Alternative Representations and Formulations for the Economic Optimization of Multicomponent Distillation Columns

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Abstract

This paper examines alternative models for the economic optimization of multicomponent distillation columns. Different column representations are modeled involving rigorous MINLP (Mixed Integer Nonlinear Programming) and GDP (General Disjunctive Programming) formulations. The different representations involve various ways of representing the choices for the number of trays and feed tray location. Also, alternatives are considered for modeling the heat exchange when the number of trays of the column must be determinated. A preprocessing procedure developed in a previous paper (Barttfeld and Aguirre, 2002a) is extended in this work to provide good initial values and bounds for the variables involved in the economic models. This initialization scheme increases the robustness and usefulness of the optimization models. Numerical results are reported on problems involving the separation of zeotropic and azeotropic mixtures. Trends about the behavior of the different proposed alternative models are discussed.

1. Introduction

The economic optimization of a distillation column involves the selection of the configuration and the operating conditions to minimize the total investment and operation cost. Discrete decisions are related to the calculation of the number of trays and feed and products locations and continuous decisions are related to the operation conditions and energy use involved in the separation.

There are two major formulations for the mathematical representation of problems involving discrete and continuous variables: Mixed-Integer Nonlinear Programming (MINLP) and General Disjunctive Programming (GDP) where the logic is represented through disjunctions and propositions (Grossmann, 2001). Both approaches have been employed in the literature to model distillation columns. The MINLP formulation has been used with economic objective functions (Viswanathan and Grossmann,1990; Viswanathan and Grossmann,1993; Bauer and Stilchmair, 1998; Aguirre et al., 2001; Dunebier and Pantelides, 1999). Two different representations arise from this formulation according to the way the discrete decisions related to the tray optimization are modeled. In one a binary variable with a value of "1" is assigned to each tray of the column denoting its existence, and with a value of "0" its absence (Viswanathan and Grossmann,1990). In the other representations, binary variables are used for the discrete decisions related to the location of the reflux, reboil or both (Viswanathan and Grossmann,1993; Bauer and Stilchmair, 1998; Aguirre et al., 2001). MINLP problems can be solved for instance with the computer code DICOPT (Viswanathan and Grossmann, 1990), which is an implementation of the Outer Approximation/Equality Relaxation (OA/ER) algorithm (Kocis and Grossmann, 1987). The computational expense in solving these models depends largely on the problem structure. There is also the computational difficulty that each constraint must be solved even if the stage "disappears" from the column. It would be desirable to eliminate these constraints, not only to reduce the size of the NLP subproblems, but also to avoid singularities that are due to the linearization at zero flows.

Motivated by the potential of using logic to improve the modeling and solution of network systems, a logic-based MINLP algorithm has been developed by Turkay and Grossmann (1996). This algorithm has been successfully applied for solving GDP models of conventional distillation columns (Yeomans and Grossmann, 2000a; 2000b), as well as reactive distillation columns (Jackson and Grossmann, 2001). Different approaches can be used with this formulation depending on which trays are defined as permanent in the configuration. It is this issue that we will be analyzing in depth in this work.

Another major difficulty that arises in the MINLP and GDP approaches is dealing with the nonlinearities that are involved in distillation models, which complicates the convergence of solvers and often leads to infeasible solutions. Therefore, developing methods for the initialization and bounding of the variables involved in the problem is an essential part for the successful application of optimization formulations and algorithms for distillation columns.

Fletcher and Morton (2000) examined the infinite reflux case for generating good initial values for the NLP solution of general distillation columns. Buggemann and Marquardt (2001) have proposed a short cut method based on the Rectification Body Method (RBM) that provides qualitative insights for rigorous simulations. The method gives information on the minimum energy demand involved in a separation by a trial and error procedure. Given the products and feed compositions as well as the operating pressure, an estimate of the energy demand is determinated to calculate the pinch points to construct the rectification bodies related to both column sections. The energy involved in the separation under minimum reflux is achieved when the bodies intersect in exactly one point. An automatic initialization scheme based on the successive solution of NLP and MINLP optimization problems was presented in a previous paper (Barttfeld and Aguirre, 2002a). These authors developed rigorous and robust optimization models that approach reversible conditions in order to initialize and bound zeotropic distillation models. No external parameters have to be tuned in the model to achieve convergence.

The main objective of this paper is to study the different representations and models that can be used for the optimization of a single distillation column. General models comprising different column configurations will be presented for the MINLP and GDP formulations involving the separation of zeotropic and azeotropic mixtures. In order to increase the robustness of convergence of the proposed models, a general preprocessing phase is adapted and extended to GDP formulations. In this preliminary phase, thermodynamics is combined with mathematical programming. In a second step, a particular initialization scheme is derived for each mathematical formulation.

This paper is organized as follows. We first examine in section 3 the different representations to model the economic optimization problem for a given separation task. In section 4, the general models for both the MINLP and GDP formulations comprising all the alternative column representations are presented. In section 5, the solution procedures for the proposed formulations are presented. Preprocessing techniques are included to reduce difficulties related to the economic optimization task. In this section, reversible distillation theory is combined with mathematical programming tools. In section 6, several case studies are analyzed. Finally, several extensions and conclusions of this work are discussed.

2. Problem Definition

The problem addressed in this paper can be stated as follows. Given is a multicomponent feed with known flow and composition, and given are the desired products specifications. The problem then consists in selecting the number of trays, feed location, condenser and reboiler duties and areas of a distillation column so as to minimize the total annualized investment and operating cost. In order to tackle this problem we examine different representations for the column and their formulations in order to develop robust MINLP and GDP models.

3. Representation and Formulation Alternatives

In this section the different distillation columns representation are presented for the MINLP and GDP models.

MINLP Representation:

As was previously mentioned, two different MINLP column configurations can be employed to solve the economic optimization problem. However, the representation involving binary variables denoting the location for the reflux and reboil (Viswanathan and Grossmann, 1993) has been shown to be computationally more efficient than the original model proposed by Viswanathan and Grossmann (1990) where a binary variable is associated to each tray to denote its existence. For this reason, in this work heat exchange variable location will be considered to optimize the number of trays with the MINLP formulation. In Figure 1, three possible representations are shown for this alternative. If the condenser location is fixed, variable location for the feed stream and the reboiler have to be considered, as is shown in Figure 1 (a). It must be noted that above the tray where the reboiler is chosen, all trays are existing stages and mass transfer takes place. All trays located below the reboiler are nonexistent stages where a liquid flows down and no vapor flows up. In Figure 1 (b), an analogous situation is depicted showing the case of variable condenser location. The trays located below the condenser tray are existing trays, while above it are nonexisting stages where an upcoming vapor flow is bypassed. No liquid flow is going downwards trough them. In Figure 1 (c), the two previous situations are combined. Both, condenser and reboiler have variable location placement while the feed stream is fixed. Below the reboiler location the liquid flow is bypassed and above the condenser a vapor flows upwards. The configuration proposed by Viswanathan and Grossmann (1993) involving variable reflux location is depicted in Figure 2. While the representations in Figures 1 (c) and Figure 2 appear to be equivalent, there are some differences as will be described bellow.

Several remarks can be made about the representations in Figure 1:

- Due to the existence of the variable heat exchange location in all nonexistent trays one of the internal flows of the column takes a value of zero.

- If liquid distillate product is specified and the column representation involves variable condenser location, a fixed condenser must be placed at the column top to condense the upcoming vapor flow.
- Vapor liquid equilibrium (VLE) conditions are enforced in all trays of the column, even in nonexisting trays where no mass transfer takes place. This means that VLE equations, which are high nonlinear expressions, have to be satisfied in nonexisting trays.
- In all configurations one reference point (fixed tray) is needed and there exists at least one variable location for the heat exchange.

From Figure 1 and 2, it follows that there are two possible representations to model variable trays elimination with the MINLP formulation as is shown in Figure 3. In part (a) of this picture, a condenser and a reboiler are placed in all candidate trays for exchanging energy. This means that a variable reflux (reboil) stream is considered by moving the condenser (reboiler). Otherwise, in the representation of variable reflux location (Figure 3 (b)), the condenser and reboiler are fixed equipments in both column extremes. The reflux (reboil) flow location is variable and not the condenser (reboiler) itself. These two alternatives are the same if one fixed equipment is considered at each column ends. However, when heat exchange variable locations are modeled as part of the tray optimization procedure some differences arise. In one case, the problem consists in finding the optimal location for the energy exchanged, while in the other the optimal location for a "secondary" feed stream (reflux) is considered. The variable heat exchange representation has an important advantage. The energy can be exchanged at intermediate trays temperatures, possibly leading to more energy efficient designs.

GDP Representations:

The possible column representations for the GDP formulations are depicted in Figure 4. In all cases, heat exchange takes place in existing trays (fixed) located at both column ends. This fact avoids that all internal flows become zero in nonexisting trays. In Figure 4 (a) an additional tray location is considered as permanent at the column feed point. Then, the resulting representation has three fixed trays. All stages between these permanent trays are conditional trays and boolean variables are related to their existence. Also, through logic constraints, the column "grows" around the feed tray. For existing trays, vapor and liquid equilibrium equations are enforced. For nonexisting trays, vapor and liquids flows bypass each other without mass and heat transfer. Both of these conditions are enforced with disjunctions.

Another possibility is shown in Figure 4 (b) where two trays (extreme stages) are permanent and all trays between them are considered conditionals (Jackson and Grossmann, 2001). The feed tray location is variable and the column can grow from the top (bottom) stage downwards (upwards).

The representations of Figure 4 have the following characteristics:

- There are nonzero liquid and vapor flows in all column trays. The reason is that in nonexisting trays both the internal liquid and vapor flows are bypassed.
- Due to the use of disjunctions at each tray, the VLE equations are only applied to existing trays. This means that these equations do not need to be satisfied in nonexisting stages.
- In the GDP configurations, a minimum of two reference points in the column are needed.

Finally, we should note that heat exchange can be considered in nonexisting trays by simply adding the possibility of exchanging heat in existing trays (see Jackson and Grossmann, 2001).

4. Single Columns Models

In this section, the general MINLP and GDP models are presented for all the representations discussed in section 3.

A distillation column model can be formulated in two different ways:

1. Employing total flows, e.g. L_n, and mole fractions related to each flow, e.g. $x_{n,i}$.

2. Employing individual flows, e.g. $LIQ_{n,i}$ defined as $LIQ_{n,i} = L_n \; x_{n,i}$.

The first alternative has the advantage of providing a convenient framework for the evaluation of the thermodynamic properties and bounds can be expressed in a more natural form. The major disadvantage of this type of formulation is that bilinear (nonconvex) terms are involved in the mass and energy balances for each components. The individual component flow formulation gives rise to a larger number of linear equations, although it requires separate equations for defining the compositions. In this work, the MINLP problem will be formulated in terms of total flows but results involving individual component flows will be also presented. In contrast, the proposed GDP formulation will involve individual flows to write the MILP master problem easily using convex envelopes (Quesada and Grossmann, 1995).

