Disjunctive Programming Models for the Optimal Design of Distillation Columns and Separation Sequences†

Hector Yeomans and Ignacio E. Grossmann*

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

A disjunctive programming model is presented for the design of ideal and nonideal distillation columns in which the feed tray location, number of trays, and operating and design parameters are determined. The proposed model is based on the identification and application of MESH equations for conditional trays in order to reduce the size of the nonlinear subproblems and to increase robustness. A logic-based outer approximation algorithm is proposed to solve the problem, where the mixed-integer linear programming (MILP) master problem based on the convex hull formulation of disjunctions is replaced with a big-M formulation. The algorithm is also modified with the introduction of two initialization schemes and the inclusion of convex envelopes to improve lower bounding in the MILP master problem. It is shown that the combination of a disjunctive model and the appropriate logic-based solution algorithm can greatly improve the robustness of the design procedure. The proposed disjunctive column model is extended to the synthesis of distillation column sequences, based on the state-equipment network representation. The robustness and computational efficiency of the model is tested with four examples involving single-column and distillation sequence configurations.

1. Introduction

Distillation is one of the most important unit operations in the chemical process industry. The importance of distillation is due to the widespread use across all sectors of the chemical industry, as well as the large impact it has on the investment and energy cost of a chemical plant. The economic importance of distillation separations has been a driving force for the research in synthesis procedures for more than 30 years (Nishida et al.[1] and Westerberg[2]). Among the various synthesis approaches, mathematical programming has been receiving much attention, particularly for the synthesis of distillation sequences. Sargent and Gaminibandara[3] proposed the optimization of a superstructure that modeled Petlyuk columns using a nonlinear programming (NLP) model. Andrecovich and Westerberg[4] proposed a mixed-integer linear programming (MILP) model for synthesizing sharp separation sequences. Paules and Floudas[5] and Aggarwal and Floudas[6] developed mixed-integer nonlinear programming (MINLP) models for heat-integrated and nonsharp distillation sequences using linear mass balances. Novak et al.[7] and Yeomans and Grossmann[8] proposed superstructure MINLP optimization approaches using short-cut models for heat-integrated distillation. Recently, Smith and Pantelides[9] and Bauer and Stichlmair[10] developed MINLP models using rigorous tray-by-tray models for zeotropic and azeotropic mixtures. Also, Dunnebier and Pantelides[11] have recently used rigorous tray-by-tray MINLP models to solve complex column configuration distillation sequences.

Except for the few research efforts mentioned above, most of the mathematical programming models developed so far have relied on simplified performance models of the distillation columns, including linear mass balance equations, short-cut models (Underwood[12]), and aggregated models (Papalexandri and Pistikopoulos[13] and Caballero and Grossmann[14]). While some of these methods can provide useful results in terms of preliminary designs or bounds, it is clear that it would be desirable to directly incorporate rigorous models in the synthesis procedures in order to increase their industrial relevance and scope of application, particularly for nonideal mixtures. Regarding the rigorous MINLP synthesis models by Bauer and Stichlmair, Smith and Pantelides, and Dunnebier and Pantelides, all of them use modifications of the single-column MINLP model proposed by Viswanathan and Grossmann[15] for optimizing feed tray location and number of trays. These rigorous MINLP synthesis models exhibit significant computational difficulties, such as the introduction of equations that can become singular, the solution of many redundant equations, and the requirement of a good initialization point. The high levels of nonlinearities and nonconvexities in the MESH equations and thermodynamic equilibrium equations, as well as the convergence difficulties when deleting nonexisting columns or column sections, are problems common to the tray-by-tray models based on the model by Viswanathan and Grossmann. These difficulties translate into high computational times and the requirement of good initial guesses and bounds on the variables to achieve convergence.

The objective of this paper is to present new models for rigorous column design and superstructure optimization for distillation sequences that can reduce or eliminate the computational difficulties mentioned above. A nonlinear tray-by-tray model based on generalized disjunctive programming, GDP (Raman and Grossmann[16]), as well as a description of the solution algorithm, will be presented first for a single column. The single-column model will then be incorporated in a state-equipment

† To Professor Bob Seader for his inspiring work in process synthesis.

* To whom correspondence should be addressed. E-mail: grossmann@cmu.edu.

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network (SEN) superstructure for the synthesis of distillation sequences. Finally, several examples for single- and multiple-column problems are presented to illustrate the effectiveness of the GDP model.

2. Problem Statement

The first objective of this paper is to develop a GDP model for the optimal design of distillation columns, using rigorous tray-by-tray calculations. This problem can be stated as follows. Given is a set of feeds with known composition and a set of distillate and bottoms products with required purity and recovery. Given is also a specified maximum for the number of trays in the column. The problem then consists of determining the optimal number of trays and feed tray locations of a column, as well as the design and operating parameters, such as reflux ratio, column diameter, condenser and reboiler areas, and their heat duties. The objective is to minimize the total annualized cost of equipment and utilities. The proposed distillation column model will be based on simple-column configurations with one reboiler and one condenser.

The second objective of the paper, which will be addressed later, is to include the proposed model, suitable for ideal as well as nonideal separations, in a SEN superstructure for synthesizing distillation sequences (see Yeomans and Grossmann[8,17]).

3. Single Distillation Column Design

The basic modeling element for a rigorous distillation column is the equilibrium stage, represented by a tray in the column. If simple-column configurations are assumed, the minimum number of stages a distillation column can have is three: one feed stage, a condenser stage, and a reboiler stage. Because these trays are ever present in the column, they are considered as permanent elements in the model. For clarity purposes, it will be initially assumed that only one feed stream is given. This assumption will be removed later to accommodate the case of multiple feeds.

To achieve a specified separation, a certain number of trays have to be included in the distillation column. The number and distribution of the trays in the rectification (between the condenser and feed tray) and stripping (between the feed tray and reboiler) sections of the column is a function of the relative volatilities and compositions of the components present in the feed. The number of trays and their distribution can be estimated with short-cut models (Yeomans and Grossmann[8]). When a maximum number of potential trays above and below the feed is specified, an upper bound for the number of trays in the column is given. In this way, the selection of those trays above and below the feed that are not required (a discrete decision) will define the actual number of trays needed in the optimal column, as well as the optimal feed location.

Allowing intermediate trays to disappear in a column is achievable in a MINLP model by relaxing the constraints and equations that take place in the given tray by means of big-M constraints. Viswanathan and Grossmann[18] initially used this approach, but it had poor numerical performance. An improved approach was later introduced by Viswanathan and Grossmann,[15] who considered multiple feed positions for the reflux and boilup (see Figure 1) and assigned 0−1 variables to each

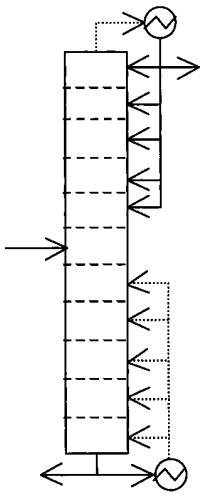

Figure 1. Viswanathan and Grossmann superstructure for a single feed column.

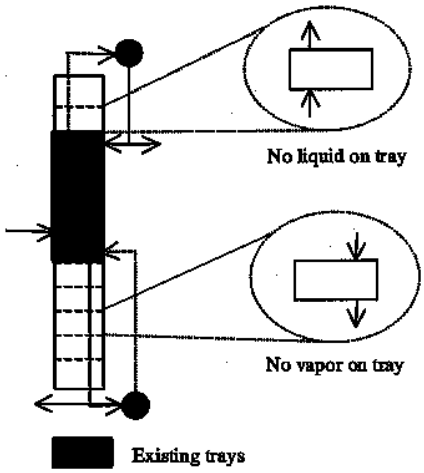

Figure 2. Inactive trays in the Viswanathan and Grossmann model.

of those potential streams. With this approach there is no need to relax equations for the nonexisting trays in the column. However, the resulting MINLP model that has to be solved is very large, because equations must be converged whether the corresponding tray exists or not. This means redundant equations (e.g., phase equilibrium) with zero liquid or vapor flow must hold in the nonexisting or inactive trays (see Figure 2). Also, the corresponding liquid and vapor flows that take a value of zero can give rise to singularities, causing convergence difficulties.

