpy balances of all the input and output ports can be generated similarly.

In the particular case of modeling distillation columns with R -graphs, a unit containing equilibrium stages and the two transport units belonging to it do not exist simultaneously in a considered structure, as it was explained in Section 2. This constraint can be expressed by a pair of "exclusive or" (XOR) relations between the logic variables in the following form:

$$Z_{s,k}^U \oplus Z_{s,k}^L \quad s \in S, k \in K \quad (22)$$

$$Z_{s,k}^U \oplus Z_{s,k}^V \quad s \in S, k \in K \quad (23)$$

The objective function is given in our model as the total cost of the column. Since the variable cost is calculated in the condenser and the reboiler (c^C and c^R), and the fix cost related to the units is calculated in the unit relations of each unit, the total cost is simply expressed as the sum of these cost parts:

$$C = c^R + c^C + c^F + \sum_{s \in S} \sum_{k \in K} c_{s,k} \quad (24)$$

4. MINLP Representation (MR)

According to the definition given by Farkas and co-workers²² the MINLP Representation (MR) can be created automatically

from the GR. The logic relations are transformed to algebraic equations, and the logic variables (Z) are substituted by binary ones (z). When transforming the GR to MR, the equations of the permanent units, the material balances of the input and output ports, and the objective function, remain unchanged. In contrary, some relations of the conditional units are converted to equations including binary variables by certain transforming techniques.

Several transformation techniques can be applied for this aim. The most widespread techniques are the so-called Big M, Multi M, and the Convex Hull formulations.

The logic relations are transformed here to algebraic equations using Big M technique. This transformation is shown here on the example of the third unit, containing four equilibrium stages, in a column section. When the unit exists in a structure then the unit equations have to be satisfied, and if it does not exist then the component flowrate, enthalpies, and cost variables, take zero value, according to the unit relations of the third unit in GR (eq 8).

This behavior of the flowrate variables are expressed by taking over the material balances from GR, and introducing additional equations that enforce input flowrate variables to take zero when the actual unit does not exist. Not only the input flowrate variables but all the inner and output molar flowrate variables take zero in this way, as a consequence of the balances, when the unit does not exist. Equations 25–29 list the material balances taken over from BGR, and eq 30 is the applied Big M equation forcing the input molar flowrate variables to take zero when the unit does not exist. The binary variable $z_{s,k}$ expresses the existence of the unit; i.e., its value is zero when the unit does not exist. When the unit exist, i.e., the binary variable is unity, the input molar liquid and vapor variables can take positive value; M^{LV} is the upper bound of the right-hand side expression in eq 30. The input liquid and vapor flowrate variables appear in the same Big M constraint in order to use as few equations containing binary variables as possible.

$$V_{i,s,k}^{in} + L_{i,j+1,s,k} = V_{i,j,s,k} + L_{i,j,s,k} \\ i \in I, j \in J4^{first}, s \in S, k \in \{k | k \in K, k = 3\} \quad (25)$$

$$V_{i,j-1,s,k} + L_{i,j+1,s,k} = V_{i,j,s,k} + L_{i,j,s,k} \\ i \in I, j \in J4^{inner}, s \in S, k \in \{k | k \in K, k = 3\} \quad (26)$$

$$V_{i,j-1,s,k} + L_{i,s,k}^{in} = V_{i,j,s,k} + L_{i,j,s,k} \\ i \in I, j \in J4^{last}, s \in S, k \in \{k | k \in K, k = 3\} \quad (27)$$

$$L_{i,s,k}^{out} = L_{i,j,s,k} \\ i \in I, j \in J4^{first}, s \in S, k \in \{k | k \in K, k = 3\} \quad (28)$$

$$V_{i,s,k}^{out} = V_{i,j,s,k} \\ i \in I, j \in J4^{last}, s \in S, k \in \{k | k \in K, k = 3\} \quad (29)$$

$$\sum_{i \in I} (L_{i,s,k}^{in} + V_{i,s,k}^{in}) \leq M^{LV} \cdot z_{s,k} \quad s \in S, k \in K \quad (30)$$

The molar enthalpy variables are managed similarly. The enthalpy balance is taken over invariantly from GR (eqs 31–35), but an additional Big M constraint is used to force the input molar enthalpy variables to take zero when the unit does not exist. As a consequence of the form of eqs 31–33, however, the flowrates may take zero when the unit does not exist, because of eq 30, and the enthalpy balances may be satisfied with nonzero molar enthalpies of the streams around the

equilibrium stages. If this happens, then the output stream enthalpy variables have positive value because of eqs 34 and 35. In such a case, the streams from nonexisting unit have positive enthalpy, involving problems in further calculations. To prevent occurring this problem, not only the input but as well the output stream enthalpy variables appear in the Big M constraints (eq 36). As a result, all the input and output stream enthalpy variables of the unit (not of the equilibrium stages inside the unit) are set to zero when the unit does not exist. The enthalpy reference is chosen such a way that no enthalpy variable can take negative value. As a result, no enthalpy variable differs from zero when the unit does not exist. The enthalpy variables of the equilibrium stages in the unit may take positive value in this case, but it does not involve any problem in the calculations.