Consider the following set definitions for the formulation of the models: *C* is the set of components *i* present in the feed. *N* represents the set of trays *n* in the column. Let the subset *feed* be the candidate feed trays *n*, *reb* the candidate trays for placing a reboiler, *cond* the candidate trays for placing a condenser, *top* the column top tray and *bot* the column bottom tray. Then $prod = top \cup bot$. Let η_i represent the minimum recovery fraction of component *i* in the distillate or bottom product. Consider that the trays (n = 1, 2, …, $Nmax$) in the column are numbered from top to bottom, so that the condenser is in tray 1 and the reboiler in tray N_{max}. Let n_{min} a lower bound on the number of trays of a column section.

The objective of the problem is to minimize the total annualized cost (*TAC*) of equipment and utilities. The investment costs are given by the function *f*(*NT,Dcol,Ar,Ac*) that involves the number of trays of the column *NT*, its diameter *Dcol,* and the condenser and reboiler areas, *Ar* and *Ac,* respectively. Q_C and Q_H *tot* are the corresponding condenser and reboiler loads, and C_w and C_s are the steam and cooling utility costs. The objective function for the economic problem can be then stated as follows:

$$\min \; TAC \;=\; f(NT, Dcol_n, Ar, Ac) \;+\; C_w\, Q_C \;+\; C_s\, Q_H \qquad (1)$$

4.1. MINLP Model

The detailed MINLP model that incorporates all the alternative representations shown in Figure 1 is as follows. Consider the single stage superstructures in Figure 5, where both alternatives for modeling variable heat exchange location are shown. Figure 5 (a) considers the variable condenser (reboiler) location, while Figure 5 (b) is the superstructure for variable reflux (reboil) location. Note that in the superstructure of Figure 5 (b) the heat exchange only takes place in the top and bottom trays of the column. This last alternative was employed by Viswanathan and Grossmann (1993), and Yeomans and Grossmann (2000a, 2000b). Although results for both approaches will be presented, for the model presentation only the tray superstructure of Figure 5 (a) will be considered.

The set of constraints for the model can be classified in two groups. The first group includes constraints with only continuous variables and a second group includes constraints related to discrete decisions that involve binary variables. The constraints involving only continuous variables include the general column mass and energy balances ((2)-(12)), purity and recovery requirements for products (13), the VLE equations (14), the definition of the liquid and vapor enthalpies (15), the sum of mole fractions (16), the calculation of the number of stages (17), and column diameter (18) and heat exchange areas definitions (19)-(20). The constraints are given as follows:

$$\sum_{n \in feed} F_n \; zf_{n,i} \; = \sum_{n \in prod} (PL_n \; x_{n,i} + \; PV_n \; y_{n,i}) \tag{2}$$

$$\sum_{n \in feed} F_n \; hf_n + Q_{H\ tot} \; - \; Q_{C\ tot} = \sum_{n \in prod} (PL_n \; hl_n \; + PV_n \; hv_n) \tag{3}$$

$$\sum_{n \in feed} F_n = Fo \tag{4}$$

$$\sum_{n \in feed} hf_n = hfo \tag{5}$$

$$zf_{n,i} = zfo_i \qquad \forall n \in feed, \forall i \in C \tag{6}$$

$$\left. \begin{array}{l} F_n \; zf_{n,i} + L_{n-1} \; x_{n-1,\,i} + V_{n+1} \; y_{n+1,\,i} \; = \; L_n \;\; x_{\,n,i} + \; V_n y_{\,n,i} \\ F_n \, hf_n + \; V_{\,n+1} \;\; hv_{n+1} \; + \; L_{\,n-1} \;\; hl_{n-1} = \; L_n \, hl_{\,n} + \; V_{\,n} \; hv_{\,n} \end{array} \right\} \forall \, n \in feed \tag{7}$$

$$\left. \begin{array}{l} L_{\,n-1} \; x_{n-1,\,i} + V_{n+1} \; y_{n+1,\,i} \; = \; L_n \;\; x_{\,n,i} + \; V_n y_{\,n,i} \\ V_{\,n+1} \;\; hv_{n+1} \; + \; L_{\,n-1} \;\; hl_{n-1} = \; L_n \, hl_{\,n} + \; V_{\,n} \; hv_{\,n} \end{array} \right\} \forall n \tag{8}$$

$$\left. \begin{array}{l} V_{n+1} \; y_{n+1,\,i} \; = \; (L_n + PL_{\,n}) \, x_{\,n,i} + PV_{\,n} \; y_{\,n,i} \\ V_{\,n+1} \;\; hv_{n+1} \; = \; (L_n + PL_{\,n}) \;\; hl_{\,n} + PV_{\,n} \; hv_{\,n} + k_c \;\; Q_n \end{array} \right\} \forall n \in top \tag{9}$$

$$L_{\,n-1} \; x_{n-1,\,i} \; = \; PL_{\,n} \; x_{\,n,i} + (V_n + PV_{\,n}) y_{\,n,i} \qquad \forall n \in bot \tag{10}$$

$$V_{\,n+1} \;\; hv_{n+1} \; = \; (L_n + PL_{\,n}) \;\; hl_{\,n} + PV_{\,n} \; hv_{\,n} + Q_n \qquad \forall n \in cond \tag{11}$$

$$Q_n \; + L_{n-1} \;\; hl_{\,n-1} \; = \; PL_{\,n} \, hl_{\,n} + (V_n + PV_{\,n}) \; hv_{\,n} \qquad \forall n \in reb \tag{12}$$

$$\left. \begin{array}{l} \displaystyle\sum_{n \in top\ or\ bot} (PL_n \; x_{n,i} + \; PV_n \; y_{n,i}) \geq \; \eta_i \; Fo \;\; zfo_{\,i} \\ \displaystyle\sum_{n \in top\ or\ bot} [\, (1 - qd) \; x_{n,i} + qd \;\; y_{n,i}] \; \geq \tau_i \end{array} \right\} \forall \, i \tag{13}$$

$$\left.\begin{aligned} f^L_{n,i} &= f^V_{n,i} \\ f^L_{n,i} &= f(T_n, P_n, x_{n,i}) \\ f^V_{n,i} &= f(T_n, P_n, y_{n,i}) \end{aligned}\right\} \forall n,i \tag{14}$$

$$\left.\begin{aligned} hl_n &= f(T_n) \\ hv_n &= f(T_n) \end{aligned}\right\} \forall n \tag{15}$$

$$\left.\begin{aligned} \sum_{i=1}^{C} x_{n,i} &= 1 \\ \sum_{i=1}^{C} y_{n,i} &= \end{aligned}\right\} \forall n \tag{16}$$

$$NT = f(bc_n, br_n) \tag{17}$$

$$Dcol = f(T_n, P_n, V_n) \tag{18}$$

$$Ar = f(Qhtot, T_n) \tag{19}$$

$$Ac = f(Qctot, T_n) \tag{20}$$

The constraints involving binary variables that model the variable location for the heat exchange equipments and variable feed location are as follows. A binary variable bc_n (br_n) is defined denoting the existence of a condenser (reboiler) in tray n of the set *cond* (*reb*) if this variable is 1. A binary variable bf_n is also considered for denoting the existence of the feed stream entering tray n of the candidate set of trays *feed*. The equations describing the heat loads and feed and their relation to the binary variables are as follows:

$$\begin{aligned} Q_C &= \sum_{n \in cond} Q_n + k_c \sum_{n \in top} Q_n \\ Q_n &\le bc_n \quad Q_{\max} \qquad \forall n \in cond \\ \sum_{n \in cond} & bc_n = 1 \end{aligned} \tag{21}$$

$$\begin{aligned} Q_H &= \sum_{n \in reb} Q_n \\ Q_n &\le br_n \quad Q_{\max} \qquad \forall n \in reb \end{aligned} \tag{22}$$

$$\sum_{n \in reb} br_n = 1$$

$$F_n \leq bf_n \; F_{\max} \qquad \forall n \in feed$$

$$\sum_{n \in feed} bf_n = 1 \tag{23}$$

Note that k_c is a scalar, which is "1" if the alternative for the column representation involves variable condenser and liquid distillate product. Otherwise, k_c is zero.

The model for variable reboiler configuration is derived by defining the following set of trays and the scalar k_c:

$$cond = \{n : n = 1\}$$

$$reb = \{n : 2n_{\min} \leq n \leq N_{\max}\}$$

$$feed = \{n : n_{\min} \leq n \leq nfo\}$$

$$k_c = 0$$

The condenser is located on the top tray. If n_{min} is a lower bound of the number of trays in each section of the column and nfo is the lowest feed tray location, the candidate reboiler trays as well as the candidate feed trays are defined as is shown in Figure 6 (a). The number of trays is defined as a function of the binary variable related to the reboiler location:

$$NT = \sum_{n \in reb} br_{reb} \; n \tag{24}$$

From Figure 6 (b), the variable condenser alternative (involving liquid distillate product) is derived by defining the sets of trays as follows:

$$cond = \{n : 2 \leq n \leq (N_{\max} - 2\,n_{\min})\}$$

$$reb = \{n : n = N_{\max}\}$$

$$feed = \{n : nfo \leq n \leq (N - n_{\min})\}$$

$$k_c = 1$$

The reboiler is fixed in the bottom tray of the column while the condenser and the feed candidate trays are defined by the equation (25):

$$NT = N_{\max} - \sum_{n \in cond} bc_{cond}\ n\ +\ 1 \tag{25}$$

For the alternative where both heat exchangers are variable and the feed tray is kept fixed in tray *nfo*, the candidates trays are defined according to Figure 6 (c):

$cond = \{n : 2 \le n \le (nfo - n_{\min})\}$

$reb = \{n : (nfo + n_{\min}) \le n \le N_{\max}\}$

$feed = \{n : n = nfo\}$

$k_c = 1$

and the number of trays is given by:

$$NT = \sum_{n \in reb} br_{reb}\ n\ -\ \sum_{n \in cond} br_{cond}\ n\ +\ 1 \tag{26}$$

It must be noted the general formulation given by (1) to (26) covers all the alternatives representations of Figure 1.

4.2. GDP Model

As was previously mentioned two different types of trays are involved in this formulation. In Figure 7, the superstructures for permanent and conditional trays are shown. The top and bottom stages of the GDP column representation are modeled as permanent trays (Figure 6 (a)) where heat exchange takes place and vapor or liquid products are withdrawn. These trays are modeled as equilibrium stages, where the vapor and liquid flows leaving a permanent tray are in equilibrium. Conditional trays (Figure 6 (b)) are intermediate trays of the column whose existence is defined according to the truth value of the corresponding boolean variable. If a tray is selected it becomes in an equilibrium stage. Otherwise, the vapor and liquid streams are bypassed.

The general GDP formulation is presented next for the alternatives shown in Figure 4. Let the set of trays be defined as $pt = \{n : n = 1,\ n = N_{\max}\}$ and the set of intermediate trays as $it = \{n : 2 \le n \le (N_{\max} - 1)\}$.