3.1. Single-Column Superstructure. The approach proposed in this paper eliminates the difficulties mentioned above by the identification and explicit specification of the tasks that take place in the permanent and conditional trays. Figure 3 shows the column representation for this approach. Consider the conditional trays. For each existing tray the mass-transfer task is accounted for and modeled with the MESH equations: the component mass balances, the tray energy balance, the equilibrium equations, and the summation of liquid and vapor mole fractions to 1. For a nonexisting or inactive tray the task considered is simply an input−output operation with no mass transfer, which gives rise to trivial mass and energy balance equations (inlet and outlet flows and enthalpies are the same for the liquid

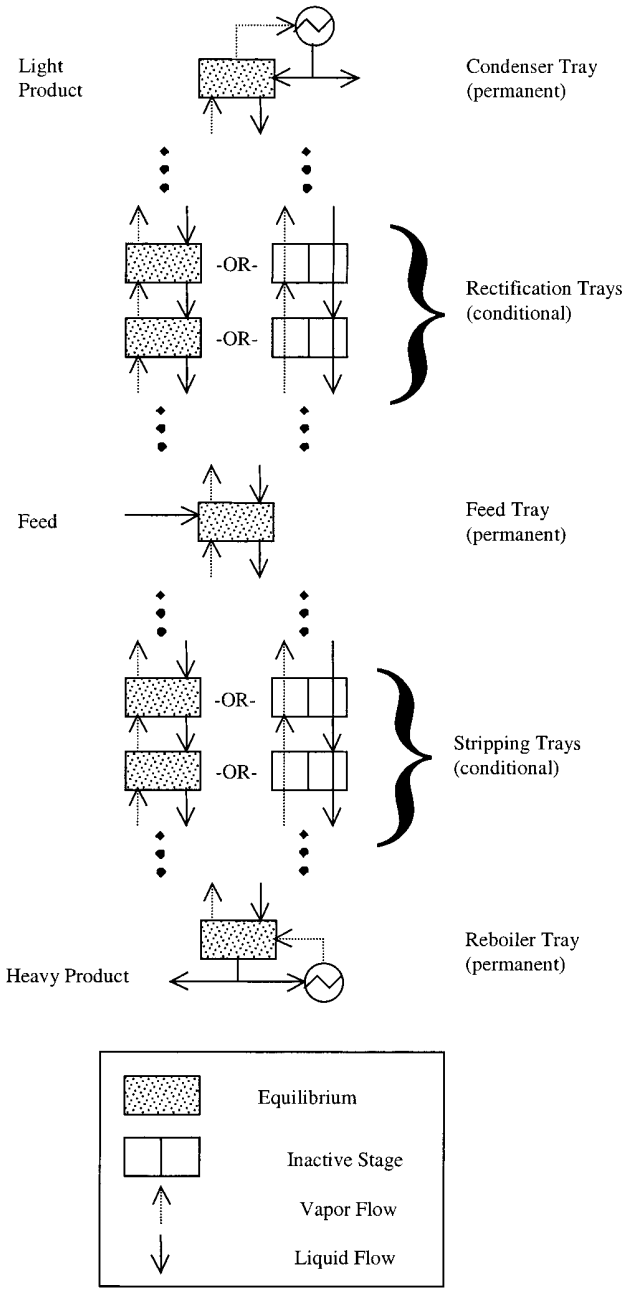

Figure 3. Single distillation column representation.

flows and the vapor flows). Because the MESH equations include the solution for trivial mass and energy balances, the only difference between existing and nonexisting trays is the application of the equilibrium equations. As for the permanent trays, all of the equations for an existing tray apply.

The advantage of the proposed modeling approach is that the MESH equations of the nonexisting trays do not have to be converged, and no flows in the column are required to take values of zero, making the convergence of the optimization procedure more reliable. Also, by using GDP as the modeling tool, the computational expense of solving the problem can be reduced, as will be shown in the next sections.

3.2. GDP Model. In this section we present the detailed GDP model for the representation of the column in Figure 3.

Consider the following set definitions for the model: C is the set of components i present in the feed. TC represents the set of trays t in the column. NFT is the feed tray $t \in$ TC. NCT is the tray $t \in$ TC corresponding to the condenser of the column. NRT represents the tray $t \in$ TC of the reboiler. TM is the subset of trays $t \in$ TC that are conditional in the rectification and stripping sections of the column. According to the above set definitions, TC = NFT ∪ NCT ∪ NRT ∪ TM.

Let ξ_i represent the minimum recovery fraction of species i and τ_i the minimum purity of species i in the distillate and/or bottoms. For simplicity in the presentation of the model, we assume only specifications in the distillate. Consider that the trays of the column ($n = 1, 2, ..., N$) are numbered from bottom to top, so that the reboiler is tray 1 and the condenser tray is number N.

The objective of the problem is to minimize the total annualized cost (TAC) of equipment and utilities. f(NT, DC, AR, AC) represents the annualized cost function of the column, which depends on the number of trays (NT), column diameter (DC), reboiler area (AR), and condenser area (AC). QR and QC are the corresponding heat loads of reboiler and condenser, and CS and CW are the steam and cooling utility costs. The objective function of the problem can be stated as

$$\min \text{TAC} = f(\text{NT,DC,AR,AC}) + \text{CS} \times \text{QR} + \text{CW} \times \text{QC} \quad (1)$$

The set of constraints for the model can be classified in two groups. The first group includes constraints with only continuous variables that are valid for any column configuration. The second group includes constraints related to discrete decisions that contain continuous and Boolean variables. The constraints in the second group are valid for specific column configurations, depending on whether vapor−liquid equilibrium (VLE) equations are applied to the tray or not.

We define the following continuous variables for the constraints in the model:

Nomenclature

F_n^i = molar feed flow of component i in tray n
FT = total molar flow of feed (single-column feed)
L_n^i = molar liquid flow of component i out of tray n
LIQ_n = total molar flow of liquid out of tray n
V_n^i = molar vapor flow of component i out of tray n
VAP_n = total molar flow of vapor out of tray n
D_i = molar flow of component i in the distillate
DIS = total molar flow of distillate
B_i = molar flow of component i in the bottoms
BOT = total molar flow of bottoms
R = reflux ratio (L_N/DIS)
T_n^{L} = temperature of liquid out of tray n
T_n^{V} = temperature of vapor out of tray n
P_n = pressure in tray n
x_n^i = liquid mole fraction of component i out of tray n
x_F^i = liquid mole fraction of component i in feed
y_n^i = vapor mole fraction of component i out of tray n
STG_n = counter for the existence of a tray
QR = reboiler heat load
QC = condenser heat load
f_i^{L} = fugacity of component i in the liquid phase
f_i^{V} = fugacity of component i in the vapor phase
hD_i = liquid molar enthalpy of component i in the distillate

hB_i = liquid molar enthalpy of component i in the bottoms

hL_n^i = liquid molar enthalpy of component i out of tray n

hV_n^i = vapor molar enthalpy of component i out of tray n

hF_i = liquid molar enthalpy of component i in the feed

U = overall heat-transfer coefficient for reboiler (R) and condenser (C)

