Optimal Synthesis of Multicomponent Zeotropic Distillation Processes. 1. Preprocessing Phase and Rigorous Optimization for a Single Unit

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Separations performed by distillation involve large operation costs due to either large heat loads or large amounts of solvent used in azeotropic mixtures. Thermodynamic aspects helpfully lead the process synthesis to energetically efficient designs. The reversible distillation sequence model (RDSM) is employed in this work as a theoretical and ideal thermodynamic model. The aim of the paper is to present an automatic methodology for the synthesis of simple distillation columns that approximate reversible conditions. A preprocessing phase is considered where proper values to initialize and bound the variables involved in the rigorous model are calculated by successively solving auxiliary optimization models. In all cases studied, the solutions obtained are very similar to those in the so-called reversible separation. This fact is used as a test criterion for global optimality of the solutions.

1. Introduction

The cost of a chemical process is often dominated by the cost for the separation and purification of the products, which is usually done by distillation.

Distillation is an expensive unit operation in terms of capital and operating costs. The efficient use of energy and the continuous improvement of equipment are required in view of environmental regulations and increasing energy costs. For that reason, in recent years, numerical methods such as mixed integer nonlinear programming (MINLP) became available for distillation process optimization and synthesis to carry out this operation at minimum cost.

We are interested in the synthesis of thermodynamically efficient distillation sequences. A measure of the efficiency of a process will be given along this work by the entropy production due to the irreversibilities that take place in the system. The lower entropy production means the larger efficiency of the system. The most efficient scheme is the RDSM (reversible distillation sequence model) where no entropy creation occurs. The reversible[1,2] or "preferred" separation[3] is performed in each unit of the sequence. This theoretical model was employed several times for the development of minimum reflux methodologies[4-7] as well as to determine feasible distillation regions for homogeneous azeotropic distillation.[8,9]

We propose to approximate this ideal thermodynamically optimum model by using finite adiabatic columns, each one with one condenser at the top and one reboiler at the bottom stage. Then, the finite approximation to the RDS (reversible distillation sequence) will be the most efficient scheme from the entropy production point of view.

Because we are interested in the RDS design where the reversible separation task is performed, the reversible approximation for each single unit of the sequence

has to be studied. It is worth noting that the procedure for performing the reversible separation task through an optimization problem is not a trivial problem. Therefore, a design methodology for the efficient design of each single unit is presented in this paper. A single distillation unit is isolated from the RDS and a methodology for closely approximating the RDC (reversible distillation column) by a simple adiabatic unit is considered.

To overcome the convergence problems of the formulations, a previous solution phase is considered. In the preprocessing phase, information related to the theoretically reversible model is computed. Initial values and bounds are computed to be used in the single column rigorous model. In this work, the preprocessing phase and a rigorous tray-by-tray model of a single column are presented. Neither external information nor parameters have to be tuned. By initializating and bounding the variables involved in the rigorous single column model with the preliminary information computed in the preprocessing phase, global convergence and global optimal solutions can be assured despite of the nonconvex characteristics of the formulation.

The synthesis problem considered in this work is stated in section 2. In section 3, the reversible distillation model is briefly introduced and its adiabatic approximation is analyzed. The pinch regions that take place in a RDC are considered as well as relevant pinch points of the reversible path. The preprocessing models for computing the theoretically reversible product composition as well as the saddle pinch points are presented in section 4.2. Departing from this information, we formulate a rigorous tray-by-tray MINLP model to approximate reversible conditions in single column. Commercial simulators are used to compare the results obtained with the proposed procedure. A new methodology to construct product pinch point curves by solving an optimization problem is also presented. Finally, the conclusions of this work and some possible extensions are discussed.

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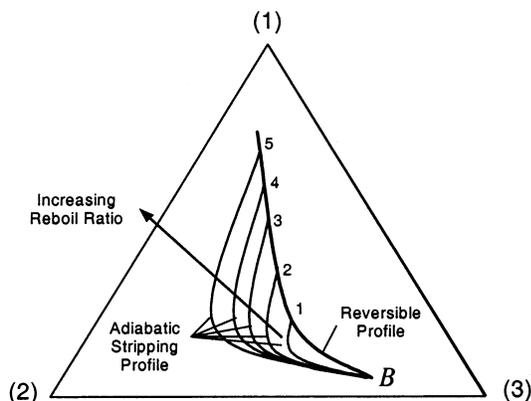
Figure 1. Relation between adiabatic and reversible concentration profiles for the stripping section of a distillation column.