The general constraints for the column diameter, condenser and reboiler areas and the number of trays in the column are given by the following:

$$Dcol = f(T_n^V, P_n, V_n) \tag{27}$$

$$Ar = f(Qhtot, T_n^L) \tag{28}$$

$$Ac = f(Qctot, T_n^V) \tag{29}$$

$$NT = \sum_n stg_n \tag{30}$$

The permanent trays are modeled according to Figure 6 (a):

$$\left.\begin{array}{l}
LIQ_{n,i} = L_n \; x_{n,i} \\
VAP_{n,i} = V_n \; y_{n,i} \\
PLIQ_{n,i} = PL_n \; x_{n,i} \\
PVAP_{n,i} = PV_n \; y_{n,i} \\
\sum_{i=1}^{C} x_{n,\,i} = 1 \\
\sum_{i=1}^{C} y_{n,\,i} = 1 \\
f_{n,i}^L = f_{n,i}^V \\
f_{n,i}^L = f(T_n, P_n, x_{n,i}) \\
f_{n,i}^V = f(T_n, P_n, y_{n,i}) \\
hliq_{n,i} = f(T_n, LIQ_{n,i}) \\
hvap_{n,i} = f(T_n, VAP_{n,i}) \\
hpliq_{n,i} = f(T_n, PLIQ_{n,i}) \\
hpvap_{n,i} = f(T_n, PVAP_{n,i})
\end{array}\right\} \forall\, n \in pt,\, i \in C \tag{31}$$

$$\left.\begin{array}{l}
LIQ_{n,i} - VAP_{n+1,i} - PLIQ_{n,i} - PVAP_{n,i} = 0 \\
hliq_{n,i} - hvap_{n+1,i} - hpliq_{n,i} - hpvap_{n,i} - Q_n = 0
\end{array}\right\} \forall\, n \in pt,\; n \in top \tag{32}$$

$$\left.\begin{array}{l}
VAP_{n,i} - LIQ_{n-1,i} - PLIQ_{n,i} = 0 \\
hvap_{n,i} - hliq_{n-1,i} - hpliq_{n,i} + Q_n = 0
\end{array}\right\} \forall\, n \in pt,\, n \in bot \tag{33}$$

$$Q_C = \sum_{n \in top} Q_n \tag{34}$$

$$Q_H = \sum_{n \in bot} Q_n \tag{35}$$

$$\left.\begin{array}{l}\sum_{n\in top\ or\ bot}(PLIQ_{n,i}\ +\ PVAP_{n,i})\geq\varepsilon_i\ Fo\ \ zf_i\\\sum_{n\in top\ or\ bot}[\,(1-qd)\ x_{n,i}+qd\ \ y_{n,i}]\ \geq\tau_i\end{array}\right\}\ \forall i\in C \tag{36}$$

$$stg_n=1 \qquad \forall n\in pt \tag{37}$$

Conditional trays are modeled according to Figure 7 (b). It is important to note that in a conditional tray a temperature for the liquid and for the vapor is defined instead of a tray temperature as it occurs in conventional distillation columns representations. In case the tray is selected, the emerging liquid and vapor temperature are the same and equal to the temperature of the tray. Otherwise, each bypassed stream keeps its own temperature.

$$\left.\begin{array}{l}FEED_{n,i}+LIQ_{n,i}+VAP_{n,i}-LIQ_{n-1,i}-VAP_{n+1,i}=0\\hfeed_{n,i}+hliq_{n,i}+hvap_{n,i}-hliq_{n-1,i}-hvap_{n+1,i}=0\end{array}\right\}\ \forall n\in it,\,n\in feed \tag{38}$$

$$\left.\begin{array}{l}LIQ_{n,i}+VAP_{n,i}-LIQ_{n-1,i}-VAP_{n+1,i}\ =0\\hliq_{n,i}+hvap_{n,i}-hliq_{n-1,i}-hvap_{n+1,i}=0\\\sum_{i=1}^{C}x_{n,\,i}\ =1\\\sum_{i=1}^{C}y_{n,\,i}\ =1\\hl_{n,i}=f(T_n^L,LIQ_{n,i})\\hv_{n,i}=f(T_n^V,VAP_{n,i})\end{array}\right\}\ \forall n\in it,\,i\in C \tag{39}$$

The discrete choices are modeled with disjunctions. The boolean variables W_n denote the existence of a conditional tray. If a value of true is assigned to this variable the tray is selected and VLE equations are applied to this tray. Otherwise, the vapor and liquid streams are bypassed through it and no mass transfer process takes place. Also, existent trays are candidate trays for having a feed steam. The boolean variables Bf_n are set to true if the feed $F_{n,i}$ enters stage n. The disjunction for each conditional tray is as follows:

$$\begin{bmatrix} W_n \\ f^L_{n,i} = f(T_n, P_n, x_{n,i}) \\ f^V_{n,i} = f(T_n, P_n, y_{n,i}) \\ f^L_{n,i} = f^V_{n,i} \\ T^V_n = T^L_n \\ \\ LIQ_{n,i} = L_n \ x_{n,i} \\ VAP_{n,i} = V_n \ y_{n,i} \\ stg_n = 1 \\ \\ \begin{bmatrix} Bf_n \\ FEED_{n,i} = Fo \ zf_i \\ hfeed_{n,i} = Fo \ hf \end{bmatrix} \vee \begin{bmatrix} \neg Bf_n \\ FEED_{n,i} = 0 \\ hfeed_{n,i} = 0 \end{bmatrix} \end{bmatrix} \vee \begin{bmatrix} \neg W_n \\ f^L_{n,i} = 0 \\ f^V_{n,i} = 0 \\ T^V_n = T^V_{n+1} \\ T^L_n = T^L_{n-1} \\ V_n = V_{n+1} \\ L_n = L_{n+1} \\ x_{n,i} = x_{n-1,i} \\ y_{n,i} = y_{n+1,i} \\ stg_n = 0 \end{bmatrix} \qquad \forall\, n \in it \qquad (40)$$

where the first term is activated when $W_n = True$, and the second when $W_n = False$.

The design specifications and logic propositions are given by expression (41), which involves only boolean variables.

$$\Omega(W_n, Bf_n) = True \qquad \forall\, n \in it \qquad (41)$$

The equations in these expressions depend on the column representation that is used. For the fixed feed representation in Figure 4 (a) the following logic propositions are defined:

$$W_n \Rightarrow W_{n+1} \qquad \forall\, n \in it,\ 2 \le n \le (nfo - 1) \qquad (42)$$

$$W_n \Rightarrow W_n \qquad \forall\, n \in it,\ (nfo + 1) \le n \le (N_{\max} - 1) \qquad (43)$$

Equations (42) and (43) avoid the possibility of obtaining multiple solutions with the same objective function value and enforce that the selected trays be activated above and below the feed tray (Yeomans and Grossmann, 2000a). It should be noted that in this alternative, the set of feed trays $feed$ is defined as $feed = \{n : n = nfo\}$.

In the representation of Figure 4 (b.1), where variable feed location is allowed, the selected trays are activated above the reboiler tray:

$$W_n \Rightarrow W_{n+1} \qquad \forall\, n \in it,\ 2 \le n \le (N_{\max} - 1) \tag{44}$$

In this representation, the set of feed trays $feed_n$ is defined as $feed = \{n : nfo \le n \le (N_{\max} - n_{\min})\}$.

Analogous expressions can be derived for the representation in Figure 4 (b.2).

In the variable feed location alternative, only existing trays are candidate for having a feed stream entering:

$$Bf_n \Rightarrow W_n \qquad \forall\, n \in it, \tag{45}$$

5. Solution of Models

In this section, the algorithms and procedures employed for solving the models presented in the previous section are described.

As was previously mentioned, independently of the formulation or the column representation employed, the initialization procedure of distillation models is a relevant point that must be considered. For that reason, in this work we extend the preprocessing phase as a preliminary solution phase to the economic optimization. The general preprocessing procedure that is applied to both formulations is described in section 5.1. In section 5.2 the solution procedure for each formulation is outlined.

5.1. General Preprocessing Phase

In the preprocessing phase initial values and bounds are systematically generated by solving optimization problems. The main idea of this phase is to generate a feasible design as an initial guess to the economic optimization problem. Ideally, good initial values and bounds have to be provided for the most relevant decision variables, such as the energy demand, internal liquid and vapor flows.

The same column topology used in the preprocessing phase has to be used in the economic topology. This means that the same upper bound on the number of trays has to be employed as well as the potential feed and product location.

We select as initial design one that involves minimum reflux conditions as well as minimum entropy production. This reversible separation provides a feasible design and hence a good initial guess to the economic optimization. Economic solutions involve a fewer number of trays than the ones of the initial solution guess. Therefore, the problem consists in optimizing the number of trays once the preprocessing phase has been solved.

An adiabatic column involving minimum heat loads and a number of stages large enough can approximate a reversible column. In spite of the difference in the energy distribution between a reversible theoretical column and its finite approximation, the products composition and flows as well as the energy demands are often very close to the theoretical values. A detailed discussion of the reversible separation task, reversibility conditions as well as an approach using a finite adiabatic column can be found in Barttfeld and Aguirre (2002a).

The general preprocessing phase procedure is shown in Figure 8. After solving a flash calculation for the feed, a model is solved for calculating the theoretical reversible products composition and flows and the minimum energy demand involved in the reversible separation task. An optimization problem for computing the theoretical model is presented for zeotropic mixtures in Barttfeld and Aguirre (2002a). A general method for multicomponent mixtures based on this previous model is employed in this work. The proposed method can deal with azeotropic mixtures with no need of knowledge of the volatility order of the components for a given azeotopic feed composition. This means that no preliminary simulations are needed to determine the feasible distillations regions. In the zeotropic case this model reduces to the previous formulation. The mathematical model which, corresponds to an NLP, can be found in Appendix A.

Once the reversible model has been solved, overall mass and energy balances can be formulated involving the column top (bottom) and the column point where the heaviest (lightest) component disappears. The saddle pinch points that take place during the reversible separation approach are computed solving the same optimization problem presented in the work by Barttfeld and Aguirre (2002a).

With the results of the reversible separation it is possible to calculate the minimum energy demand involved in the separation where the lightest (heaviest) component is completely recovered in the distillate (bottom) product. The rectifying (stripping) saddle pinch point that takes place in the adiabatic approach to a reversible column is preserved in the separation involving a low (high) boiler rich distillate (bottom) fraction (Stilchmair and

Fair, 1998). With the saddle pinch point information, the minimum energy demand involved in these separations then can be easily calculated. The NLP model for these calculations is presented in Appendix A.

Up to this point, well-behaved optimization problems are solved to compute relevant information to rigorously approach the reversible and low (high) boiler rich distillate (bottom) separations under minimum reflux conditions. A tray-by-tray distillation column is considered next. An upper bound on the number of stages is selected according to the pinch point zones development criteria (Barttfeld and Aguirre, 2002b). This model involves the constraints presented in the previous section (according with the formulation employed) except for these ones related to costs and column dimensions. For a column with an upper bound of 50 trays and a ternary mixture, the model involves 2250 constraints and 2750 variables. An additional constraint describing the reversible mass balance line is included:

$$y_i^F - x_{top,i} = \alpha \ (x_i^F - y_i^F) \qquad (46)$$

where x_i^F and y_i^F are the feed liquid and vapor composition, $x_{top,i}$ is the distillate composition and α represents the ratio between the liquid flow leaving the rectifying section and the distillate product flow. This equation is obtained from witting total and component mass balances for a reversible rectifying column section. An analogous expression can be written for a reversible stripping section.