$$\sum_{i \in I} (V_{i,s,k}^{in} \cdot hV_{i,s,k}^{in} + L_{i,j+1,s,k} \cdot hL_{i,j+1,s,k}) = \\ \sum_{i \in I} (V_{i,j,s,k} \cdot hV_{i,j,s,k} + L_{i,j,s,k} \cdot hL_{i,j,s,k}) \\ j \in J4^{first}, s \in S, k \in \{k | k \in K, k = 3\} \quad (31)$$

$$\sum_{i \in I} (V_{i,j-1,s,k} \cdot hV_{i,j-1,s,k} + L_{i,j+1,s,k} \cdot hL_{i,j+1,s,k}) = \\ \sum_{i \in I} (V_{i,j,s,k} \cdot hV_{i,j,s,k} + L_{i,j,s,k} \cdot hL_{i,j,s,k}) \\ j \in J4^{inner}, s \in S, k \in \{k | k \in K, k = 3\} \quad (32)$$

$$\sum_{i \in I} (V_{i,j-1,s,k} \cdot hV_{i,j-1,s,k} + L_{i,s,k}^{in} \cdot hL_{i,s,k}^{in}) = \\ \sum_{i \in I} (V_{i,j,s,k} \cdot hV_{i,j,s,k} + L_{i,j,s,k} \cdot hL_{i,j,s,k}) \\ j \in J4^{last}, s \in S, k \in \{k | k \in K, k = 3\} \quad (33)$$

$$hL_{i,s,k}^{out} = hL_{i,j,s,k} \\ i \in I, j \in J4^{first}, s \in S, k \in \{k | k \in K, k = 3\} \quad (34)$$

$$hV_{i,s,k}^{out} = hV_{i,j,s,k} \\ i \in I, j \in J4^{last}, s \in S, k \in \{k | k \in K, k = 3\} \quad (35)$$

$$\sum_{i \in I} (hL_{i,s,k}^{in} + hV_{i,s,k}^{in} + hL_{i,s,k}^{out} + hV_{i,s,k}^{out}) \leq 4 \cdot nc \cdot M^h \cdot z_{s,k} \\ s \in S, k \in K \quad (36)$$

The concentration, fugacity, temperature, and pressure variables of the equilibrium stages have to satisfy the unit relations (eq 8 for $k = 3$; the mass- and heat transfer equations between trays, equality of fugacities, summation of mole fractions, etc.) when the unit exists. However, there is not any constraint to them when the unit does not exist. Each unit communicates with its environment only through its input ($L_{i,s,k}^{in}$, $V_{i,s,k}^{in}$, $hL_{i,s,k}^{in}$, $hV_{i,s,k}^{in}$) and output ($L_{i,s,k}^{out}$, $V_{i,s,k}^{out}$, $hL_{i,s,k}^{out}$, $hV_{i,s,k}^{out}$) variables. If they are set to zero, i.e., when the unit does not exist, then the inner variables belonging to the trays inside the unit can take any value. These variables can also be constrained to take zero when the unit does not exist. But such constraints could be too strict, and would involve problems in the MINLP optimization to find the optimal solution. Therefore, only those constraints are provided which enforce the equations in GR to be satisfied when the unit exists.

This is achieved with Big M formula by inserting two inequalities to each variable. Such a pair of equations expressing the molar liquid enthalpy in function of the temperature is, for example, as follows:

$$-M^h(1 - z_{s,k}) \leq hL_{i,j,s,k} - \Phi_i^h(T_{j,s,k})$$

$$i \in I, j \in J4, s \in S, k \in \{k \mid k \in K, k = 3\} \quad (37)$$

$$hL_{i,j,s,k} - \Phi_i^h(T_{j,s,k}) \leq M^h(1 - z_{s,k})$$

$$i \in I, j \in J4, s \in S, k \in \{k \mid k \in K, k = 3\} \quad (38)$$

The binary variable ($z_{s,k}$) takes unity, and the left-hand side of eq 37 and the right-hand side of eq 38 takes zero when the unit exists; therefore, the molar liquid enthalpy becomes equal to the function calculated from the temperature.

Analogous Big M equations may be written for the other equations containing logic expression(s) in the GR, such as the equality of the fugacities (eq 9), the summation of the mol fractions (eq 9), and calculation of the unit costs (eq 9). According to our experiences, however, the relaxation is improved when the latter equations are satisfied independently from the existence of the unit. Therefore, the final version of the model contains these constraints in form of equations that are always satisfied.

The logic equations describing the requirement that the transfer units and equilibrium units cannot exist at the same time (eqs 23 and 24 in GR) are transformed to algebraic equation:²³

$$z_{s,k} + z_{s,k}^L = 1 \quad s \in S, k \in K \quad (39)$$

$$z_{s,k} + z_{s,k}^V = 1 \quad s \in S, k \in K \quad (40)$$

In this way, the MR represents the considered structures only. Considered structures are all the structures that are physically feasible and can be taken account from engineering point of view as possible solutions.²²

The unit relations of the transport units are transformed to algebraic equations by applying the same principles as above. That is, the material and enthalpy balances are taken over from GR, and Big M constraints are added for the input variables, as follow.

The equations of the liquid transport units are listed below:

$$tL_{i,s,k}^{in} = tL_{i,s,k}^{out} \quad s \in S, k \in K \quad (41)$$

$$htL_{i,s,k}^{in} = htL_{i,s,k}^{out} \quad s \in S, k \in K \quad (42)$$

$$\sum_{i \in I} tL_{i,s,k}^{in} \leq nc \cdot M^L \cdot z_{s,k}^L \quad s \in S, k \in K \quad (43)$$

$$\sum_{i \in I} htL_{i,s,k}^{in} \leq nc \cdot M^h \cdot z_{s,k}^L \quad s \in S, k \in K \quad (44)$$

The equations of the vapor transport units have the same form.

The material and enthalpy balances have to be satisfied even when the unit does not exist (eqs 41 and 42). The Big M constraints need to be applied for the input variables (eqs 43 and 44) because the output variables take zero when the input variables are zero, because of the form of the balances.

The above representation is constructed automatically from the GR. The numerical behavior of the MINLP representation can, however, be greatly enhanced with some following modifications. For this aim, we take into account some specific properties of the actual chemical engineering problem to further improve the numerical behavior of the MINLP by tailoring its actual form.