2. Problem Statement

The problem addressed in this paper can be stated as follows. Given are a multicomponent feed composition, flow rate, and an upper bound on the number of trays for the column. The problem then consists of determining the feed tray location as well as the operating parameters (such as the reflux ratio and condenser and reboiler heat duties) for achieving the maximum reversible products under minimum reflux conditions. An infinite reversible distillation column involving minimum energy demand and maximum efficiency will be approximated by an adiabatic unit.

3. Adiabatic Approximation of a RDC

A reversible column is an ideal distillation unit, which operates without entropy production. The main sources of irreversibilities and the conditions that must be prevailed in a distillation column to avoid entropy production can be found in our previous work.[4]

To avoid irreversibilities, equilibrium has to take place in the unit between counter current liquid and vapor streams and the driving forces for heat and mass transfer processes must be zero. Thus, a reversible column will be infinitely long with a continuous distribution of heat exchangers along its length.[2]

Reversibility conditions require the feed to be introduced without entropy of mixing. This fact leads to the main restriction of reversible columns. A unit that operates reversibly can only separate the most and least volatile component of the feed stream. The best possible reversible separation is the one where the most volatile component does not appear in the bottom product and the least volatile is completely removed from the distillate. Then, the reversible separation task is a special case of a nonsharp separation where the reversible mass balance line and the feed equilibrium vector are coincident. Note that the feed equilibrium vector departs from the liquid feed composition pointing toward its equilibrium vapor composition.

A reversible column can be modeled by a fairly simple flash-type formulation[2-4] and can be approximated by an adiabatic unit because both models present some interactions. The reversible feasible region is completely contained in the adiabatic one and each adiabatic composition profile finishes at a pinch point. In Figure 1, the relationship between both model profiles is qualitatively shown for a three-component mixture in the composition space (the volatility of the components decreases from 1 to 3). Note that departing from the
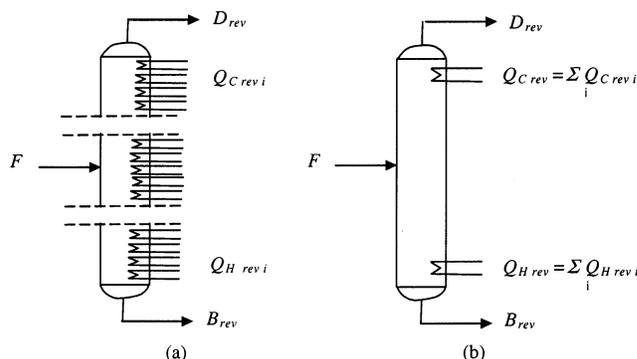
Figure 2. Adiabatic approximation of a hypothetical reversible column.
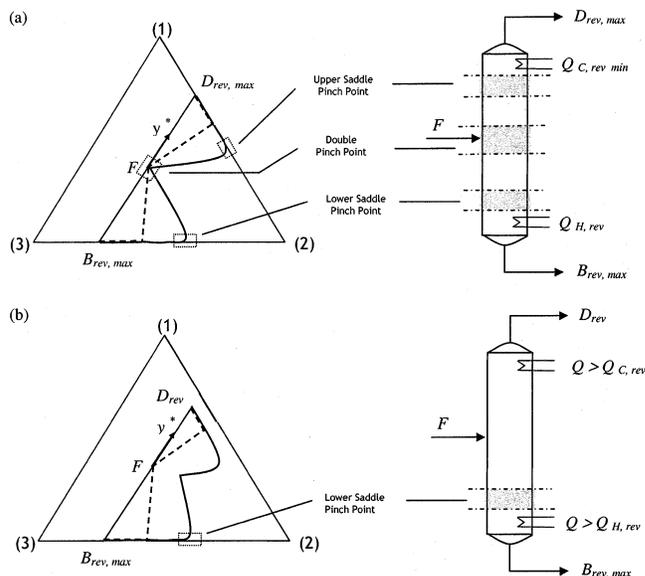
Figure 3. Saddle pinch points regions of the RDS adiabatic approximation.