Then, the following objective function is minimized over the feasible region previously described (see Appendix A for the definition of *s* and *cmax*):

$$z = s \ (x_{bot,c\max} - x_{top,c\max}) \qquad (47)$$

Expression (47) enforces the product compositions to move towards the mass balance line extremes, while constraint (46) forces the separation mass balance line direction to coincide with the reversible direction.

Starting from this solution, the separation involving a low boiler rich distillate or higher boiler rich bottom fraction under minimum reflux conditions can be rigorously approximated. In this solution, the cost-based and dimensional equations are included as constraints to obtain upper bounds of the cost related variables. Since we obtain information about the theoretical minimum energy demands of the separations that are taking place, these rigorous solutions are not difficult to obtain.

When azeotropic mixtures are involved, the same preprocessing procedure is employed. However, no calculations involving the low (high) boiler-rich distillate separation are computed or rigorously approximated. That is because, in some cases, saddle pinch points do not exist due to the presence of distillation boundaries.

5.2. MINLP Model Solution

The MINLP formulation is solved according to the following procedure (see Figure 9):

1. Solve the general preprocessing phase.
2. Using as a starting point the solution from step 1, initialize the MINLP as follows:
   2.1. Solve the model as a Relaxed MINLP (RMINLP). A lower bound on the total cost for the separation is obtained.
   2.2. Reduce the candidate trays for variable heat exchange equipments or feed tray location, according to the case, using information of the solution obtained in point 2.1.
3. Solve the model as an MINLP problem (e.g. using DICOPT).

Using the procedure described above, the MINLP formulation can be solved with a reduced number of binary variables. The reason is that the RMINLP optimal solution in step 2.1 yields a number of trays that is often very close to the integer optimal design. This relaxation also provides a good lower bound on the objective function value. Therefore, the solution of the relaxed problem can be employed to reduce the domain of the variable tray location such that they contain few additional trays compared to the ones at the relaxation solution. The procedure for reducing the domain will be illustrated on the numerical results section.

Since we are dealing with a highly nonconvex problem, the master MILP problem of the Outer Approximation (OA) algorithm will not produce in general valid lower bounds of the problem (Viswanathan and Grossmann, 1990). Therefore, the stopping criterion adopted for the MINLP formulation is based on the lack of improvement in the objective of the NLP subproblems. Also, it is clear that due to the nonconvexities the global optimum of the NLP cannot be guaranteed.

5.3 GDP Model Solution

The GDP model is solved with the decomposition algorithm proposed by Yeomans and Grossmann (2000a), which is a modified version of the logic-based Outer Approximation (OA) algorithm (Turkay and Grossmann, 1996). This algorithm solves the problem by iterating between reduced NLP subproblems and MILP master problems. Thus, the GDP model proposed in section 5.2 is rewritten as a NLP and MILP formulations. A general procedure for making this transformation can be found in Turkay and Grossmann (1996).

The GDP formulation is solved according to the following procedure (see Figure 10):

1. Solve the general preprocessing phase.
2. Solve the GDP preprocessing phase as follows:
   2.1. Solve an NLP subproblem with all trays exiting.
   2.2. Solve an NLP subproblem with not all trays existing.
3. Solve the synthesis problem applying the GDP algorithm.

After solving the general preprocessing phase, two NLP subproblems are solved to provide linearizations to start the first MILP master problem. The NLP subproblem with all existent trays (applying VLE in all trays) provides linearizations for all the nonlinear equations in the original model. This problem requires solving the largest possible problem but it is not computationally expensive because of the previous preprocessing phase. The second NLP problem provides extra linearizations for the MILP master problem. In this problem, some existent trays are selected as active and the purity specifications for the products is the same as the one of the desired products. We have found that including these extra linearizations improves the solutions achieved during the GDP solution.

The domain reduction procedure was also applied to the GDP formulation as an alternative solution scheme as the one proposed above. The model presented in section 4.2 was reformulated as an MINLP model by replacing each boolean variables by binary variables and using big-M constraint (Lee and Grossmann, 2000). We observed that the relaxation of this model does not provide a good selection of trays to reduce the domain of the binary variables. This is due to the big-M formulation of the disjunctions, which renders the relaxation to yield physically infeasible solutions. For this reason, the GDP formulations were solved in the full space domain (see Figure 10).

The GDP algorithm stops when the maximum number of iterations is achieved (typically ten). This stopping criterion is adopted since the subproblems of the GDP formulation do not involve a long solution time, as it will be shown in the numerical examples in next section. Also, as in the MINLP case, global optimality cannot be guaranteed.

6. Numerical Examples

The MINLP and GDP models derived in section 5 are tested with three ternary mixtures. The low boiler-rich distillate separation is specified for cases involving zeotropic mixtures, while the reversible product compositions are specified for azeotropic mixtures. A constant pressure of 1.01 bar is considered. In all cases, a feed flow of 10 mole/s and saturated liquid products are considered. The minimum number of trays n_{min} is 5. The thermodynamic properties are taken form Reid et al. (1987).

Three examples are presented. Example 1 involves the separation of n-pentane, n-hexane and n-heptane and uses ideal equilibrium. Example 2 deals with the separation of toluene, benzene and o-xylene and also uses ideal equilibrium. Finally, example 3 is concerned with the separation of methanol, ethanol and water using the ideal gas model for the vapor phase and the Wilson model for the liquid phase. In all cases, the VLE equations involve the transformation of variables suggested by Bauer and Stilchmair (1998) in order to improve the convergence of the NLP problems. This transformation yields more linear equations when modeling the VLE equations.

All the examples were implemented and solved in GAMS (Brooke et al, 1998) in a PIII, 667 MHz with 256 MB of RAM. The code DICOPT was employed for solving the MINLP problem. CPLEX was used for solving the mixed integer linear programming (MILP) problems and CONOPT for the NLP subproblems.

6.1. Example 1: n-pentane/n-hexane/n-heptane

A feed with composition of 0.2/0.2/0.6 is given. The required purity for the distillate product is 98% of n-pentane with a minimum recovery of 98%. The upper bound for the number of trays is 50.

The preprocessing phase solution for the MINLP formulation is shown in Table 1. Note that the NLP tray-by-tray models involve the upper bound on the number of trays, fixed condenser, reboiler and feed tray location. In Table 2, the model description and the optimal economic solutions are reported for the MINLP representations involving variable condenser, variable reboiler and variable condenser and reboiler locations. The reason why the solutions are different in each of the cases is due to the nonconvexities that are involved in the MINLP models.

The solutions in Table 2 were obtained solving the MINLP models presented in section 4.1. These formulations involve total flows and compositions and the variable location equipments alternative for modeling the heat exchange. As discussed in section 5.2, in the MINLP formulations of Table 2, the relaxation of the problems were first solved, and the candidate trays for exchanging heat or having a feed were redefined before solving the problem as an MINLP (see solution scheme of Figure 9). This domain reduction procedure considerably decreases the number of binary variables involved in the formulation and enhances its robustness. To show the candidate trays redefinition procedure consider the example of variable reboiler location of Table 2 with the feed initially located on tray 25. The candidate stages for placing a reboiler were initially defined from tray 10 to 50 and the candidate trays for having a feed were defined from stage 5 to 25 (see section 4.1). This formulation involves 62 binary variables. The relaxation of this model was first solved. In the relaxed solution, the feed is located in tray 9, the reboilers are placed from tray 17 to 19 and an the objective function had a value of 49,558 \$/yr. In most cases, the MINLP relaxation has the feed entering in one tray while the reboilers are usually distributed. After the relaxation is solved, the lower reboiler location *ntr* and the feed tray *ntf* are defined as parameters of the MINLP model. Before solving the model as an MINLP problem, the candidate feed and reboiler trays are redefined as follows: $reb = \{n : 2n_{\min} \le n \le ntr + 2\}$ and $feed = \{n : ntf - 2 \le n \le ntf + 2\}$. For this example *ntf*= 9 and *ntr*=19, therefore, the candidate reboiler trays are $reb = \{n : 10 \le n \le 21)\}$ and the candidate feed trays are $feed = \{n : 7 \le n \le 11\}$. Note that after the domain reduction procedure, the MINLP problem involves only 17 of the 62 original binary variables. The integer solution has the feed located in tray 9 and the reboiler is placed on tray 18 with an objective function value of 49,580 \$/yr (see Table 2).

If the models are solved directly as MINLP problems (without solving its relaxation), the formulations are very difficult to solve. In some cases, an integer solution is found before the maximum number of iterations is reached. These solutions are similar to the ones employing the complete preprocessing procedure of Figure 9. However, robustness cannot be ensured.

Comparing the results for the three possible MINLP alternative configurations in Table 2, the representation involving variable condenser and reboiler location yields the highest cost. The other two representations yield similar results, however, the representation involving variable feed and reboiler location yields lower costs (18 to 22 trays, 49,580$/year to 50,080$/year). According to our experience, in most cases, the variable reboiler representation yields lower cost solutions. However, in some cases, the representations involving one variable heat exchange equipment require the longest solution times. This is because in these representations there is a superposition between the candidate trays for exchanging heat and having a feed stream. If the condenser and reboiler are variable, the candidate trays where the energy can be added are different than the ones from where it can be removed (see Figure 6).

The individual component flows formulation was also analyzed. We observed that the solutions obtained with this model are the same as the ones for total flows reported in Table 2. However, the NLP solution times are in general longer. The solution time for the formulation involving individual flows and variable reboiler location is 72.75 sec for the NLP problems and 2.25 sec for the MILP problems versus 44.74 sec. for the NLP and 18.45 sec. for the MILP with the total flow and composition model. The difference is because the NLP models involving individual flows are more difficult to initialize. However, the MILP models with individual flows are easier to solve because a larger number of linear equations and bilinear terms (defining the individual component flows) are involved. Therefore, the formulation involving individual flows is convenient when the solution times of the MILP models are longer than the time of the NLP problems.

The alternative for modeling the heat exchange involving variable reflux and reboil streams location was also tested (see Figure 2). For the same feed composition the solution obtained is shown in Table 3. This configuration has a significantly larger number of trays (32) and higher cost (61,280$/year) than in the previous cases. Note that the configuration achieved involves a stripping section with 9 trays which is approximately the same number as in the MINLP solutions of Table 2. However, the rectifying section has a large number of stages (22 trays). Furthermore, we observed that employing this formulation, the convergence of the NLP subproblems is more difficult than in the previous cases where variable heat location was considered.

To show the effect of the preprocessing phase in the MINLP formulation, we also considered a feed with composition 0.33/0.33/0.34. In Table 4, the solutions for the variable reboiler representation are presented for the model with and without the preprocessing phase. In this case, the model that does not include the previous initialization procedure reaches the maximum number of iterations, and only one integer solution was found by the solver, which is the one reported in Table 4. This solution has a larger number of trays than the solution of the model with preprocessing (32 vs. 15). Furthermore, higher energy duties are also obtained. This is because the model has no information about the minimum energy demand of the separation. Arbitrary bounds for the heat duties have to be used. From these results, it is clear that the preprocessing phase helps to improve solutions of the MINLP formulation.