The equations used for calculating the fix cost of the conditional units are strongly nonlinear. The effect of this nonlinearity is decreased first. Calculation of the cost depending

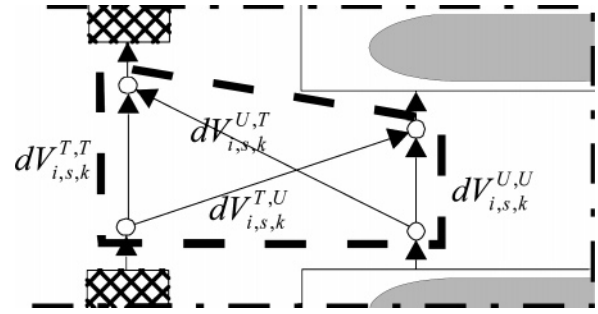


Figure 4. Omitting the edge variables.

on the number of stages, for each conditional unit separately, consumes a great effort of computation. Combining these cost functions into a single equation is a much better idea. Accordingly, instead of summing up the earlier calculated cost parts as in eq 24, all the parts are calculated in the objective function,

$$C = \Phi^{cC}(QC) + \Phi^{cR}(QR) + \Phi(N,DC) \quad (45)$$

where N is the number of the equilibrium stages in the column and DC is the diameter calculated from the maximum vapor flowrate in each section.

Second, the number of variables is decreased by omitting the variables belonging to the edges of the R -graph. According to Figure 4, a material balance is written around the dashed line:

$$V_{i,s,k-1}^{out} + tV_{i,s,k-1}^{out} = V_{i,s,k}^{in} + tV_{i,s,k}^{in}$$

$$i \in I, s \in S, k \in \{k \mid k \in K, k \neq \text{first}\} \quad (46)$$

Similarly, all the balances between units are written in a simpler form, omitting the dL , dhL , and dhV edge variables.

Third, in order to further decrease the number of binary variables, the binary variables of the transport units are expressed using the ones belonging to units containing equilibrium stages:

$$z_{s,k}^L := 1 - z_{s,k} \quad s \in S, k \in K \quad (47)$$

$$z_{s,k}^V := 1 - z_{s,k} \quad s \in S, k \in K \quad (48)$$

Fourth, the form of the big-M equations like in eqs 37 and 38 are modified in order to decrease the number of equations containing binary variable. The equation rearranged to one side is taken equal to the difference of two non-negative continuous variables Δ (eq 49). A Big M constraint, including the binary variable of the unit, is added to these two variables Δ (eq 50). These Δ variables take zero, and the difference of two zero values in eq 50 will take zero, when the unit exists; therefore, the molar liquid enthalpy has to equal the function calculated from the temperature. When the unit does not exist, these Δ variables can take any non-negative value below their upper limit. The difference of two non-negative values in the right-hand side of eq 49 can take any value in this case; therefore, the original equation need not be satisfied, and the liquid enthalpy variable can take greater or lower value than that calculated from the temperature.

$$hL_{i,j,s,k} - \Phi_i^h(T_{j,s,k}) = \Delta_{s,k}^{h,+} - \Delta_{s,k}^{h,-}$$

$$i \in I, j \in J4, s \in S, k \in \{k \mid k \in K, k = 3\} \quad (49)$$

$$\Delta_{s,k}^{h,+} + \Delta_{s,k}^{h,-} \leq M^k(1 - z_{s,k}) \quad s \in S, k \in K \quad (50)$$

Equations 37 and 38 containing a binary variable z are transformed to eqs 49 and 50 with introducing two continuous

variables (Δ -s). As a result, only one of the two new equations contains the binary variable, namely, eq 50. This modification results in shorter runtime.

The same Δ variables are used also for the equations containing vapor enthalpy variables (eq 51). The relaxation of the equations is a bit worse in this case because the upper bounds are not fitted to different variables, but the number of equations containing binary variables is further decreased:

$$hV_{i,j,s,k} - \Phi_i^H(T_{j,s,k}) = \Delta_{s,k}^{h,+} - \Delta_{s,k}^{h,-} \quad i \in I, j \in J4, s \in S, k \in \{k \mid k \in K, k = 3\} \quad (51)$$

According to the formulas (eqs 25–36 and 49–51 and analogous equations), all the unit relations are satisfied when the equilibrium unit exists, and its inlet and outlet streams are of zero flowrate and zero molar enthalpy when the unit does not exist. All the conditional unit relations containing equilibrium stages, not only those of the third unit in the above example, are transformed to algebraic equations in the same way.

5. Modified MINLP Algorithm for Handling Complex Distillation Systems

When solving complex distillation process optimization problems containing several distillation column with a huge number of stages (see an example in Section 6.3), the researcher encounters serious numerical problems relating the large number of nonlinear equations and strong nonlinearities.

For example, when applying our model to the problem presented in Section 6.3, we experienced such difficulties (see the model statistics presented in Table 5). The problem scale is so large that the problem cannot be solved with the traditional tools (GAMS 20.0., SBB or DICOPT MINLP solver using Outer Approximation algorithm; see Figure 5a). The main issue is the huge number of the nonlinear equations. The solver has serious difficulties with solving the NLP subproblems; they were alleged to be infeasible, although they must have feasible solution. Even the relaxed NLP was impossible to solve without good initial values. The user can provide good initial values for the (first) relaxed NLP, but that will be missed during the solution process.

This is particularly true in the case of our model. If during the execution of the Outer Approximation one of the MIP master problem concludes that the number of the stages in either column-section should be changed from 8 to 7 then the whole structure is changed, and the actual values of the continuous variables become suddenly very far from their feasible value. This is not so for the models of Yeomans^{8,9} and Viswanathan^{4–6} in case of smaller design problems. However, when large scale problems are to be solved, with as many as 160 stages, even the NLP subproblems become too difficult to solve. In order to solve them, the NLP solver needs good initial values therefore, the MINLP algorithm should be changed toward that solution.