bottom product B, different adiabatic profiles can be computed depending on the reboil ratio involved. If the reboil ratio is increased, stationary points from 1 to 5 are achieved. Therefore, for the same amount of energy, the stationary concentration obtained in an adiabatic unit corresponds to a pinch point of the reversible path. The difference between both models lies in the energy distribution, and as a consequence, the composition paths to reach the reversible product composition are not the same. However, the energy involved in both cases is the same. In Figure 2, a reversible column (see Figure 2a) and its adiabatic approximation (see Figure 2b) are shown.

It is interesting to note that two pinch point regions take place in the adiabatic approximation of a reversible column, as shown in Figure 3a for a ternary mixture. The broad line connecting the reversible products D_{rev} and B_{rev} corresponds to the adiabatic concentration profile whereas the striped path represents the composition change in the reversible operation.

A double pinch point around the feed stage takes place if the separation is performed at minimum energy consumption. If heat loads greater than the minimum ones are involved, this region will not occur and the branches of the composition profile of the adiabatic separation will not intersect at the feed composition, as shown in Figure 3b.
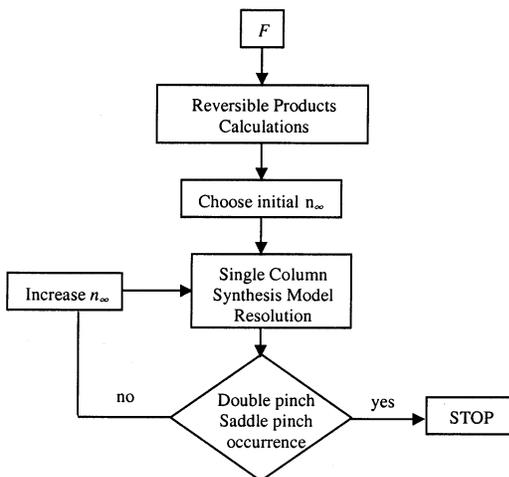
Figure 4. Infinite stage number selection.

Saddle pinch point regions toward the column extremes take place in an adiabatic column if the lightest (heaviest) component is completely removed from the bottom (distillate) product. According to Figure 3a, component 3 (1) has been totally removed from the top (bottom) product. Therefore, a saddle pinch point takes place in each section of the column. However, if a ternary distillate and a binary bottom are obtained as products from a ternary feed, only one saddle pinch emerges in the stripping section, where a large number of stages are required (see Figure 3b).

4. Single Distillation Column Design

4.1. Superstructure. Every single column of the RDS can be modeled with the methodology we present in this paper. As in any other separation carried out by distillation, there exists a tradeoff between the number of stages and the reflux ratio when the separation task is defined. For approximating a reversible column involving minimum energy demand, a superstructure with infinite number of stages is required. An upper bound on the number of trays is estimated for each unit in order for the pinch zones to be correctly developed within the unit[10] (see Figure 3b). The column with the upper bound on the number of trays is the "infinite" adiabatic column, which approximates the reversible unit.

It is worth noting that if a unit with not enough stages is used to approximate each column of the RDC, the reversible products are achieved, but in one of the two following schemes:

1. The least (most) volatile component is not completely removed from the distillate (bottom) product if the reflux involved is the minimum. Even a small trace of these components causes the deformation of the saddle pinch regions. Therefore, the maximum reversible products are not achieved.

2. The specification of the products is the maximum reversible composition, but the heat loads involved in the separation process are not minimal. As a consequence, the double pinch point around the feed stage disappears.