The mixture with composition 0.2/0.2/0.6 was also used to test the GDP formulations in order to compare them with the previous MINLP representations. The results for the fixed feed tray location including the preprocessing are presented in Table 5. It should be noted that the size of the preprocessing NLP problems for the GDP formulation are the same as the ones in the MINLP (see Table 1). In this case, however, the number of 0-1 variables is not reduced (see solution scheme of Figure 10).

According to our experience, the GDP model with variable feed location exhibits worse numerical behavior than the model with fixed feed location. For this example, starting with a column with 50 initial trays with the feed initially located in tray 25, the solution obtained with the variable feed model involves a column with 41 trays, with the feed located in tray 26 and with a total cost of 72,160$/yr. In contrast, the optimal solution of the fixed feed tray model requires 24 trays with the feed in tray 16 and a cost of 51,520$/year. From these results, it is clear that the fixed feed column representation provides significantly cheaper solutions. Note, also, that the MINLP solutions reported in Table 2 yields a lower cost (49,580$/yr), which is most probably due to the nonconvexities and the reduction scheme of binary variables in the MINLP model.

It is interesting to analyze the behavior of the GDP formulation without including the preprocessing phase. For the same number of iterations, the fixed feed location GDP model is solved for the same mixture composition than before (see Table 5) and the best solution achieved involves a total cost of 58,800$/yr. This means that including the proposed preprocessing in these formulations, solutions with lower total costs are also found. It should be noted that it is difficult to set bounds and initial values without the preprocessing phase for the initial NLP problems of the GDP problem since individual component flows are involved in the formulation. In some cases that were studied, the procedure of finding a feasible solution takes a long time. Therefore, the preliminary calculations avoid this trial-and-error procedure for selecting proper bound and initial values.

According to our experience, the preprocessing phase provides a good initial guess for the optimization problem in both formulations. However, it should be noted that the GDP formulation is not as strongly dependent of a good starting point as the MINLP formulation. Also, even though the GDP formulation achieves a better solution if the preprocessing phase is included, the solution time of the NLP and MILP subproblems remains the same if bounds and initial values are set arbitrarily. In contrast, we observed that the MINLP solution is very dependent of the initial guess provided, not only in the costs involved in the solution designs but also in the solution time (see Table 4).

For this example we can observe that the MINLP variable reboiler representation and fixed feed GDP representation yield similar costs (49,580$/year vs. 51,520$/year). However, the detailed designs are not the same (18 vs. 24 trays) and the solution time of the GDP formulation is considerably smaller (15.7 sec vs. 64.3 sec).

6.2. Example 2: butane/toluene/o-xylene

A second example to illustrate the performance of the models presented in this work involves the separation of butane, toluene and o-xylene with ideal equilibrium. This mixture has a closer volatility difference between the components than in the previous example. This fact makes the problem more difficult to solve.

A mixture with composition 0.33/0.33/0.34 was considered. The required purity for the distillate product is 98% of butane and a minimum recovery of 98%. The upper bound for the number of trays is 60. The results are presented in Table 6 for the MINLP formulation with variable reboiler location. As can be seen the predicted design involves a minimum cost of 79,962$/yr. For this case, the MINLP relaxation provides a bound on the objective function of 79,223$/yr.

For the same feed composition the representation involving variable reflux and reboil location was tested (see Figure 2). The solution achieved has 34 final trays (24 in the rectifying section and 10 in the stripping section) and a cost of 90,640 $/yr. The same behavior in the distribution of trays was observed in the previous case studied. Therefore, from these results we can conclude that the representation involving variable location for the heat exchange equipment yields better results.

In Table 7, the solution is reported for the GDP model with fixed feed location, which predicted 27 trays. As can be seen the corresponding cost of 85,752$/yr is higher than the solution obtained with the variable reboiler MINLP (79,962 $/yr). The solution time is however much smaller (14.8 sec. vs. 648 sec).

6.3. Example 3: methanol/ethanol/water

This example illustrates the performance of the models with an azeotropic mixture. A mixture with composition 0.2/0.2/0.6 was considered. The reversible products compositions are specified and an upper bound for the number of trays of 60 is considered. The results obtained with the MINLP representation involving variable reboiler location are reported in Table 8. The solution obtained with the GDP formulation involving fixed feed tray location is presented in Table 9. For this example, the solution obtained with the GDP formulation again involves higher cost than with the MINLP formulation (133,680$/yr and 50 trays vs. 116,320$/yr and 41 trays) although the CPU time is again lower (26.1 sec vs. 501 sec).

It is important to point out that the product composition achieved with the models is located in a different distillation boundary than the feed composition. A product composition can cross a distillation boundary if its total reflux profile and pinch point curve finishes in different distillation regions (Castillo et al, 1998). In the example presented above, the distillate pinch point curve finishes in the same distillation region where the feed is located. However, the residue curve going through the distillate composition of the solution achieved finishes on the other side. Therefore, we can conclude that for this example, the model we presented allows the distillate product to cross the distillation boundaries and it locates the distillate composition inside the region of the simplex bounded by the distillation boundary of the system and the envelope of inflexion tangent points (Wahnschafft et al, 1992).

It should be mentioned that we assumed that the infinite reflux composition profile can be represented by a residue curve near the distillation boundary. This means that we are approximating the distillation line going through the distillate composition by the residue curve.

7. Conclusions

This paper has presented different alternatives for representing and formulating the economic optimization problem of a single multicomponent distillation column. The different alternatives involve different ways of representing the choices for the number of trays in the column and the energy demand. Rigorous MINLP and GDP formulations were developed in each of the cases. In order to increase the robustness in the solution of these formulations, a general automatic preprocessing phase was considered.

Three example problems were solved to evaluate the robustness and performance of the models. According to our experience, the most efficient MINLP representation involves variable reboiler and feed tray location, and the most convenient formulation involves total flows and variable energy demand for the variable reboiler location representation. In the GDP formulation, the representation with fixed feed tray location yields designs involving lower costs.

Numerical results were presented to show the performance of the proposed formulations. For the examples studied, the MINLP formulation with preprocessing and domain reduction yields designs involving lower total costs. In the azeotropic example, the distillate composition achieved in the economic solution crosses the distillation boundary. This is an important fact when distillation sequences are considered because it allows obtaining pure products.

In all cases, the MINLP solution times are considerably longer than the ones of the GDP models. We observed that the robustness of the MINLP formulations depends very much on the solution scheme. If a good initial guess is generated with the preprocessing phase and the domain reduction for the binary variables is applied, an integer solution is obtained in few iterations. However, the total solution time is long because the convergence of the NLP subproblems is usually very difficult to achieve. Also, the MILP subproblems include constraints, which were generated by linearizing the original constraints of the problem at zero flows.

According to our experience, the GDP formulation is more robust and faster than the MINLP model. We observed that the GDP formulation is not as strongly dependent of the initial guess as the MINLP formulation. If a good initial solution guess is provided, the convergence of the initial NLP problems is guaranteed without tuning external parameters and also, better solutions can be found. It should be noted that the relaxed solution of the GDP formulation does not provide a useful distribution of trays as it was the case of the relaxed MINLP solution. Consequently, cheaper solutions were found with the MINLP models.

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Nomenclature

Ac	condenser area (m^2)
Ar	reboiler area (m^2)
bc_n	binary variable denoting the existence of a condenser in tray *n*
bf_n	binary variable denoting the existence of a feed stream entering in tray *n*
Bf_n	boolean variable related with the existence of a feed entering a tray *n*
br_n	binary variable denoting the existence of a reboiler in tray *n*
C	number of components
Cs	cost of the steam
Cw	cost of cooling water
Dcol	column diameter
fLn,i	fugacity of component *i* in the liquid leaving tray *n*.
fVn,i	fugacity of component *i* in the vapor leaving tray *n*.
Fo	feed flow (mol/sec)
F_n	feed flow entering on stage *n* (mol/sec)
FEEDn,i	feed flow of component *i* entering on stage *n* (mol/sec)
hfo	feed enthalpy (KJ/mol)
hfn	enthalpy of the feed stream entering in tray *n* (KJ/mol)
hfeedn,i	feed molar enthalpy of component *i* entering in tray *n* (KJ)
hln	enthalpy of the liquid leaving tray *n* (KJ/mol)
hliqn,i	liquid molar enthalpy of component *i* leaving tray *n* (KJ)
hvn	enthalpy of the vapor leaving tray *n* (KJ/mol)
hvapn,i	vapor molar enthalpy of component *i* leaving tray *n* (KJ)
Ln	liquid flow leaving tray *n* (mole/sec)
LIQn,i	liquid flow of component *i* leaving tray *n* (mol/sec)
n	tray
nfo	initial feed tray location
nmin	lower bound on the number of trays
Nmax	upper bound on the number of trays
NT	number of trays in the column
Pn	total pressure in tray *n* (bars)
PLn	liquid product flow leaving tray *n* (mol/sec)

$PLIQ_{n,i}$	liquid product flow of component i leaving tray n (mol/sec)
PV_n	vapor product flow leaving tray n (mol/sec)
$PVAP_{n,i}$	vapor product flow of component i leaving tray n (mol/sec)
qd	distillate product vapor fraction
Q_n	energy demand on tray n (KJ/sec)
Q_C	condenser heat duty (KJ/sec)
Q_H	reboiler heat duty (KJ/sec)
$refL_n$	liquid reflux stream (mole/sec)
$refV_n$	vapor reflux stream (mole/sec)
stg_n	counter for the existence of a tray n
T_n	temperature of tray n (^oK)
$T^L{}_n$	temperature of the liquid flow leaving tray n (^oK)
$T^V{}_n$	temperature of the vapor flow leaving tray n (^oK)
V_n	vapor flow leaving tray n (mole/sec)
$VAP_{n,i}$	vapor flow of component i leaving tray n (mol/sec)
$x_{n,i}$	liquid composition of component i leaving tray n (mole fraction)
W_n	boolean variable related to tray n existence
$y_{n,i}$	vapor composition of component i leaving tray n (mole fraction)
zfo	feed composition (mole fraction)
$zf_{n,i}$	feed composition of component i entering tray n (mole fraction)
ε_i	recovery factor of component i
τ_i	Minimum mole composition of component i in the product

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Appendix A: General Preprocessing Phase Models.