Another issue is the strong nonconvexity of the problem. When applying the lower estimation obtained from the MILP master problems, it is possible to cut off some feasible solutions or even all of them. Thus, another modification of the algorithm is needed, in order to decrease this effect.

Apparently, the DICOPT or SBB solvers are unsuitable to handle the problem, because of their black-box nature. Another advanced tool can be used to realize these ideas. That can be the Paragon Decision's developer system called AIMMS. AIMMS has a GMP library through which the user have direct access to mathematical program instances generated by AIMMS, allowing the user to implement advanced algorithms in an

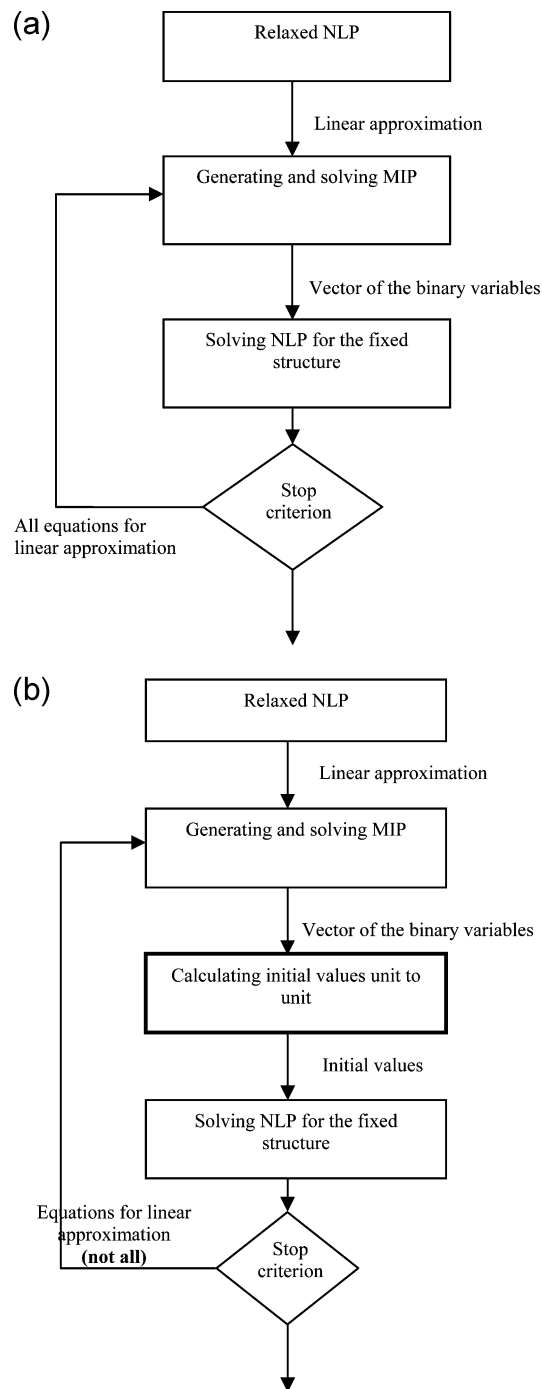


Figure 5. (a) Original OA algorithm and (b) modified OA algorithm.

efficient manner. The GMP routines can be used for nonlinear models, as well. The basic outer approximation algorithm can be completely implemented using functionality provided by the GMP library. According to the requirement of the problem, the user is able to implement modified or customized algorithms.²⁴

5.1. Modified Algorithm. In order to get good initial values, we inserted a new step between the MIP master problem and the NLP subproblem in each iteration. We calculate appropriate values for the variables stage to stage using the binary vector obtained from the MIP master problem. By this way, the initial infeasibility of the NLP subproblem can be smaller with orders of magnitude, and the solution time is decreased strongly. For handling the problem of cutting off possible feasible solutions when generating the MIP master problems, we omit those nonlinear equations which are the main source of the strong

nonconvexity. The Antoine equations, the Wilson equations calculating the activity coefficients, are thus eliminated. The resulted system for the unit containing four equilibrium stages consists of eqs 8–6 to 8–10, 8–17, 8–18, and the objective function. The Wilson equations calculating the activity coefficients (eq 8–19) and the Antoine equations (eq 8–20) are omitted. The scheme of the new algorithm is depicted in Figure 5b.

5.2. Modified Algorithm in Practice—Calculating the Initial Values. Initial values are computed to units top down in the columns. Each unit constitutes a distinct NLP problem. The NLP gets the data of leaving vapor streams and the entering liquid streams as parameters from the previous NLP problem (from the preceding unit above). The NLP problem is solved with these fixed values. Constant molar overflow assumption is used in order to obtain an unambiguously determined problem. The NLP for the unit containing four equilibrium stages when it exists consists of eqs 8–1 to 8–7, 8–11 to 8–20, 10–3 to 10–6, and the additional eqs 52 and 53 introduced for fixing the inlet liquid and outlet vapor flow:

$$L_{i,s,k}^{in} = L_{i,s,k+1}^{out} + tL_{i,s,k+1}^{out} \quad i \in I, s \in S, j \in J4, k \in \{k \in K \mid k = 3\} \quad (52)$$

$$V_{i,s,k}^{out} = V_{i,s,k+1}^{in} + tV_{i,s,k+1}^{in} \quad i \in \{i \in I \mid i \notin HV\}, s \in S, j \in J4, k \in \{k \in K \mid k = 3\} \quad (53)$$