These last situations enhance the number of trays in the superstructure. In Figure 4, an algorithm to compute the upper bound in the number of stages is
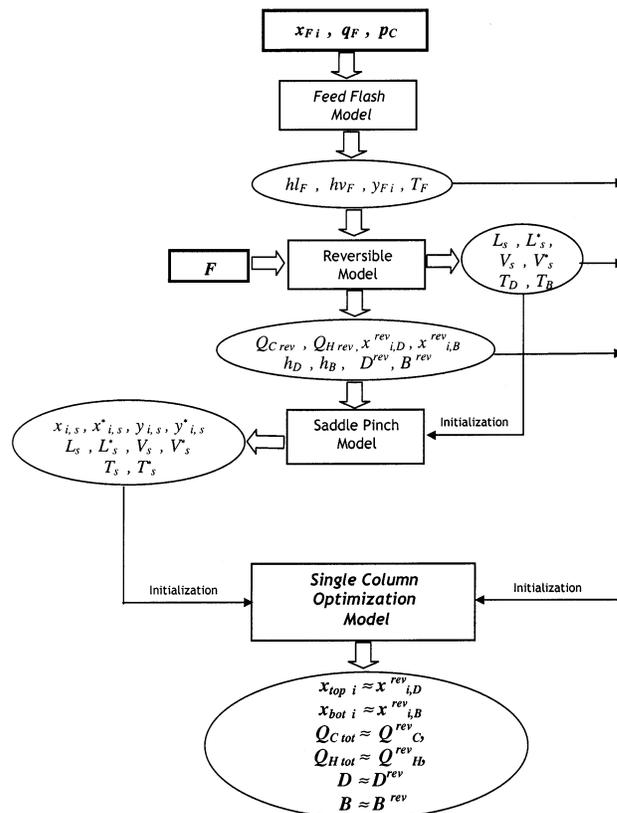
Figure 5. Schematic diagram of the preprocessing phase procedure.

presented. Note that the number of trays depends on the relative volatility difference between the components of the feed stream. A feed with components with a narrow volatility difference will be a "difficult separation task"; then a larger number of stages is required than in the case where this difference is bigger.

4.2. Preprocessing Phase. In this preliminary phase, optimization problems describing control volumes of a RDC operating at minimum reflux conditions are successively solved. The results of the preprocessing phase problems provide initial values and bounds for the synthesis model variables. Thermodynamic insights provide proper bounds and reduce the synthesis problem feasible region. Thus, a reduced-size superstructure of the separation process remains and it needs to be analyzed by rigorous optimization methods. These preliminary calculations also provide useful parameters to construct objective functions and constraints for the rigorous single column formulation. Neither simplifying assumptions regarding mass and energy balances nor iterative procedures or shortcut methods are considered in this preliminary phase.

Basically, two auxiliary NLP problems are involved in the formulation of the preprocessing phase, as shown in the scheme of Figure 5.

By defining the nature and composition of the mixture, its vapor fraction and the operating pressure, the vapor−liquid equilibrium (VLE) is calculated by solving a flash type model. The VLE is rigorously formulated. The vapor pressure is modeled according to Wagner's equation.[11,12] As we are dealing with zeotropic mixtures, both the liquid and the vapor enthalpies are modeled with polynomial expressions of temperature.

A NLP problem is first solved to compute the theoretical product composition and flow rates as well as the energy demand involved in the reversible separation. According to Figure 6, the RDC mathematical model (RM) for an ideal mixture containing NC components is as follows:

RM:

$$\min z_{\text{RM}} = x_{\text{NC,D}}^{\text{rev}} + x_{1,\text{D}}^{\text{rev}} \tag{1}$$

subject to

$$L + D^{\text{rev}} = V \tag{2}$$

$$Lx_i + D^{\text{rev}}x_{i,\text{D}}^{\text{rev}} = Vy_i \tag{3}$$

$$Lh_{\text{L}} + D^{\text{rev}}h_{\text{D}} + Q_{\text{C}}^{\text{rev}} = Vh_{\text{V}} \tag{4}$$

$$\sum_{i=1}^{\text{NC}} x_{i,\text{D}}^{\text{rev}} = 1 \qquad \sum_{i=1}^{\text{NC}} y_{i,\text{D}}^{\text{rev}} = 1 \tag{5}$$