Theoretical Reversible Products Calculation

Consider the following definition of variables and parameters involved in the model:

D^{rev}	distillate product flow (mole/sec)
B^{rev}	bottom product flow (mole/sec)
fLi	fugacity of component i in the liquid
fVi	fugacity of component i in the vapor
hB	bottom product enthalpy (KJ/sec)
hD	distillate product enthalpy (KJ/sec)
hL	liquid flow enthalpy (KJ/sec)
hV	vapor flow enthalpy (KJ/sec)
L	liquid flow leaving the rectifying section (mole/sec)
L^*	liquid flow entering to the stripping section (mole/sec)
q_F	feed vapor fraction
$Q^{rev}{}_C$	reversible condenser duty (KJ/sec)
$Q^{rev}{}_H$	reversible reboiler duty (KJ/sec)

V	vapor flow entering to the rectifying section (mole/sec)
V^*	vapor flow leaving the stripping section (mole/sec)
x_i	liquid composition of component i (mole fraction)
y_i	vapor composition of component i (mole fraction)
$z^{rev}{}_{i,D}$	reversible distillate product composition
$z^{rev}{}_{i,B}$	reversible bottom product composition

The model for calculating the reversible product composition flows and energy demand according to Figure 11 is as follows:

$$\min \quad s\ (z^{rev}_{c\max,B} - z^{rev}_{c\max,D}) \tag{A1}$$

$s.t.$

$$dif_i = abs(y_{i,F} - x_{i,F}) \tag{A2}$$

$$difmax = \max_i (dif_i\ ) \tag{A3}$$

$$s = \frac{(y_i^F - x_i^F)}{difmax} \tag{A4}$$

Rectifying Section:

$$L\ +\ D^{rev}\ = V \tag{A5}$$

$$L\ \ x_i + D^{rev}\ z^{rev}_{i,D} = V\ y_i \tag{A6}$$

$$L\ \ h_L + D^{rev}\ \ h_D + Q^{rev}_C = V\ h_V \tag{A7}$$

$$\sum_{i=1}^{NC} x^{rev}_{i,\,D} = 1 \qquad \sum_{i=1}^{NC} y^{rev}_{i,\,D} = 1 \tag{A8}$$

$$z^{rev}_{i,D} = (1-qd)\ x^{rev}_{i,D} + qd\ \ y^{rev}_{i,D} \tag{A9}$$

Stripping Section:

$$L^* = V^* + B^{rev} \tag{A10}$$

$$L^*\ x_i = V^*\ y_i + B^{rev}\ \ z^{rev}_{i,\,B} \tag{A11}$$

$$L^*\ h_L + Q^{rev}_H = V^*\ h_V + B^{rev}\ \ h_B \tag{A12}$$

$$\sum_{i=1}^{NC} x_{i,B}^{rev} = 1 \qquad \sum_{i=1}^{NC} y_{i,B}^{rev} = 1 \tag{A13}$$

$$z_{i,B}^{rev} = x_{i,B}^{rev} \tag{A14}$$

Feed Section:

$$L + (1-q_F)\, Fo = L^* \tag{A15}$$

$$V + q_F\, Fo = V^* \tag{A16}$$

$$f_i^L = f_i^V \tag{A17}$$

$$f_i^L = f(T,P,x_i)\ ,\ f_i^V = f(T,P,y_i) \tag{A18}$$

$$h_L = f(T),\ h_V = h_V\ (T) \tag{A19}$$

$$h_D = f(T),\ h_B = f(T) \tag{A20}$$

The constraints of this optimization problem are the overall mass and energy balances that are formulated in both sections of a reversible unit, like the one shown in Figure 11. Since a previous feed flash calculation is solved, the vapor and liquid streams enthalpies h_V and h_L, respectively, are known. This is because each point of a reversible column composition profile is a pinch point, where all streams are in equilibrium. Therefore, in a stage above (below) the feed tray, the vapor entering (leaving) and the liquid leaving (entering) have the same composition than the vapor and liquid fractions of the feed.

The unknowns in this model are the reversible products flows D^{rev} and B^{rev} and compositions $z_{i,D}^{rev}$ and $z_{i,B}^{rev}$, and the energy demand Q_C^{rev} and Q_H^{rev} as well.

The objective function is formulated in such a way that the model allows the calculation of the reversible products even for azeotropic mixtures. An earlier version of this problem employed an objective function where the lightest component composition was minimized in the bottom product and the heaviest component composition minimized in the distillate (Barttfeld and Aguirre, 2002). But when azeotropic mixtures are involved, the volatilities change with the composition of the mixture. Therefore, the lightest and heaviest components definition depend on the distillation region in which the feed composition is located. To avoid the use of topological information of the mixture involved, a general objective function is employed. The absolute difference between the vapor and liquid feed compositions y_i^F and x_i^F, respectively, are computed for each component *i* and denoted by dif_i. The largest value of dif_i is $difmax$. The component *i* for which its value of dif_i is equal to $difmax$ is the one that presents more variation between its composition in the vapor and liquid phases. Then, *cmax* will be the lightest component if $y_i^F - x_i^F \geq 0$ and the heaviest one if $y_i^F - x_i^F \leq 0$. This sign is kept in the parameter *s*. It must be noted that only one reference component is needed in the objective function. If $s \geq 0$ $(s \geq 0)$ *cmax* is the lightest (heaviest) component and its composition is minimized in the bottom (distillate) product and maximized in the distillate (bottom) product.

Minimum Energy Demand Calculation for the Low boiler-rich Distillate (High boiler-rich Bottom Fraction) Separation

For zeotropic mixtures, after calculating the reversible products, the saddle pinch points that take place in the adiabatic approach to a reversible column can be calculated. A simple model for calculating the rectifying and stripping saddle pinch points can be found in our previous work (Barttfeld and Aguirre, 2002).

Employing saddle pinch point information, the minimum energy demand for the low boiler-rich distillate (high boiler-rich bottom) separation can be easily computed. The formulations will be illustrated for the low boiler-rich distillate separation. Analogous expressions can be written for the high boiler-rich bottom separation.

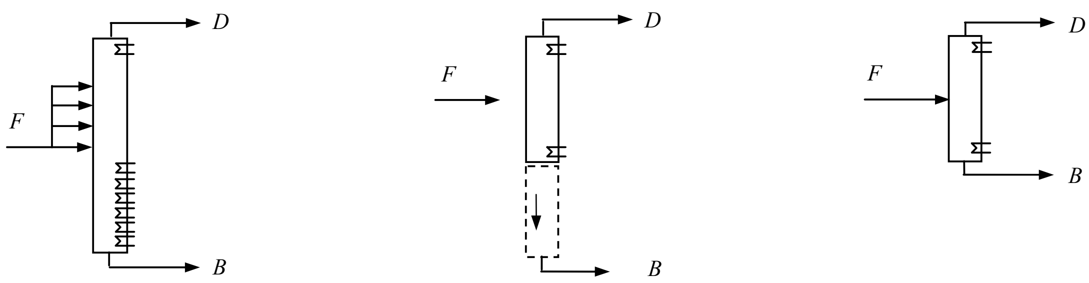
Consider a rectifying section, like the one depicted in Figure 12. The rectifying (stripping) saddle pinch point that takes place in the adiabatic approach to the reversible separation is preserved during the separation where a low (high) boiler pure distillate (bottom) product is achieved. Using this information, an energy balance can be derived for calculating the energy demand involved in the condenser (reboiler) in the low (high) boiler rich distillate (bottom) separation:

$$Ls\ h_L^s + D\ h_D + Q_C = Vs\ h_V^s \tag{A21}$$

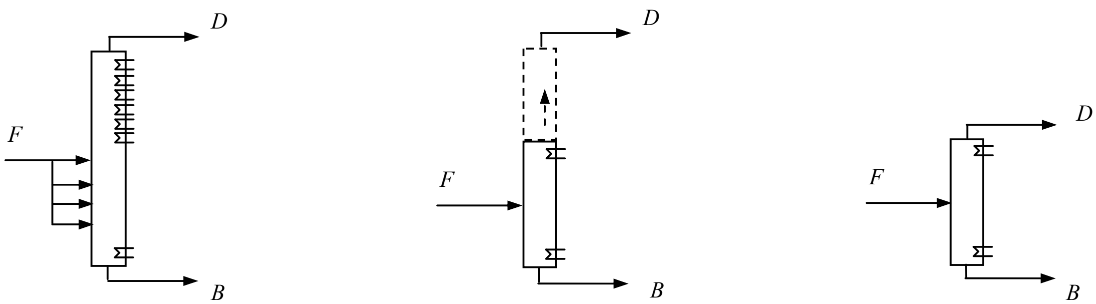
with $D = Fo\ zfo_a$. For calculating the reboiler (condenser) energy duty, a total energy balance of the column can be formulated:

$$Fo \; hfo + Q_H - Q_C = D \; h_D + B \; h_B \tag{A22}$$

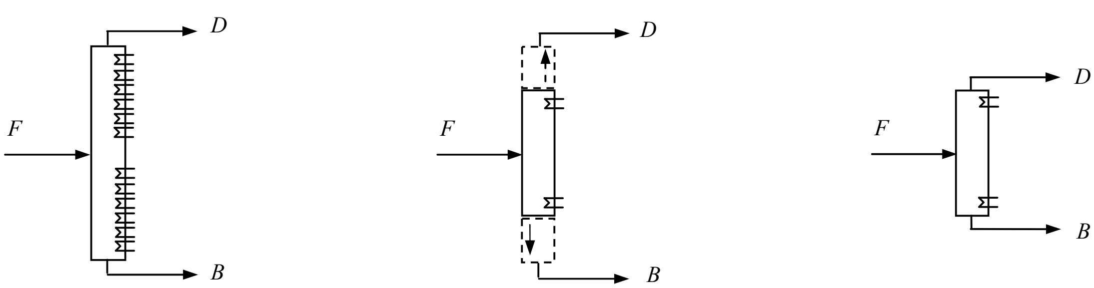
with $B = Fo\,(1 - zfo_a)$.



(a) Variable reboiler location



(b) Variable condenser location



(c) Variable reboil and condenser location

Figure 1: MINLP distillation column representations

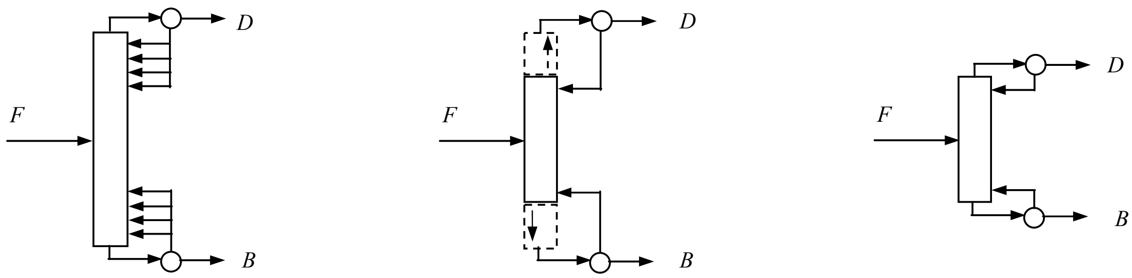
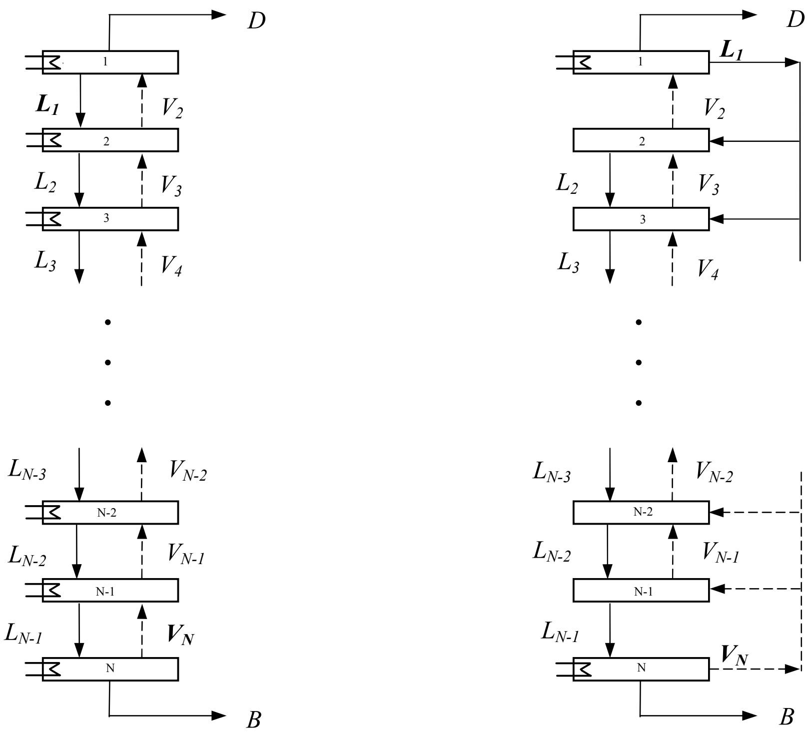