When the unit does not exist, then the NLP consists of eqs 8–11, 8–12, 8–23 to 8–32, 10–1, 10–2, and the additional eqs 54 and 55 introduced for fixing the inlet liquid and outlet vapor flow:

$$tL_{i,s,k}^{in} = L_{i,s,k+1}^{out} + tL_{i,s,k+1}^{out} \quad i \in I, s \in S, j \in J4, k \in \{k \in K \mid k = 3\} \quad (54)$$

$$tV_{i,s,k}^{out} = V_{i,s,k+1}^{in} + tV_{i,s,k+1}^{in} \quad i \in I, s \in S, j \in J4, k \in \{k \in K \mid k = 3\} \quad (55)$$

In both cases, constant molar overflow assumption, and eqs 56 and 57, are used instead of the heat balances:

$$VAP_{j,s,k} = \sum_{i \in I} V_{i,s,k}^{out} \quad s \in S, j \in J4, k \in \{k \in K \mid k = 3\} \quad (56)$$

$$LIQ_{j,s,k} = \sum_{i \in I} L_{i,s,k}^{in} \quad s \in S, j \in J4, k \in \{k \in K \mid k = 3\} \quad (57)$$

The objective function is the input vapor flow of the heavy entrainer, i.e., eq 58:

$$obj = V_{i,s,k}^{in} \quad i \in HV, s \in S, j \in J4, k \in \{k \in K \mid k = 3\} \quad (58)$$

Because of some numerical inaccuracy that may cause difficulties under certain circumstances, the process of calculating initial values may require some ingenuity. In case of extractive distillation with heavy entrainer, the volatility of the entrainer is considerably smaller than the others (see example 3 in Section 6.3). It is then a straightforward idea to fix the amount of the heaviest component at zero in the leaving vapor stream of the unit at the top. However, the tolerance of the solver allows it to be equal to E-15. This small difference can cause that the amount of the heaviest component in the leaving liquid stream of the actual unit will be significantly different from zero in the solution. Thus,

there can practically be multiple solutions. This problem is avoided by including the entering vapor stream of the heaviest component in the objective function, as in eq 65. The entering vapor stream will be zero of all the units, thus when turning over the fixed values of the streams from one NLP to the next, the amount of the entrainer in the entering vapor stream should not be fixed (that is why eq 60 is valid for the lighter components only). Being this far the heaviest component in the mixture, this difference between the units will cause a very small initial infeasibility when starting to solve the NLP subproblem.

6. Examples

The MR developed according to Section 4 is tested from computational point of view on three different separation examples. The new model was originally intended to compare with the GDP model of Yeomans and Grossmann.⁹ Since GDP solver is not available for us, that GDP model has been transformed to MINLP model using Big M technique, and the results obtained with that MINLP model are compared to the results obtained with our MR model

All the examples are solved on a Sun Sparc workstation using GAMS.²⁵ The MINLP solver is DICOPT++; it applies the Outer Approximation (OA) algorithm for solving mixed-integer nonlinear problems. The NLP subproblems are solved with CONOPT2; the MILP subproblems are solved with CPLEX.

In all the examples, the cost function of Luyben and Floudas²⁶ are applied,

$$C = \frac{\beta_{tax}(C_{LPS} \cdot QR + C_{CW} \cdot QC)V + UF \cdot \Phi^{fix}(N, DC)/\beta_{pay}}{1000} \quad (59)$$

$$\Phi^{fix}(N, DC) = 12.3[615 + 324DC^2 + 486(6 + 0.76N)DC] + 245N(0.7 + 1.5DC^2) \quad (60)$$

where β_{tax} is the tax factor (=0.4); C_{LPS} is the cost of the low-pressure team (=1.1488 × 10⁻⁶ \$/kJ); C_{CW} is the cost of the cooling water (=3.73 × 10⁻⁸ \$/kJ); UF is the update factor (=1.292); β_{pay} is the payback period (=4 yr).

The column diameter is calculated as

$$DC = 2\sqrt{\frac{A}{\pi}} \quad (61)$$

where A is the cross section of the column (m²).

The cross section of the column is determined by using the F_f -proccession,²⁷

$$A = \frac{\dot{m}_v}{F_{max} \sqrt{\rho_v}} \quad (62)$$

where \dot{m}_v is the mass flowrate of the vapor from the reboiler (kg/s); F_{max} is the F -factor (=2.2√ Pa); and ρ_v is the density of the vapor (kg/m³).

The original objective function is divided by 1000 for better scaling.

6.1. Example 1. The problem is separation of a benzene/toluene mixture. Equimolar feed is considered, i.e., the charge composition is $x_{ch} = [0.5, 0.5]$. The feed is 100 kmol/h. The specified purity is 0.98 benzene in the distillate and 0.98 toluene in the bottom product. Atmospheric column is used, $P = 760$ Torr. The mixture is assumed be ideal, and constant molar overflow is also assumed.

Table 1. Model Characteristics of Example 1

model	no. of eqs	no. of nonlin. eqs	no. of vars.	no. of bin. vars.
Yeomans-base MINLP	2051	514	1272	60
new	1592	519	1449	10

Table 2. Computational Results of Example 1

model	<i>N</i>	<i>DC</i>	<i>Ref</i>	objective function	no. of iters.	solution time (CPU s)
Yeomans-base MINLP	13	1.38	2.83	83.15	150	79 565
new	16	1.18	1.76	73.12	150	13 643

Table 3. Model Characteristics of Example 2

model	no. of eqs	no. of nonlin. eqs	no. of vars.	no. of bin. vars.
Yeomans-base MINLP	2177	640	1398	60
new	1718	645	1575	10

Table 4. Computational Results of Example 2

model	<i>N</i>	<i>DC</i>	<i>Ref</i>	objective function	no. of iters.	solution time (CPU s)
Yeomans-base MINLP	47	0.89	2.38	121.9	150	181 564
new	26	0.95	2.87	100.8	150	10 929

Table 5. Model Statistics of the Problem

no. of eqs	no. of nonlinear eqs	no. of variables	no. of binary variables
12 307	6 439	10 920	35

The vapor/liquid equilibrium is calculated according to the Raoult–Dalton equation,

$$f_i^V = P y_i \quad (63)$$

$$f_i^L = x_i p_i^0(T) \quad (64)$$

where $p_i^0(T)$ is the vapor pressure of component i . Vapor pressure $p_i^0(T)$ is calculated with the Antoine equation,

$$\log(p_i^0 \text{ (mmHg)}) = A_i - \frac{B_i}{C_i + T \text{ (}^\circ\text{C)}} \quad (65)$$

where A_i , B_i , and C_i are the Antoine constants of component i . The applied constants²⁸ are collected in Table A1 of the Appendix. The maximum number of equilibrium stages in the column is set to 63 (31 above, 31 below the feed, and the feed stage).