The overall constraints include the general column mass balance, the purity and recovery requirements, the calculation of the number of stages, column diameter, reboiler, and condenser areas. These constraints are as follows:

$$\left.\begin{aligned} &F_i = D_i + B_i \\ &D_i \geq \xi_i F_i \\ &y_N^i \geq \tau_i \end{aligned}\right\} \quad i \in C$$

$$\mathrm{NT} = \sum_{n \in \mathrm{TC}} \mathrm{STG}_n \tag{2}$$

$$\mathrm{DC} \geq g(T_n^{\mathrm{V}}, P_n, \mathrm{VAP}_n) \qquad n \in \mathrm{TC}$$

$$\mathrm{AR} = \mathrm{QR}/U^{\mathrm{R}}(T^{\mathrm{S}} - T_1^{\mathrm{L}})$$

$$\mathrm{AC} = \mathrm{QC}/U^{\mathrm{C}}(T_N^{\mathrm{V}} - T^{\mathrm{cw}})$$

The feed tray is considered a fixed part of the column. There is no discrete choice associated with it, so the feed tray constraints are valid for any column configuration. The component mass balances, the energy balance, the summation of mole fractions, and the equilibrium equations are given by the following equations:

$$\left.\begin{aligned} &F_n^i + L_{n+1}^i + V_{n-1}^i - L_n^i - V_n^i = 0 \\ &F_n^i = \mathrm{FT} x_F^i \\ &L_n^i = \mathrm{LIQ}_n x_n^i \\ &V_n^i = \mathrm{VAP}_n y_n^i \\ &\sum_{i \in C} \{F_n^i \mathrm{hF}_i + L_{n+1}^i \mathrm{hL}_{n+1}^i + V_{n-1}^i \mathrm{hV}_{n-1}^i - \\ &\quad L_n^i \mathrm{hL}_n^i - V_n^i \mathrm{hV}_n^i\} = 0 \\ &\mathrm{hL}_n^i = f(T_n^{\mathrm{L}}) \\ &\mathrm{hV}_n^i = f(T_n^{\mathrm{V}}) \\ &\mathrm{hF}_i = f(T_n^{\mathrm{L}}) \\ &\sum_{i \in C} x_n^i = 1, \qquad \sum_{i \in C} y_n^i = 1 \\ &f_{i,n}^{\mathrm{L}} = f_{i,n}^{\mathrm{V}} \\ &f_{i,n}^{\mathrm{L}} = f(T_n^{\mathrm{L}}, p_n, x_n) \\ &f_{i,n}^{\mathrm{V}} = f(T_n^{\mathrm{V}}, p_n, x_n) \\ &T_n^{\mathrm{L}} = T_n^{\mathrm{V}} \\ &\mathrm{STG}_n = 1 \end{aligned}\right\} \quad n \in \mathrm{NFT} \tag{3}$$

The condenser and reboiler trays are also fixed in the column. Equation 4 includes the MESH equations for the condenser tray, and eq 5 includes the corresponding constraints for the reboiler tray:

$$\left.\begin{aligned} &V_n^i - L_{n+1}^i - D_i = 0 \\ &\sum_{i \in C} (V_n^i \mathrm{hV}_n^i - L_{n+1}^i \mathrm{hL}_{n+1}^i - D_i \mathrm{hD}_i) = \mathrm{QC} \\ &D_i = \mathrm{DIS}_n y_n^i \\ &D_i = RL_n^i \\ &\mathrm{hD}_i = f(T_n^{\mathrm{L}}) \\ &L_n^i = \mathrm{LIQ}_n x_n^i \\ &V_n^i = \mathrm{VAP}_n y_n^i \\ &T_n^{\mathrm{L}} = T_n^{\mathrm{V}} \\ &\sum_{i \in C} x_n^i = 1, \quad \sum_{i \in C} y_n^i = 1 \\ &f_{i,n}^{\mathrm{L}} = f_{i,n}^{\mathrm{V}} \\ &f_{i,n}^{\mathrm{L}} = f(T_n^{\mathrm{L}}, P_n, x_n) \\ &f_{i,n}^{\mathrm{V}} = f(T_n^{\mathrm{V}}, P_n, x_n) \\ &\mathrm{hL}_n^i = f(T_n^{\mathrm{L}}) \\ &\mathrm{hV}_n^i = f(T_n^{\mathrm{V}}) \\ &\mathrm{STG}_n = 1 \end{aligned}\right\} \quad n \in \mathrm{NCT} \tag{4}$$

$$\left.\begin{aligned} &L_{n+1}^i - B_i - V_n^i = 0 \\ &\sum_{i \in C} (L_{n+1}^i \mathrm{hL}_{n+1}^i - V_n^i \mathrm{hV}_n^i - B_i \mathrm{hB}_i) = \mathrm{QR} \\ &B_i = \mathrm{BOT} x_n^i \\ &\mathrm{hB}_i = f(T_n^{\mathrm{L}}) \\ &L_n^i = \mathrm{LIQ}_n x_n^i \\ &V_n^i = \mathrm{VAP}_n y_n^i \\ &T_n^{\mathrm{L}} = T_n^{\mathrm{V}} \\ &\sum_{i \in C} x_n^i = 1, \quad \sum_{i \in C} y_n^i = 1 \\ &f_{i,n}^{\mathrm{L}} = f_{i,n}^{\mathrm{V}} \\ &f_{i,n}^{\mathrm{L}} = f(T_n^{\mathrm{L}}, P_n, x_n) \\ &f_{i,n}^{\mathrm{V}} = f(T_n^{\mathrm{V}}, P_n, x_n) \\ &\mathrm{hL}_n^i = f(T_n^{\mathrm{L}}) \\ &\mathrm{hV}_n^i = f(T_n^{\mathrm{V}}) \\ &\mathrm{STG}_n = 1 \end{aligned}\right\} \quad n \in \mathrm{NRT} \tag{5}$$

As mentioned before, the MESH equations for the intermediate trays in the rectification and stripping sections (for the case of a single feed) are valid for any column configuration, excluding the equations related to the VLE. Equation 6 includes the mass balances and

$$\left.\begin{aligned} &L_{n+1}^i + V_{n-1}^i - L_n^i - V_n^i = 0 \\ &\sum_{i \in C} (L_{n+1}^i \mathrm{hL}_{n+1}^i + V_{n-1}^i \mathrm{hV}_{n-1}^i - \\ &\quad L_n^i \mathrm{hL}_n^i - V_n^i \mathrm{hV}_n^i) = 0 \\ &\mathrm{LIQ}_n = \sum_{i \in C} L_n^i \\ &\mathrm{VAP}_n = \sum_{i \in C} V_n^i \\ &\sum_{i \in C} x_n^i = 1, \quad \sum_{i \in C} y_n^i = 1 \\ &\mathrm{hL}_n^i = f(T_n^{\mathrm{L}}) \\ &\mathrm{hV}_n^i = f(T_n^{\mathrm{V}}) \end{aligned}\right\} \quad n \in \mathrm{TM} \tag{6}$$

energy balance for the intermediate trays, as well as the summation of mole fractions.