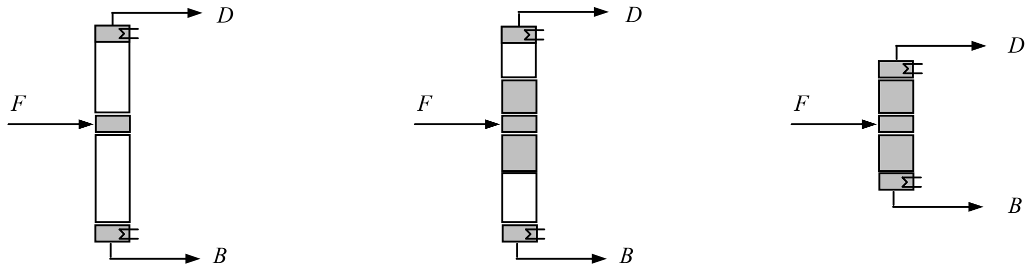
Figure 2: Variable reflux and reboil location with fixed heat exchangers



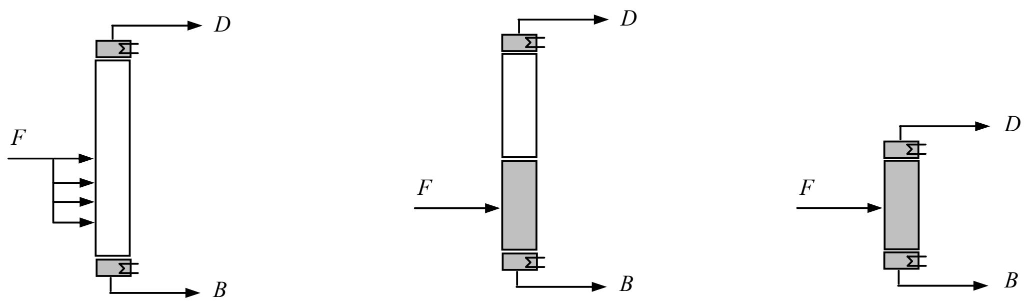
(a) Variable condenser location

(b) Variable reflux/reboil location

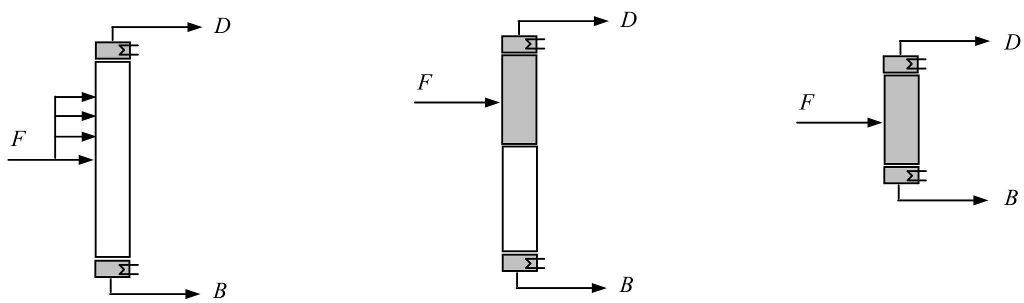
Figure 3: Different representations for the MINLP tray optimization



(a) Fixed feed location



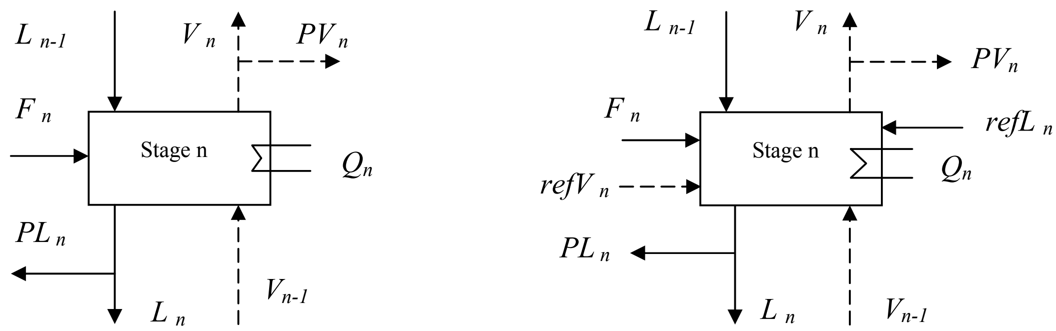
(b.1)



(b.2)

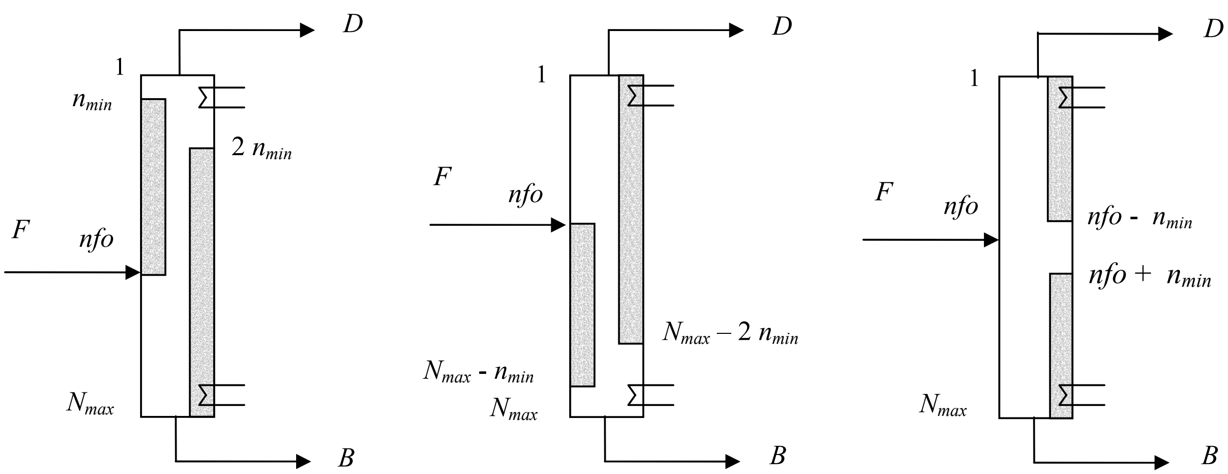
(b) Variable feed location

Figure 4: GDP distillation column representations



(a) Variable heat exchange location (b) Variable reflux location

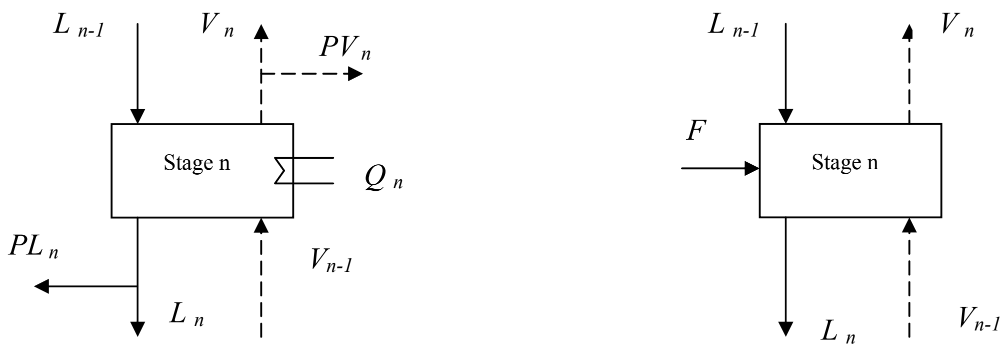
Figure 5: MINLP single tray superstructures