The initial values (before the first iteration) of the variables are calculated by modeling the process using the maximum number of stages and the specified product purity. The modeling software for calculating initial values is ChemCAD. The stop criterion is the specified maximum number of iterations.

Data characterizing the models are listed in Table 1, as follows: number of equations, number of nonlinear equations among them, number of variables, and number of binary variables among them. The new model uses slightly more variables and less equation than the Yeomans model, but the number of binary variables is decreased significantly since the new model is a binarily minimal one.

Table 2 collects the data of the optimal solution: the number of equilibrium stages, the column diameter (m), the reflux ratio, and the total cost of the column in [1000 USD/yr]. The last two columns show the number of main iterations, and the computation time needed to find the optimal solution. The new

model finds a better solution in 150 iterations than the Yeomans-based MINLP model, and the solution time is also significantly shorter, with almost 83%.

6.2. Example 2. Equimolar ethanol/water mixture is to be separated. The feed flowrate is 100 kmol/h. The required purity is 0.85 ethanol in the distillate and 0.999 water in the bottom product. The CMO and constant atmospheric pressure assumptions are used. The phase equilibrium is calculated with the modified Raoult–Dalton equation,

$$f_i^V = P y_i \quad (66)$$

$$f_i^L = \gamma_i x_i p_i^0(T) \quad (67)$$

where γ_i is the activity coefficient of component i calculated by the Margules equations:

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \quad (68)$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})x_2]x_1^2 \quad (69)$$

The vapor pressure is modeled with the Antoine equations (eq 75). The model parameters²⁷ are listed in Tables A3 and A4 of the Appendix.

The maximum number of stages is set to 63. The initial values (before the first iteration) of the variables are calculated by modeling the process using the maximum number of stages and the specified product purity. The modeling software for calculating initial values is ChemCAD. The stopping criterion was a specified maximum number of iterations.

The model characteristics are collected in Table 3, and the computational results in Table 4. The new model finds a better solution 94% faster than the Yeomans-based MINLP model.

For the sake of completeness, we have to remark that the models have been tested with the SBB MINLP solver, as well. That solver uses the modified Branch and Bound algorithm, instead of OA. However, we cannot conclude unambiguous issue in this case, because of the very wide scattering of the results.

6.3. Example 3. 6.3.1. Process Description. Our goal is to separate a three-component methanol/ethanol/water mixture into its components through extractive distillation. We have three possibilities: either we can use heavy solvent (i.e., ethylene glycol) fed into the column above the feed; or we can use light solvent (i.e., methanol) fed into the column below the feed; or we can use both of them simultaneously.

The feed mixture has two components, ethanol and water. Glycol is used as a heavy solvent fed into an extractive column above the feed. The pure ethanol is obtained at the top of the column; the water-glycol mixture is obtained at the bottom of the column, and is separated in a conventional distillation column.

The feed mixture has three components, methanol, ethanol, and water. Glycol is used as a heavy solvent fed into an extractive distillation column above the feed. Methanol/ethanol mixture is obtained at the top of the column; water-glycol mixture is obtained at the bottom of the column, they will be separated in two conventional distillation columns, respectively.

The feed mixture has three components, methanol, ethanol, and water. The feed is first fed into a conventional distillation column; pure methanol is obtained at the top of the column; ethanol/water mixture is obtained at the bottom of the column. The latter is fed into an extractive distillation column in which glycol is used as a heavy solvent fed into the column above the

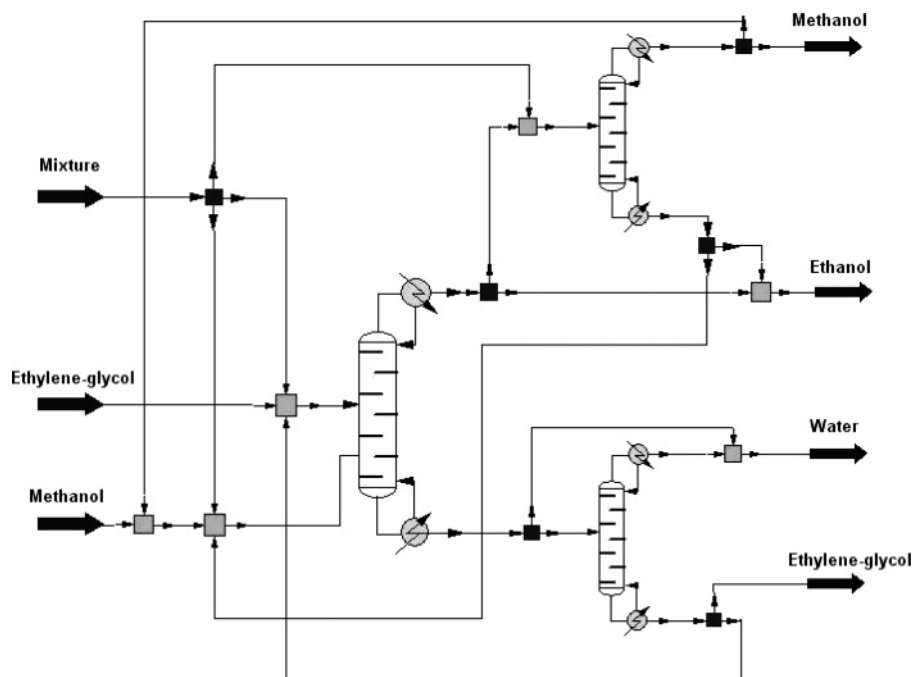


Figure 6. Superstructure of the extractive distillation system.