The constraints in eqs 1−6 involve only continuous variables and are valid for any column configuration. The constraints in eq 7 are the ones associated with the discrete choice of enforcing VLE in a tray or not. The Boolean variable Z_n takes a value of true when the tray is selected, and hence the equilibrium equations are applied in that tray. In this case the fugacities of the liquid and vapor streams are calculated, and the temperatures of liquid and vapor streams are set equal. If Z_n takes a value of false, the composition of the inlet liquid stream is set equal to the composition of the outlet liquid stream. The vapor streams are treated similarly, and the temperatures of liquid and vapor streams are set to those of the tray above and below, respectively. Because the equilibrium equations are not used, the values of the fugacity of liquid and vapor are set to zero. The disjunction is then as follows:

$$\begin{bmatrix} Z_n \\ f_{i,n}^{\mathrm{L}} = f(T_n^{\mathrm{L}}, P_n, x_n) \\ f_{i,n}^{\mathrm{V}} = f(T_n^{\mathrm{V}}, P_n, y_n) \\ f_{i,n}^{\mathrm{L}} = f_{i,n}^{\mathrm{V}} \\ T_n^{\mathrm{L}} = T_n^{\mathrm{V}} \\ \mathrm{STG}_n = 1 \\ L_n^i = \mathrm{LIQ}_n\, x_n^i \\ V_n^i = \mathrm{VAP}_n\, y_n^i \end{bmatrix} \vee \begin{bmatrix} \neg Z_n \\ x_n^i = x_{n+1}^i \\ y_n^i = y_{n+1}^i \\ L_n^i = L_{n+1}^i \\ V_n^i = V_{n-1}^i \\ T_n^{\mathrm{L}} = T_{n+1}^{\mathrm{L}} \\ T_n^{\mathrm{V}} = T_{n-1}^{\mathrm{V}} \\ f_{i,n}^{\mathrm{L}} = 0 \\ f_{i,n}^{\mathrm{V}} = 0 \\ \mathrm{STG}_n = 0 \end{bmatrix} \quad n \in \mathrm{TM} \qquad (7)$$

Because there is the possibility of deleting or deactivating different intermediate trays for the same total number of trays, it is possible to obtain multiple solutions with the same objective function value. To avoid this situation, the following logic constraints enforce the selected trays to be activated above and below the feed tray:

$$\begin{aligned} Z_n &\Rightarrow Z_{n-1}, \quad n > \mathrm{NFT} \\ Z_{n-1} &\Rightarrow Z_n, \quad n < \mathrm{NFT} \end{aligned} \qquad (8)$$

The logic relationships in eq 8 are valid only for columns with one feed. Finally, all continuous variables are positive, except for the enthalpies:

$$F, \mathrm{FT}, D, \mathrm{DIS}, B, \mathrm{BOT}, L, \mathrm{LIQ}, V, \mathrm{VAP} \in \mathrm{R}^+$$

$$R, T, P, \mathrm{NT}, \mathrm{QR}, \mathrm{QC}, x, y, f, \mathrm{STG}, \mathrm{RA}, \mathrm{CA} \in \mathrm{R}^+$$

$$\mathrm{hD}, \mathrm{hB}, \mathrm{hF}, \mathrm{hL}, \mathrm{hV} \in R$$

$$Y = \{\mathrm{True}, \mathrm{False}\}$$

4. Solution Algorithm

The proposed GDP model will be solved with a modification of the logic-based outer approximation (OA) algorithm of Turkay and Grossmann.[19] This decomposition algorithm solves the problem by iterating between reduced NLP subproblems and a MILP master problem. The NLP subproblem contains only the equations for the terms in the disjunctions that are true and provides an upper bound in the objective. The master problem predicts a combination of discrete variables, which is optimal for a global linear approximation of the problem. The MILP master problem proposed by Turkay and Grossmann[19] is constructed by applying the convex hull formulation (Balas[20]) to the linearized version of the nonlinear disjunctive problem. The combination of discrete variables produced by the master problem is used to remove the constraints from the disjunctions that do not apply to the particular tray, yielding the reduced size NLP subproblem.

One of the modifications proposed for this algorithm is the replacement of the master problem that is based on the convex hull of disjunctions by one that makes use of big-M constraints. There are two reasons for this replacement. The first is that the convex hull formulation does not yield a tight bound because of the looseness of the linearized constraints in each subregion. The second reason is that the big-M formulation does not require disaggregation of variables, and hence it involves fewer variables and constraints. A disjunction of the form

$$\begin{bmatrix} Z_k \\ A_1 x \le b_1 \end{bmatrix} \vee \begin{bmatrix} \neg Z_k \\ A_2 x \le b_2 \end{bmatrix} \qquad (9)$$

is transformed into the following constraints by means of the convex hull formulation of disjunctions (Turkay and Grossmann[21]):

$$\begin{aligned} x &= x^{\mathrm{I}} + x^{\mathrm{II}} \\ A_1 x^{\mathrm{I}} &\le b_1 z^{\mathrm{I}} \\ A_2 x^{\mathrm{II}} &\le b_2 z^{\mathrm{II}} \\ L z^{\mathrm{I}} &\le x^{\mathrm{I}} \le U z^{\mathrm{I}} \\ L z^{\mathrm{II}} &\le x^{\mathrm{II}} \le U z^{\mathrm{II}} \\ z^{\mathrm{I}} + z^{\mathrm{II}} &= 1 \end{aligned} \qquad (10)$$

where A_1 and A_2 are coefficient matrixes for two different linear sets of constraints, b_1 and b_2 are the right-hand sides of the constraint sets, x^{I} and x^{II} are variable vectors, and y^{I} and y^{II} are binary variables. It can be seen that every variable inside the disjunction term results in three variables in the MILP problem (original plus two disaggregated), as well as the inclusion of bounding constraints. For a number of synthesis problems this increase in the number of variables in the master problem is justified because the MILP relaxation becomes tighter (Turkay and Grossmann[21]). For the case of a distillation column, however, the total number of variables in the problem is very large because the constraints of each tray are linked to the trays above and below it. This linkage requires every variable in the disjunctions of every tray to be disaggregated into four variables. Furthermore, even if all of the disaggregated variables are included, there is virtually no improvement in the lower bound of the MILP relaxation.

Using the big-M transformations shown in eq 11,

$$\begin{aligned} A_1 x &\le b_1 + U(1 - z^{\mathrm{I}}) \\ A_2 x &\le b_2 + U(1 - z^{\mathrm{II}}) \\ z^{\mathrm{I}} + z^{\mathrm{II}} &= 1 \end{aligned} \qquad (11)$$

where U is a large parameter, the linearized equilibrium constraints in the left-hand term of the disjunction and

all of the constraint in the right-hand side term in eq 7 are replaced by the following in the master problem:

$$\nabla f_{i,n}^{\mathrm{L}}(\bar{T}_n^{\mathrm{L}},\bar{P}_n,\bar{x}_n)^{\mathrm{T}}\begin{pmatrix}T_n^{\mathrm{L}}\\P_n\\x_n\end{pmatrix}\le -\left[f_{i,n}^{\mathrm{L}}(\bar{T}_n^{\mathrm{L}},\bar{P}_n,\bar{x}_n) - \nabla f_{i,n}^{\mathrm{L}}(\bar{T}_n^{\mathrm{L}},\bar{P}_n,\bar{x}_n)^{\mathrm{T}}\begin{pmatrix}\bar{T}_n^{\mathrm{L}}\\\bar{P}_n\\y_n\end{pmatrix}\right] + U(1-z_n)$$

$$\nabla f_{i,n}^{\mathrm{V}}(\bar{T}_n^{\mathrm{V}},\bar{P}_n,\bar{y}_n)^{\mathrm{T}}\begin{pmatrix}T_n^{\mathrm{V}}\\P_n\\y_n\end{pmatrix}\le -\left[f_{i,n}^{\mathrm{V}}(\bar{T}_n^{\mathrm{V}},\bar{P}_n,\bar{y}_n) - \nabla f_{i,n}^{\mathrm{V}}(\bar{T}_n^{\mathrm{V}},\bar{P}_n,\bar{y}_n)^{\mathrm{T}}\begin{pmatrix}\bar{T}_n^{\mathrm{V}}\\\bar{P}_n\\y_n\end{pmatrix}\right] + U(1-z_n)$$

$$f_{i,n}^{\mathrm{L}} = f_{i,n}^{\mathrm{V}}$$

$$T_n^{\mathrm{L}} \le T_n^{\mathrm{V}} + M(1-z_n)$$

$$T_n^{\mathrm{L}} \ge T_n^{\mathrm{V}} - M(1-z_n)$$

$$x_n^i \le x_{n+1}^i + Mz_n$$

$$x_n^i \ge x_{n+1}^i - Mz_n$$

$$y_n^i \le y_{n-1}^i + Mz_n$$

$$y_n^i \ge y_{n-1}^i - Mz_n$$

$$T_n^{\mathrm{L}} \le T_{n+1}^{\mathrm{L}} + Mz_n$$

$$T_n^{\mathrm{L}} \ge T_{n+1}^{\mathrm{L}} - Mz_n$$

$$T_n^{\mathrm{V}} \le T_{n-1}^{\mathrm{V}} + Mz_n$$

$$T_n^{\mathrm{V}} \ge T_{n-1}^{\mathrm{V}} - Mz_n \qquad (12)$$

where $\bar{T}$, $\bar{P}$, $\bar{x}$, and $\bar{y}$ represent the solution of a previous NLP subproblem in the iteration sequence of the solution algorithm.