(a) Variable reboiler (b) Variable condenser (c) Variable condenser and reboiler

Candidate trays

Figure 6: Definitions of candidate trays for the MINLP representation



(a) Permanent tray (b) Conditional tray

Figure 7: GDP single tray superstructure

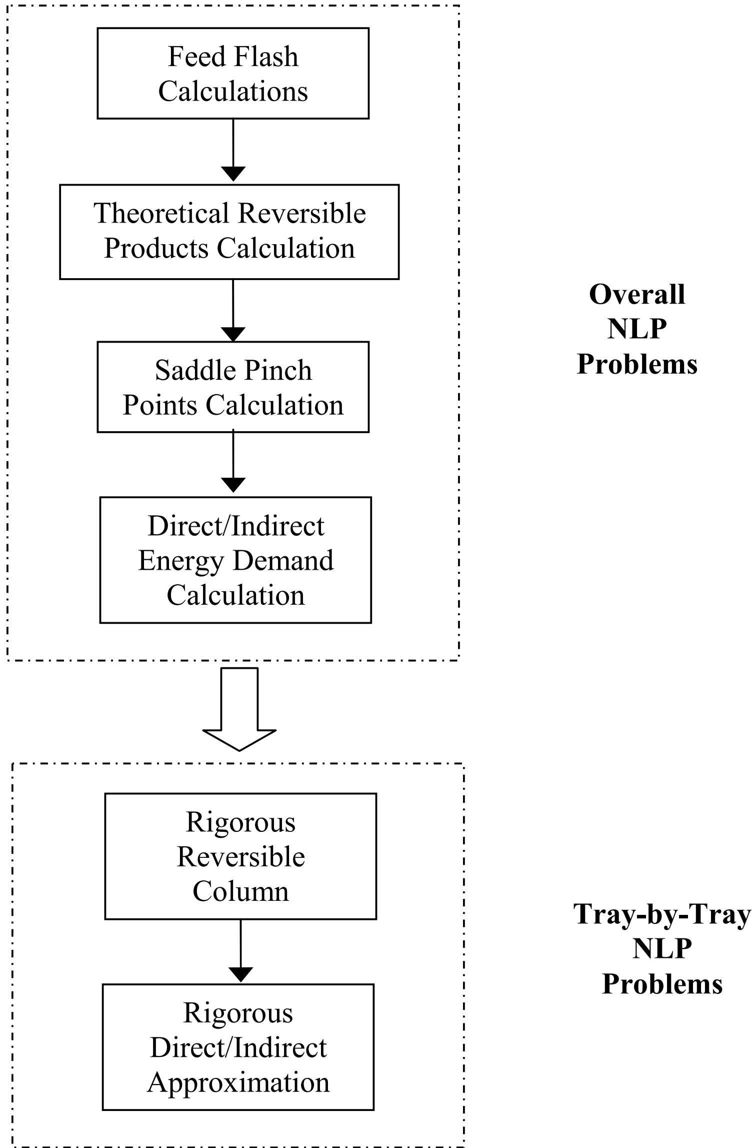


Figure 8: General preprocessing phase procedure

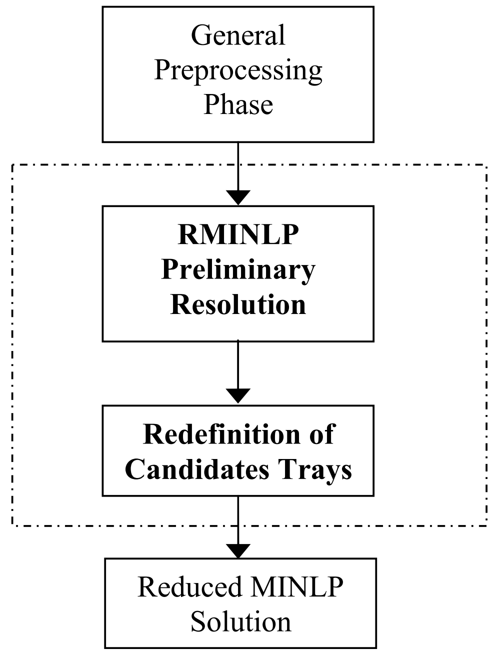


Figure 9: MINLP solution procedure

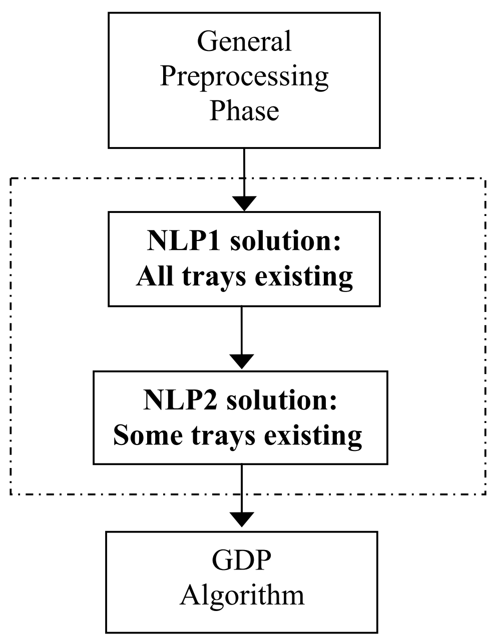


Figure 10: GDP solution procedure

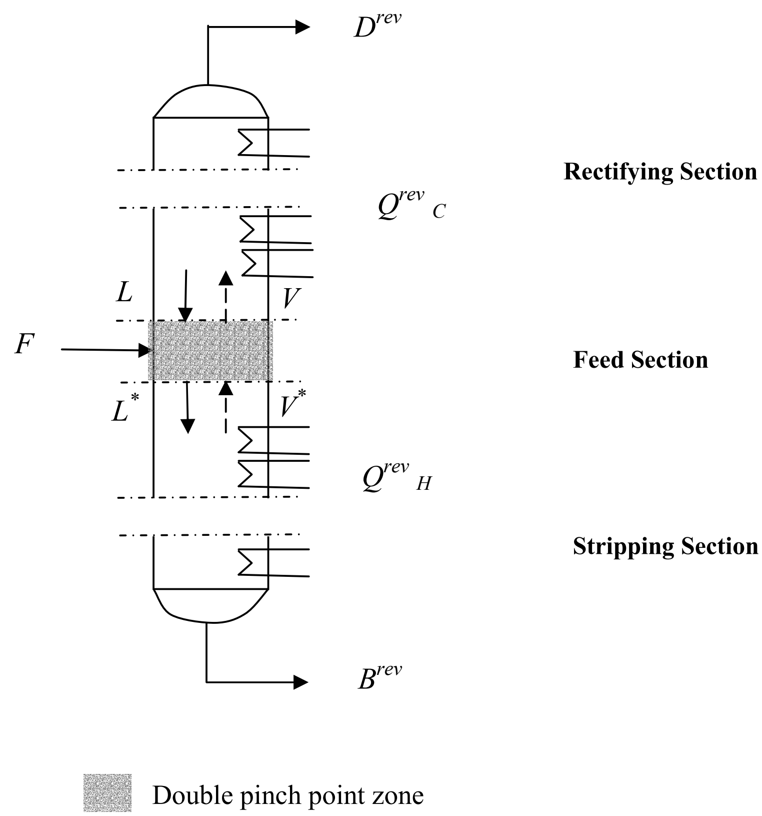


Figure11: Control volumes for the theoretical reversible product calculations

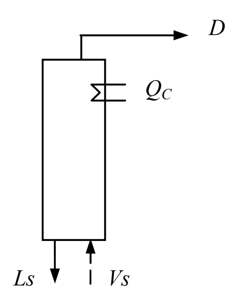


Figure 12: Lower boiler-rich distillate minimum energy demand calculation

Table1: Example 1 - MINLP preprocessing phase

Preprocessing Phase Models Description	
NLP Model	
Continuous Variables	196
Constraints	173
Nonlinear nonzero elements	279
Total CPU time (s)	**0.1**
NLP tray-by-tray Models	
Continuous Variables	2743
Constraints	2244
Nonlinear nonzero elements	6958
Total CPU time (s)	**0.61**

Table 2: Example 1 - MINLP model representation solutions

	Variable Reboil	Variable Condenser	Variable Reboiler and Condenser
Model Description			
Continuous Variables	1504	1437	1490
Binary Variables	17	19	10
Constraints	1261	1179	1243
Nonlinear nonzero elements	3867	4250	3627
RMINLP CPU time (s)	0.45	0.38	0.3
NLP CPU time (s)	44.74	8.93	51.8
MILP CPU time (s)	18.45	13.97	19.33
Major Iterations (DICOPT)	4	3	4
Total CPU time (s)	**63.64**	**23.28**	**71.44**
Optimal Solution			
Total number of trays	18	22	18
Condenser tray	1	29	15
Reboiler tray	18	50	32
Feed tray	9	38	25
Column diameter (m)	0.487	0.477	0.507
Condenser duty (KJ/s)	149.32	138.96	160
Reboiler duty (KJ/s)	171.9	161.43	182.5
Objective value ($/yr)	**49,580**	**50,080**	**51,680**

Table 3: Example 1 - MINLP model: variable reflux and reboil streams location

Model Description	
Continuous Variables	1358
Binary Variables	26
Constraints	1134
Nonlinear nonzero elements	3669
RMINLP CPU time (s)	0.35
NLP CPU time (s)	260.7
MILP CPU time (s)	62
Major Iterations (DICOPT)	14
Total CPU time (s)	**323.05**

Optimal Solution	
Total number of trays	32
Condenser tray	3
Reboiler tray	34
Feed tray	25
Column diameter (m)	0.48
Condenser duty (KJ/s)	141.1
Reboiler duty (KJ/s)	163.7
Objective value ($/yr)	**61,280**

Table 4: Example 1 - MINLP model: effect of the preprocessing phase.

	with preprocessing	**without preprocessing**
Total number of trays	15	32
Condenser tray	1	1
Reboiler tray	15	32
Feed tray	10	27
Column diameter (m)	0.505	0.59
Condenser duty (KJ/s)	206.64	275.12
Reboiler duty (KJ/s)	224.45	295.67
NLP CPU time (s)	101.39	195.37
MILP CPU time (s)	4.88	55.88
Major Iterations (DICOPT)	9	20
Total CPU time (s)	**106.27**	**251.25**
Objective value ($/yr)	**58,560**	**93,200**

Table 5: Example 1 - GDP model: fixed tray location

Preprocessing Phase: NLP tray-by-tray Models	
Continuous Variables	4508
Constraints	3967
General preprocessing CPU time (s)	0.57
NLP1 CPU time (s)	0.31
NLP2 CPU time (s)	0.56
Total CPU time (s)	**1.44**

Model Description	
Continuous Variables	2297
Binary Variables	48
Constraints	2105
Nonlinear nonzero elements	2230
Number of iterations	10
NLP CPU time (s)	4.92
MILP CPU time (s)	9.33
Total CPU time (s)	**14.25**

Optimal Solution	
Total number of trays	24
Feed tray	16
Column diameter (m)	0.421
Condenser duty (KJ/s)	134.22
Reboiler duty (KJ/s)	156.81
Objective value ($/yr)	**51,520**

Table 6: Example 2 - MINLP: variable reboiler location

Preprocessing Phase: NLP tray-by-tray Models	
Continuous Variables	3273
Constraints	2674
Total CPU time (s)	**0.68**

Model Description	
Continuous Variables	1507
Binary Variables	33
Constraints	1830
Nonlinear nonzero elements	4637
RMINLP CPU time (s)	0.52
NLP CPU time (s)	249.35
MILP CPU time (s)	398.4
Major Iterations (DICOPT)	17
Total CPU time (s)	**648.27**

Optimal Solution	
Total number of trays	26
Feed tray	13
Column diameter (m)	0.6
Condenser duty (KJ/s)	241.7
Reboiler duty (KJ/s)	258.03
Objective value ($/yr)	**79,962**

Table 7: Example 2 - GDP model: fixed tray location

Preprocessing Phase: NLP tray-by-tray Models	
Continuous Variables	4508
Constraints	3967
General preprocessing CPU time (s)	0.71
NLP1 CPU time (s)	0.46
NLP2 CPU time (s)	0.32
Total CPU time (s)	**1.49**
Model Description	
Continuous Variables	2343
Binary Variables	58
Constraints	2105
Nonlinear nonzero elements	2230
Number of iterations	10
NLP CPU time (s)	5.42
MILP CPU time (s)	9.37
Total CPU time (s)	**14.8**
Optimal Solution	
Total number of trays	27
Feed tray	16
Column diameter (m)	0.605
Condenser duty (KJ/s)	248.66
Reboiler duty (KJ/s)	265.02
Objective value ($/yr)	**85,752**

Table 8: Example 3 - MINLP: variable reboiler location

Preprocessing Phase: NLP tray-by-tray Models	
Continuous Variables	1600
Constraints	1548
Total CPU time (s)	**0.5**
Model Description	
Continuous Variables	1894
Binary Variables	67
Constraints	1817
Nonlinear nonzero elements	6953
RMINLP CPU time (s)	0.61
NLP CPU time (s)	305.13
MILP CPU time (s)	196.02
Major Iterations (DICOPT)	20
Total CPU time (s)	**501.15**
Optimal Solution	
Total number of trays	41
Feed tray	32
Column diameter (m)	0.51
Condenser duty (KJ/s)	389.32
Reboiler duty (KJ/s)	388.2
Objective value ($/yr)	**116,320**

Table 9: Example 3 - GDP model: fixed tray location

Preprocessing Phase: NLP tray-by-tray Models	
Continuous Variables	1597
Constraints	1544
Total CPU time (s)	**1.12**

Model Description	
Continuous Variables	2933
Binary Variables	60
Constraints	2862
Nonlinear nonzero elements	5656
Number of iterations	10
NLP CPU time (s)	9.14
MILP CPU time (s)	16.97
Total CPU time (s)	**26.11**

Optimal Solution	
Total number of trays	50
Feed tray	30
Column diameter (m)	0.529
Condenser duty (KJ/s)	415.3
Reboiler duty (KJ/s)	414.3
Objective value ($/yr)	**133,680**