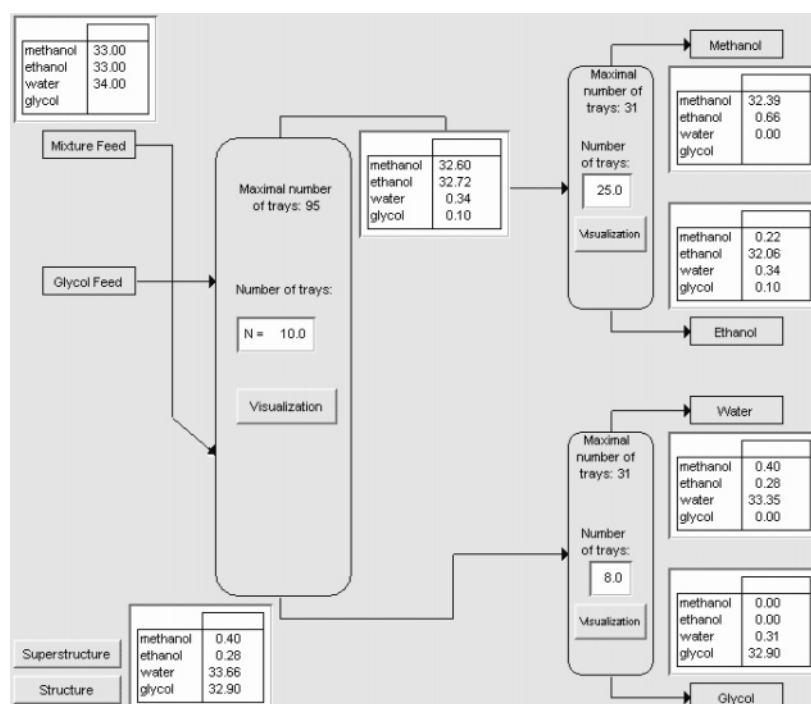


Figure 7. Structure obtained for example 3.

feed. Pure ethanol is obtained at the top of the extractive column; water/glycol mixture is obtained at the bottom of the extractive distillation column, and will be separated in a second conventional distillation column.

The feed mixture has two or three components, (methanol,) ethanol, and water. Methanol is used as a light solvent fed into an extractive distillation column below the feed. Methanol/ethanol mixture is obtained at the top of the column, and is separated in a conventional distillation column; pure water is obtained at the bottom of the extractive distillation column.

The feed mixture has three components, methanol, ethanol, and water. The methanol fraction is large enough to behave as a light solvent; there is no need to use additional methanol from

outer resource. Methanol/ethanol mixture is obtained at the top of the extractive distillation column, and is separated in a conventional distillation column; pure water is obtained at the bottom of the extractive distillation column.

The feed mixture has two or three components, (methanol,) ethanol, and water. Glycol is used as a heavy solvent fed into the extractive distillation column above or with the feed, and methanol is used as a light solvent fed into the column below or with the feed. Methanol/ethanol mixture is obtained at the top of the column; water/glycol mixture is obtained at the bottom of the column, they will be separated in two conventional distillation columns, respectively. By combining the above 6 process variants, the superstructure presented in Figure 6 is constructed.

Table 6. Solution and Solution Time Data When Different Sets of Equations Are Used for OA

	objective value	computation time (s) (no. of iterations = 10)
original	185.12	15 270
modified	183.96	3 917

Remark: Our aim is to pick up the optimal structure for ethanol dehydration. Although it is widely supposed that extractive distillation with heavy solvent is more economical than with light solvent, we suppose that if having a feed mixture with large methanol content, the optimal structure may use light solvent.

The extractive column contains three sections; each of them consists of five conditional units, i.e., 95 stages altogether. There are two feed stages between the sections; they have the same equations as it is detailed above. The equations of the condensers, the reboilers, the conventional units, and the equations for the streams between them, are unchanged. The conventional columns—used for separating methanol from ethanol and water from glycol—are uniform, with two sections; each of them includes four units, i.e., 31 stages altogether. The feed compositions in mole fractions are 0.33, 0.33, and 0.34, respectively. The feed is 100 kmol/h. The specified purity is 0.98 in each product. Atmospheric column is used, $P = 760$ Torr. The mixture is assumed to be of real behavior, the activities are calculated with Wilson equations, see the Appendix for coefficients. Heat balances are considered.

The modified outer approximation algorithm (detailed in Section 5) is applied to the problem; initial values are calculated before each NLP-subproblem. The algorithm has been implemented in AIMMS 3.7 modeling system. CPLEX 10.0. is used as MILP solver, and CONOPT 3.14A as NLP solver.

6.3.2. Results. The model statistics are collected in Table 5. The limit number of iterations is set to ten; the solution time is 3364 s, i.e. shorter than 1 h. The individual NLPs require 10–30 s, due to the good initial values. The calculation of initial values (as described in Section 5.2) requires 1–3 s in each iteration. The obtained solution structure, presented in Figure 7, applies glycol as entrainer; the extractive column contains ten stages, the conventional column used for separating the methanol/ethanol mixture and for separating the water/glycol mixture consists of 25 and 8 stages, respectively. Thus, the modified algorithm provides with good solution in reasonable time even for large size processes.