A second modification to the algorithm was made to avoid difficulties with linearizations of bilinear terms in the MILP master problem. The linearizations of bilinear terms in the disjunctive models were replaced with convex envelopes (McCormick[22] and Quesada and Grossmann[23]) in the master MILP problem. As an example of this substitution, the equation $D_i = \mathrm{DIS}x_i$ was replaced with the following convex envelopes in the master problem:

$$D_i \ge \mathrm{DIS}^{\mathrm{LO}}x_i + \mathrm{DIS}x_i^{\mathrm{LO}} - \mathrm{DIS}^{\mathrm{LO}}x_i^{\mathrm{LO}}$$

$$D_i \ge \mathrm{DIS}^{\mathrm{UP}}x_i + \mathrm{DIS}x_i^{\mathrm{UP}} - \mathrm{DIS}^{\mathrm{UP}}x_i^{\mathrm{UP}}$$

$$D_i \le \mathrm{DIS}^{\mathrm{LO}}x_i + \mathrm{DIS}x_i^{\mathrm{UP}} - \mathrm{DIS}^{\mathrm{LO}}x_i^{\mathrm{UP}}$$

$$D_i \le \mathrm{DIS}^{\mathrm{UP}}x_i + \mathrm{DIS}x_i^{\mathrm{LO}} - \mathrm{DIS}^{\mathrm{UP}}x_i^{\mathrm{LO}} \qquad (13)$$

where UP and LO represent upper and lower bounds on the variables, respectively. This substitution is appropriate, considering that good bounds on flows can be derived easily. Another advantage of using envelopes as linearizations is that they do not have to be accumulated in each iteration, as a regular Taylor series expansion would have in the original OA algorithm. These envelopes contribute to keep a low solution time of the MILP master problem.

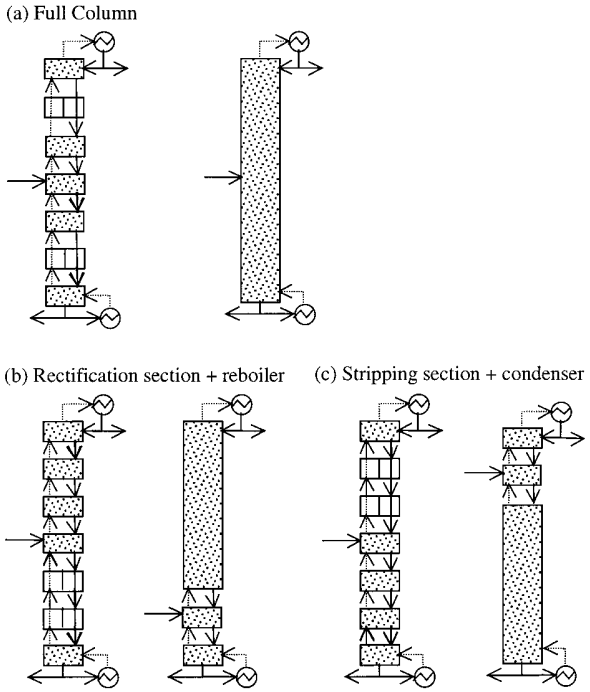

Figure 4. Initialization options for a single column.

To start the first MILP master problem, it is necessary to provide linearizations for all of the nonlinear equations in the original model. Solving the column model with the VLE equations in all trays can provide these initial linearizations, but because it represents solving the largest possible problem, it can be computationally very intensive. These linearizations can be provided with two different approaches. The first one requires a single initialization subproblem with all existing trays in the column (see Figure 4a), where the purity and recovery constraints will be relaxed. Because the objective of the initial NLP subproblem is to provide linearization values, it is not important if the solution is feasible for the original problem or not. The second approach involves solving two initialization subproblems: one for all of the existing trays in the rectification section and another one for all of the existing trays in the stripping section (see parts b and c of Figure 4). As in the first approach, purity and recovery constraints are relaxed. When problems are solved with a single column, there are no clear relative advantages of one initialization scheme over the other. However, the second approach is more appropriate when sequences are synthesized, as will be discussed later in the paper.

Overall, the proposed modifications to the logic-based OA algorithm improve its performance by reducing the size of the MILP master problem for distillation sequences, as well as the reduction of the size of the master problem as iterations progress, because fewer linearizations have to be accumulated. The smaller MILP problems, together with smaller, nonredundant NLP subproblems, make the modified logic-based OA a faster and more robust solution algorithm.

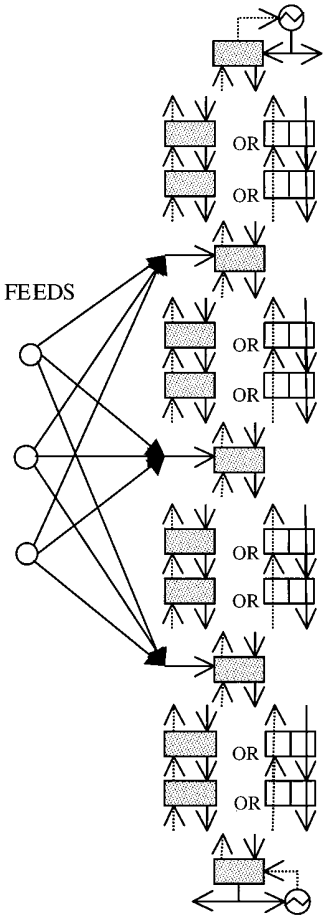

Figure 5. Column configuration for multiple feed locations.

5. Multiple Feeds and Side Draws

The model for distillation column design presented in the previous section considers that condenser, reboiler, and feed trays are permanent in the column. If multiple feeds are desired, it is only necessary to fix additional feed trays throughout the column and to consider potential assignments of the column feeds into these. Figure 5 shows the representation of a column where three feeds are possible. Note that for cases when the compositions of the feed are very different it might be possible to fix a priori the assignments (e.g., feed rich in the most volatile component at the top feed tray, equimolar in the middle feed tray, and feed rich in the heavy component in the bottom feed tray). It is in principle possible to consider as another alternative representation that every tray in the column can be a potential feed tray, as in the Viswanathan and Grossmann model. This modification was not implemented because allowing a feed to go into every tray requires multiple binary variables that indicate a given feed is supplied at a given tray. Although the number of continuous variables in this alternative model will be increased significantly, it offers one advantage over the proposed method. In particular, the upper bound on the number of trays for the proposed model with multiple feeds will be larger than that used by the Viswanathan and Grossmann model, because the upper bound needs to guarantee the required number of trays is available between each potential feed location (for an example see Figure 6).

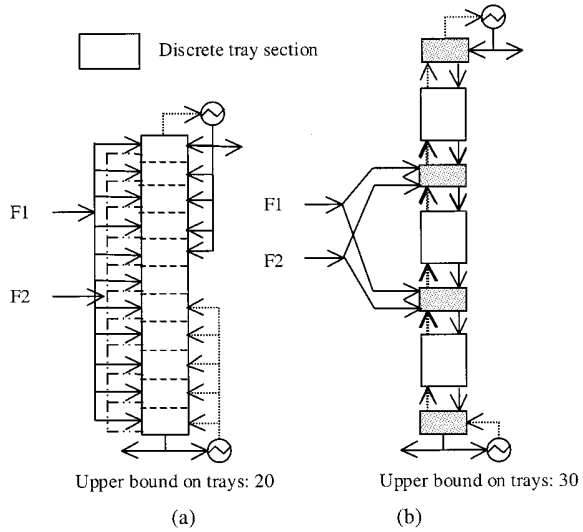

Figure 6. Comparison between (a) the Viswanathan−Grossmann model and (b) the proposed representation for multiple feeds.

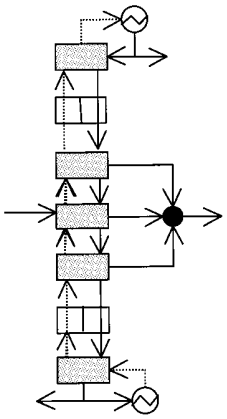

Figure 7. Potential side draws for a standard column with the proposed representation.

The case of side draws is different from the one of multiple feeds. The definition of a special side draw tray is not needed, because one can simply consider a potential extraction in each tray and the needed mixer if one single product is required (see Figure 7). Therefore, only a simple modification of the mass and energy balances on each of the intermediate trays is needed for liquid (or vapor) streams to be drawn from the column.

6. Synthesis of Distillation Sequences

The column sequence superstructure can be constructed using the state-task network (STN) or SEN representations. The reader should refer to Yeomans and Grossmann[17] for a detailed description of each one. The most suitable for the case of rigorous distillation sequences is the SEN, because the SEN representation requires the least number of equipment units in the superstructure and hence leads to a smaller model compared to the STN model (Smith and Pantelides[9]).

To construct the SEN superstructure, it is necessary to determine how many distillation columns can be used, regardless of the separation tasks that take place on each of them. The number of columns is defined in terms of the number of components available, the purity

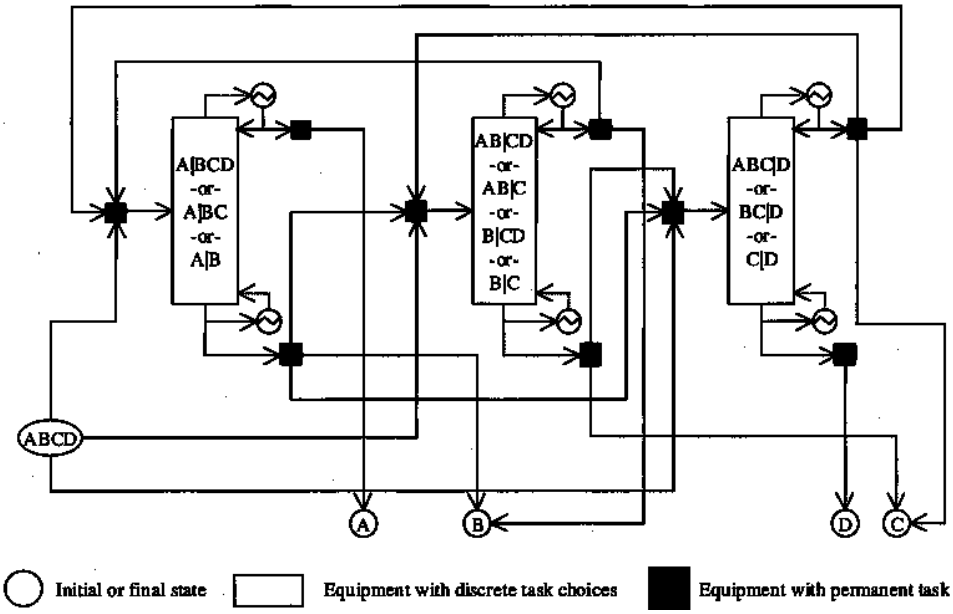

Figure 8. SEN superstructure for the separation of a four-component mixture.

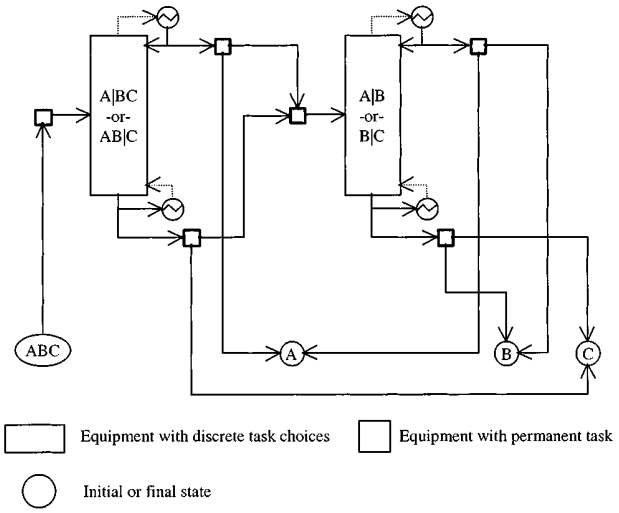

Figure 9. Alternative SEN superstructure for the separation of three components.

of the products, and the potential VLE limitations. For the case of zeotropic separations where high-purity components are required, the superstructure is composed of $n_C - 1$ columns, where n_C represents the number of components to separate. The interconnection among the columns is given by potential tasks that each column can perform. Novak et al.[7] and Yeomans and Grossmann[8] have used the assignment of tasks to each column based on the location of the separation cut (see Figure 8). This task assignment is not the simplest in terms of column connectivity, and Yeomans and Grossmann[17] proposed a different task assignment that reduces the column connectivity to the minimum. This last task assignment is the one used in this paper (Figure 9). Figures 8 and 9 show the SEN superstructure for the separation of multicomponent mixtures. Task allocation based on separation cuts assumes that the relative volatilities of the components do not change with pressure. Note that the assumption of sharp splits is not needed because a rigorous performance model is used.

6.1. GDP Model for the SEN Superstructure. Once the superstructure for the sequence of columns has been postulated, it is necessary to transform the representation into a GDP. The GDP model for distillation sequences can incorporate the proposed model for the design of a single distillation column, without any modification. This is possible because the selection of a task for a particular column in the superstructure is a decision that affects the single-column model just by changing the purity specifications and recovery, and these parameters had been considered as user-defined. Furthermore, the task selection becomes a discrete decision of higher hierarchical level, because it does not affect the model for a single column.

The complete GDP model for the synthesis of distillation sequences will include the following elements (equations are not included in detail because of space limitations):

(a) Objective function equivalent to the summation of the annualized costs of columns, as represented in eq 1.

(b) Material and energy balances for the interconnection of columns.

(c) GDP model for each column in the superstructure (eqs 2−8).

(d) The following disjunction for the selection of tasks for a particular column:

$$\bigvee_{t \in T_j} \left[\begin{array}{c} W_{tj} \\ \left. \begin{array}{l} y_{tj}^{i} \geq \xi_{ij} \\ r_{tj}^{i} \geq \tau_{ij} \end{array} \right\} i \in C \end{array} \right] \quad j \in \mathrm{COL} \tag{14}$$

where the recovery (ξ_{ij}) and purity (τ_{ij}) specifications for the distillate are in reference to component i in column j. y_{tj}^{i} and r_{tj}^{i} are the top composition and recovery of component i in column j. COL is the set of columns in the superstructure, and T_j is the set of tasks that a certain column j can perform. The Boolean variable W_{tj} is true when task t takes place in column j.