Since not all of the nonlinear equations are used for the linear approximation in the modified algorithm, the MILP values are far lower than with the original OA, and the solution time of the master problems increases less steeply, resulting in much less total solution time, as it is shown in Table 6. The objective value is better in the case of the modified algorithm, making us suspect that the original algorithm may cut off that solution.

7. Conclusion

A new, R -graph based, superstructure for designing conventional distillation columns is presented. A GDP representation (GR) of the superstructure is first constructed in such a way that only the considered substructures of the superstructure are represented. An MINLP representation (MR) can automatically be created from the GR.

The new model is tested on three examples, and the results are compared to the results of an MINLP model based on the GDP model of Yeomans and Grossmann.⁹ The new model yields shorter computation time and provides better local optima.

The model is applied to a complex extractive distillation system. The huge number of nonlinear equations caused difficulties during the solution process; therefore the original Outer Approximation algorithm is modified in order to provide good initial values for NLP solver. The modified algorithm reliably provides solution for processes containing four components and three distillation columns with altogether as much as 160 stages. The solutions time for such a complex process remains around 1 h.

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Appendix

Tables A1–A5 show the constants in the Antoine and Margules models.

Table A1. Antoine Constants in Example 1

	A_i	B_i	C_i
benzene	6.87987	1196.76	219.161
toluene	6.95087	1342.31	219.187

Table A2. Antoine Constants in Example 2

	A_i	B_i	C_i
ethanol	8.1122	1592.864	226.184
water	8.07131	1730.63	233.426

Table A3. Margules Parameters in Example 2

A12 (ethanol–water)	1.5871
A21 (water–ethanol)	0.7941

Table A4. Antoine Constants in Example 3

	A_i	B_i	C_i
methanol	8.08097	1582.271	239.726
ethanol	8.1122	1592.864	226.184
water	8.07131	1730.63	233.426
ethylene glycol	8.09083	2088.936	203.454

Table A5. Wilson Constants in Example 3

	methanol	ethanol	water	ethylene glycol
methanol	0	−21.425	−45.818	−254.45
ethanol	49.676	0	277.761	−129.204
water	441.871	819.63	0	1266.01
ethylene glycol	722.83	1539.41	−1265.74	0

Nomenclature

Abbreviations

MILP = mixed-integer linear programming
 MINLP = mixed-integer nonlinear programming
 NLP = nonlinear programming
 GDP = generalized disjunctive programming
 GR = GDP representation
 MR = MINLP representation

Parameters

$Feed$ = feed flow rate (kmol/h)
 M = Big M parameter(s)
 nc = number of components
 x_i^F = mole fraction of component i in the feed (mol/mol)

Variables

F = feed component flowrate (kmol/h)
 Dis = distillate component flowrate (kmol/h)
 Bot = bottom product component flowrate (kmol/h)
 L = liquid component flowrate for nontransport units (kmol/h)
 V = vapor component flowrate for nontransport units (kmol/h)
 tL = liquid component flowrate for transport units (kmol/h)
 tV = vapor component flowrate for transport units (kmol/h)
 LIQ = total liquid flowrate (kmol/h)
 VAP = total vapor flowrate (kmol/h)
 dF = feed stream component flowrate (kmol/h)
 dL = liquid stream component flowrate between units (kmol/h)
 dV = vapor stream component flowrate between units (kmol/h)
 x = liquid mole fraction (mol/mol)
 y = vapor mole fraction (mol/mol)
 hF = molar enthalpy of the feed (kJ/kmol)
 hD = molar enthalpy of the distillate (kJ/kmol)
 hB = molar enthalpy of the bottom product (kJ/kmol)
 hL = molar liquid enthalpy for nontransport units (kJ/kmol)
 hV = molar vapor enthalpy for nontransport units (kJ/kmol)
 htL = molar liquid enthalpy for transport units (kJ/kmol)
 htV = molar vapor enthalpy for transport units (kJ/kmol)
 hdF = component molar enthalpy of feed stream (kJ/kmol)
 hdL = component molar liquid enthalpy of stream between units (kJ/kmol)
 hdV = component molar vapor enthalpy of stream between units (kJ/kmol)
 T = temperature (K)
 P = pressure (mmHg)
 f = fugacity (mmHg)
 γ = fugacity coefficient
 p^0 = vapor pressure of pure component (mmHg)
 K = equilibrium factor
 ref = reflux ratio
 obj = objective function
 c = cost component of a unit (USD/yr)
 C = total cost (USD/yr)
 τ = purity requirement, lower bound (mol/mol)
 λ = purity requirement, upper bound (mol/mol)
 ξ = recovery ratio (mol/mol)
 N = number of equilibrium stages
 DC = column diameter (m)
 QR = effective heat transfer in reboiler (kJ/h)
 QC = effective heat transfer in condenser (kJ/h)
 Z = logic variable
 z = binary variable

Arrays

\mathbf{x} = array of liquid mole fractions (mol/mol)
 \mathbf{y} = array of vapor mole fractions (mol/mol)
 \mathbf{V} = array of component vapor flowrates for nontransport units (kmol/h)

Sets

I = set of components
 $HV \subseteq I$ = set containing the heaviest component
 J_n = sets of equilibrium stages in a unit; n is equal to the number of equilibrium stages in the particular unit
 K = set of conditional units in a column section
 S = set of column sections, 1 = lower, 2 = upper

Subscripts

i = component
 j = equilibrium stage
 k = unit
 s = column section

Superscripts

B = bottom product
 C = condenser
 $crit$ = related to maximum vapor flowrate
 D = distillate
 F = feed
 $first$ = first stage
 fix = fix cost
 in = inlet
 $inner$ = inner stages
 $last$ = last stage
 out = outlet
 R = reboiler
 T = transport unit
 U = conditional unit containing equilibrium stages

Function

Φ = function in general

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