(e) Logic relationships that enforce the consistency of tasks in columns. For the separation of a zeotropic

mixture of four components, the logic relationships are the following:

$$W_{A|BCD} \Rightarrow W_{B|CD} \vee W_{BC|D}, \quad W_{AB|CD} \Rightarrow W_{A|B} \wedge W_{C|D}, \quad W_{ABC|D} \Rightarrow W_{AB|C} \vee W_{A|BC}$$

$$W_{B|CD} \Rightarrow W_{C|D}, \quad W_{BC|D} \Rightarrow W_{B|C}, \quad W_{A|BC} \Rightarrow W_{B|C}$$

$$W_{AB|C} \Rightarrow W_{A|B}, \quad W_{B|CD} \Rightarrow W_{A|BCD}, \quad W_{BC|D} \Rightarrow W_{A|BCD},$$

$$W_{A|BC} \Rightarrow W_{ABC|D}, \quad W_{AB|C} \Rightarrow W_{ABC|D}, \quad W_{A|B} \Rightarrow W_{AB|CD} \vee W_{AB|C}$$

$$W_{B|C} \Rightarrow W_{BC|D} \vee W_{A|BC}, \quad W_{C|D} \Rightarrow W_{AB|CD} \vee W_{B|CD} \quad (15)$$

where column location of each task has been omitted for clarity purposes but can be easily derived from Figure 8.

6.2. Remarks. For the distillation of azeotropic mixtures, it is not always possible to determine beforehand if a certain separation task can be achieved, if it can actually be followed by other separations, or how many columns might be required. This information can be obtained from the analysis of the equilibrium space, which in turn can be considered in the construction of the SEN superstructure. The construction of a superstructure for separation of azeotropic mixtures is out of the scope of this paper. The reader should refer to the work of Sargent[24] and Bauer and Stichlmair[10] for this topic.

7. Numerical Examples

The single-column model derived in section 3.2 was tested with two distillation problems. The first problem (example 1) involves the separation of benzene and toluene into pure components and uses ideal equilibrium. The second problem (example 2) requires the separation of ethanol and water and uses ideal vapor phase behavior and the Wilson model (Orye and Prausnitz[25]) to calculate the liquid activity coefficients. The model for distillation sequences was tested with two problems involving the separation of three-component mixtures. Example 3 involves the separation of toluene and benzene when two feed streams of different composition are available. Example 4 is the separation of *n*-butane, *n*-pentane, and *n*-hexane, and example 5 requires the separation of a mixture of benzene, toluene, and *o*-xylene. Examples 3−5 are modeled with ideal equilibrium equations.

The first three examples were solved on a 300 MHz Pentium II PC, with 128 MB of RAM. The fourth and fifth examples were solved on a 120 MHz HP9000-C110 workstation, with 256 MB of RAM. All of the examples and the solution algorithm were coded in the GAMS modeling environment (Brooke et al.[26]). The solver CONOPT 2.0 was used for the NLP subproblems, and the solver OSL was used for the mixed-integer master problems for the first three examples. The fourth and fifth example master problems were solved with CPLEX.

7.1. Example 1: Separation of Benzene and Toluene. The feed for example 1 is a mixture of benzene and toluene in ideal equilibrium. The feeds to the column are 100 kmol/h of benzene and 50 kmol/h of toluene. The required purity for the product is 99% benzene in the overhead for a minimum recovery of 50%. The upper bound for the number of discrete choice trays was 30 per column section (30 trays above and 30 trays below the feed), giving an upper bound of 63 for the total number of trays in the column. The separation is carried out at 1.01 bar.

Table 1. Computational Results for Example 1

Model Description	
discrete variables	60
continuous variables	1670
constraints	1613
OA iterations	4
initialization NLP (s)	63
NLP subproblems (s)	214
MILP master problems (s)	105
total CPU time (s)	383
Optimal Solution	
objective (K$/year)	157.36
no. of trays	55
feed location (bottom to top)	29
column diameter (ft)	1.84
condenser area (m^3)	25.6
reboiler area (m^3)	6.95
condenser duty (MkJ/h)	4.25
reboiler duty (MkJ/h)	4.27
reflux ratio (L/D)	1.77

The computational results and optimal design characteristics for example 1 are shown in Table 1. The objective function used for this problem is the minimization of the total annualized cost (TAC). The cost data for column and trays, were obtained from Peters and Timmerhaus.[27] The column cost function is in the form $c_1 D_C^{c_2} N_T$ where c_1 and c_2 are regression parameters. The cost function for heat exchangers is in the form $c_1 A^{c_2}$, where A is the area of reboiler or condenser. The stopping criterion for the logic-based OA algorithm was no improvement of the NLP solution because the problem is nonconvex (see Viswanathan and Grossmann[18]).

It is worth noting that the number of continuous variables and the number of constraints reported in Table 1 correspond to the NLP subproblem of the optimal solution. If an MINLP problem using Viswanathan and Grossmann's would be solved instead, the number of continuous variables and constraints would be more than 2000 and the number of binary variables would be 60. The small subproblem size, along with the more robust model allows the small CPU time required for solving the problem. Notice also that the initialization scheme proposed in previous sections only requires 16% of the total solution time.

7.2. Example 2: Separation of Ethanol and Water. Example 2 consists of a mixture of ethanol and water to be separated into pure water and a mixture of ethanol and water at the azeotropic conditions. The problem was modeled assuming ideal vapor phase and using the Wilson model for the calculation of liquid-phase activity coefficients. The feed consists of 1000 kmol/h of methanol and 1000 kmol/h of water. A 99% purity of water in the bottom of the column with a minimum 60% recovery is the desired specification. The separation takes place at atmospheric pressure.

The computational and design results are summarized in Table 2. The effect of the complex equilibrium calculations can be seen in the total CPU time. Despite the smaller upper bound in the number of trays (20 discrete trays per section), the computational time is longer. Notice also that the time distribution shifts significantly toward the NLP subproblems and that three OA iterations were required. Furthermore, if more iterations are run for example 2, it exhibits infeasible subproblem solutions.

Table 2. Computational Results for Example 2

Model Description	
discrete variables	40
continuous variables	1360
constraints	1365
OA iterations	3
initialization NLP (s)	76
NLP subproblems (s)	469
MILP master problems (s)	37
total CPU time (s)	582
Optimal Solution	
objective (K$/year)	3132.4
no. of trays	39
feed location (bottom to top)	19
column diameter (ft)	5.9
condenser area (m^3)	599
reboiler area (m^3)	149
condenser duty (MkJ/h)	97.3
reboiler duty (MkJ/h)	95.6
reflux ratio (L/D)	2.214

Table 3. Computational Results for Example 3

Model Description	
discrete variables	90
continuous variables	2294
constraints	2519
OA iterations	4
initialization NLP (s)	108.4
NLP subproblems (s)	182.3
MILP master problems (s)	200.0
total CPU time (s)	490.7
Optimal Solution	
objective (K$/year)	1335.87
no. of trays	38
light feed location (from bottom)	8
heavy feed location	3
column diameter (ft)	5.623
condenser area (m^3)	237.8
reboiler area (m^3)	77.7
condenser duty (MkJ/h)	39.54
reboiler duty (MkJ/h)	39.99
reflux ratio (L/D)	1.415

7.3. Example 3: Separation of Benzene and Toluene from Two Different Feeds. This example will show the performance of the single-column model when several feed streams are available. The lightest feed stream consists of 500 kmol/h of benzene and 100 kmol/h of toluene; the heaviest feed is a 600 kmol/h equimolar feed. The column configuration is similar to the one in Figure 6b. The maximum number of stages in each of the three sections of the proposed column is 30, for a total number of 90 potential trays. The pressure for the column was fixed to 1.01 bar. The computational results and design parameters for this example are found in Table 3.

Note that the possibility of feeding the heavy feedstock in a tray above the light feedstock was not considered. This was done in order to take advantage of the existing difference in volatilities of the feeds, which mainly impacts the loads of reboiler and condenser. The results show that the assumption is correct, because there are a number of trays between each light and heavy feed location. If the assumption had been incorrect, the optimal solution would have eliminated all of the trays between both feeds.

7.4. Example 4: Separation of *n*-Butane, *n*-Pentane, and *n*-Hexane. The distillation sequence synthesis model proposed in section 6.2 was tested with the following problem. Given is a mixture of *n*-butane (50% mol), *n*-pentane (25%), and *n*-hexane (25%) in a single feed. The superstructure representation in Figure 9 is needed to determine the optimal sequence and operating conditions for the separation of the feed into pure components (95% purity of *n*-butane and *n*-pentane, 90% purity of *n*-hexane; all three 90% recovery). The objective function is to minimize the net present cost (NPC) of equipment and utility costs, and the operating pressure was assumed constant throughout the column, with a value of 3.03 bar.

Table 4. Computational Results for Example 4

parameter	value
discrete variables	56
continuous variables	1952
constraints	2107
OA iterations	6
initialization NLP (s)	47.4
NLP subproblems (s)	388.8
MILP master problems (s)	2192.0
CPU time	43 min 46 s
max trays per column	30
objective value (M$)	2.2573

Table 4 shows the computational results of the problem, and the optimal design can be found in Figure 10. Because the selection of the number of trays for a column is dominated by the selection of a task for the column, the order of the branch and bound search in the master problem was set so that the discrete variables for task selection were branched on first.

If a heuristic approach is used to select the separation sequence, the following rules would be typically used (Seader and Westerberg[28]). As a first rule, perform the cut on adjacent components that have the highest relative volatility. The relative volatilities of the cuts nC4−nC5 and nC5−nC6 are not much different, so the task selection cannot be resolved by this heuristic. The second rule requires the separation of the most abundant component first (nC4). This heuristic rule leads us to the direct separation sequence, which is the separation sequence obtained by the GDP optimization (M$2.25 NPC).

Notice that the optimal separation sequence located the feed of the second column closer to the bottoms. This is because the purity specifications are tighter for the products recovered in the distillate streams. Another alternative to solve this problem is to consider a complex column configuration (i.e., single column with side draw). Because the model requires the solutions to be standard columns, this possibility was not studied. However, the model can be modified to accommodate complex column configurations, following a superstructure representation approach similar to the one proposed by Dunnebier and Pantelides.[11]

7.5. Example 5: Separation of Benzene, Toluene, and *o*-Xylene. A second example to illustrate the performance of the separation sequence model involves the separation of a 1000 kmol/h mixture of benzene (15% mol), toluene (25%), and *o*-xylene (60%) with ideal equilibrium. The products are required with at least 95% purity and a recovery of 90%. The objective function is to minimize the NPC of the equipment and utilities.

Table 5 presents the computational results of example 5. Figure 11 shows the optimal operating conditions and sequence, which is indirect in this case. The difference in the composition distribution of the feed and the close relative volatilities of the components make the problem more difficult to solve. Because of these difficulties and the higher number of maximum allowable trays per column, the computational expenses are higher.

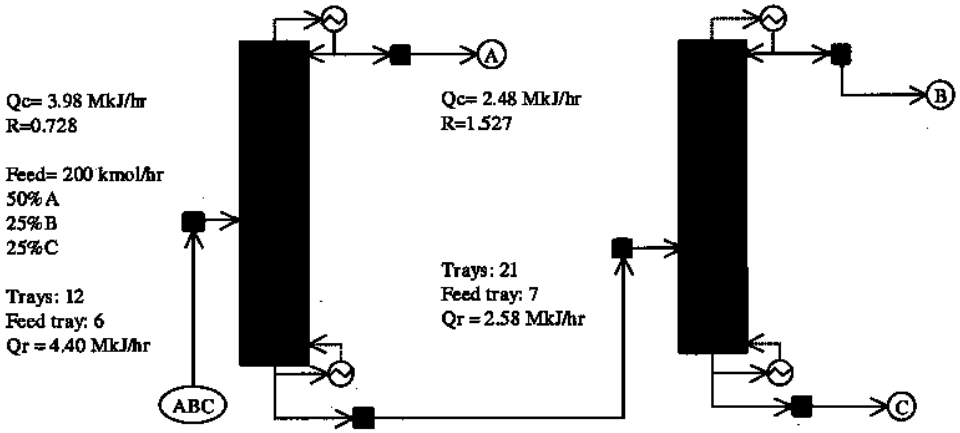

Figure 10. Optimal sequence and operating conditions for example 3 (A = *n*-butane, B = *n*-pentane, and C = *n*-hexane).

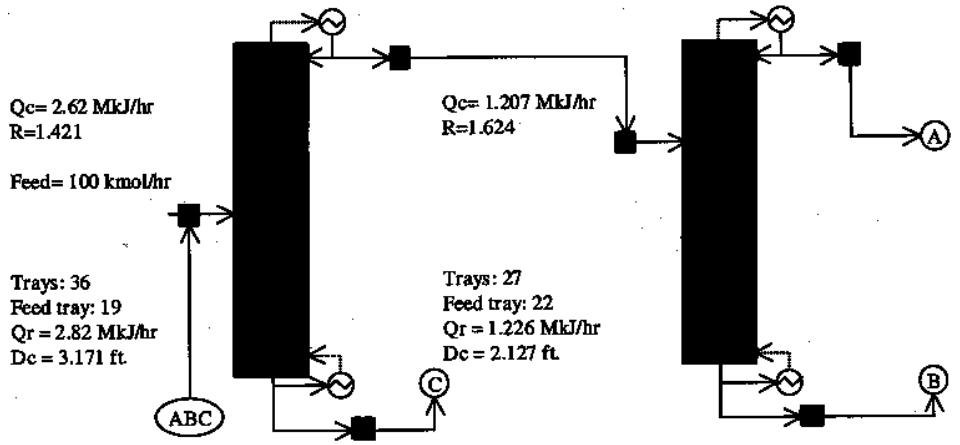

Figure 11. Optimal sequence and operating conditions for example 4 (A = benzene, B = toluene, and C = *o*-xylene).

Table 5. Computational Results for Example 5

parameter	value
discrete variables	96
continuous variables	3225
constraints	3396
OA iterations	5
initialization NLP (s)	98
NLP subproblems (s)	1445.3
MILP master problems (s)	4519.1
CPU time	101 min 2 s
max trays per column	50
objective value (M$)	1.362

7.6. Remarks. A major difficulty encountered when solving optimal distillation column design problems is the specification of the initial guess to the problem (Viswanathan and Grossmann[15] and Bauer and Stichlmair[10]). Because of the structure of the MINLP models, the initial guess usually has to be very close to a real simulation result, and it affects strongly the outcome of the solution that is obtained. One of the major benefits of the proposed model, aside from its computational performance, is its robustness. The initialization scheme of the proposed model requires only a starting point involving variable values different from zero. The problems in this paper were initialized by setting the variables of all trays to the values provided by a flash calculation of the feed.

8. Conclusions

This paper has presented a disjunctive programming model for the synthesis of distillation columns. The proposed model simultaneously optimizes the design and operating parameters of the distillation column, along with the discrete design decisions of the feed location and optimal number of trays. The representation of existing and nonexistent trays was defined in terms of the application of VLE in each tray. The proposed model was extended to the solution of multiple feed columns and distillation column sequences. If the SEN representation is used, the single-column model becomes a module in the larger distillation sequence model. It was shown that the assignment of a task to each distillation column is a higher hierarchical level discrete decision that interacts with the single-column models by means of the purity and recovery specifications.

A modified logic-based OA algorithm was proposed to solve the column model. The modifications to the solution algorithm involve two different initialization approaches and the replacement of the convex hull formulation of the master problem with a big-M formulation master problem. Also, linearizations based on convex envelopes for bilinear constraints were used to avoid singularities.

Five example problems were solved to evaluate the robustness and performance of the proposed model. The first two examples showed that it is possible to solve single-column problems with ideal or nonideal equilibrium with a moderate computational expense. The third example illustrated the case of multiple feeds. The fourth and fifth examples illustrated the application of the single-column model in the context of distillation

sequences. It is important to note that the model presented in this paper not only solves in moderate computational time, but also is more robust than standard MINLP models. This robustness is a product of the tray representation and disjunctive modeling approach, as well as of the size of the NLP subproblems that are solved when using a logic-based OA algorithm.

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