$$L^* = V^* + B^{\text{rev}} \tag{6}$$

$$L^*x_i = V^*y_i + B^{\text{rev}}x_{i,\text{B}}^{\text{rev}} \tag{7}$$

$$L^*h_{\text{L}} + Q_{\text{H}}^{\text{rev}} = V^*h_{\text{V}} + B^{\text{rev}}h_{\text{B}} \tag{8}$$

$$\sum_{i=1}^{\text{NC}} x_{i,\text{B}}^{\text{rev}} = 1 \qquad \sum_{i=1}^{\text{NC}} y_{i,\text{B}}^{\text{rev}} = 1 \tag{9}$$

$$L + (1 - q_{\text{F}})F = L^* \tag{10}$$

$$V + q_{\text{F}}F = V^* \tag{11}$$

$$K_i = K_i(x_i, y_i, T, p) \qquad i = 1, ..., \text{NC} \tag{12}$$

$$h_{\text{L}} = h_{\text{L}}(x_i, T, p) \qquad h_{\text{V}} = h_{\text{V}}(y_i, T, p) \tag{13}$$

The model is formulated to both sections of a reversible column. Equations 2−5 are the mass and energy balances and mole fraction summation of the reversible rectifying section. The equivalent expressions for the stripping section are given by (6)−(9). Equations 10 and 11 are mass balances around the feed stage of the unit. Finally, eqs 12 and 13 rigorously model the vapor liquid equilibrium and the vapor and liquid enthalpies, respectively.

It should be noted that the values of h_{L} and h_{V} are known from the feed flash model previously solved. As a RDC under minimum reflux condition is considered, a double pinch point takes place around the feed stage. Then, the composition of the vapor y_i and liquid streams x_i entering or leaving this stage in the rectifying or stripping section are specified because they have the same composition as the feed stream and the vapor in equilibrium with it, according to the feed thermal state denoted by q_{F}. It is worth noting that constant vapor or liquid flows are not assumed in this model. These flows are computed by the model previously presented.

The saddle pinch points are calculated in a second step by solving a system of nonlinear equations. The pinch point compositions can be computed using the results of the reversible model (RM). The flow rates and the composition of the reversible products as well as the
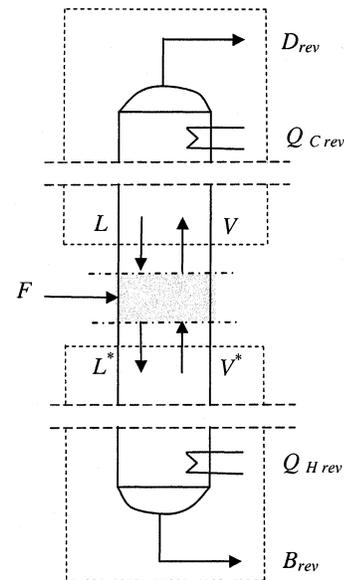
Figure 6. Balance control volume for reversible product calculations.

heat loads $Q_{\text{C}}^{\text{rev}}$ and $Q_{\text{H}}^{\text{rev}}$ are parameters in the saddle pinch point model (SPPM) calculations. The mathematical model for calculating saddle pinch points is presented next (see Figure 7):

SPPM:

$$L_{\text{s}} + D^{\text{rev}} = V_{\text{s}} \tag{14}$$

$$L_{\text{s}}x_{i,\text{s}} + D^{\text{rev}}x_{i,\text{D}}^{\text{rev}} = V_{\text{s}}y_{i,\text{s}} \tag{15}$$

$$L_{\text{s}}h_{\text{L,s}} + D^{\text{rev}}h_{\text{D}} + Q_{\text{C}}^{\text{rev}} = V_{\text{s}}h_{i,\text{s}} \tag{16}$$

$$\sum_{i=1}^{\text{NC}} x_{i,\text{s}} = 1 \qquad \sum_{i=1}^{\text{NC}} y_{i,\text{s}} = 1 \tag{17}$$

$$x_{\text{NC,s}} = 0 \qquad y_{\text{NC,s}} = 0 \tag{18}$$

$$L_{\text{s}}^* = V_{\text{s}}^* + B^{\text{rev}} \tag{19}$$

$$L_{\text{s}}^*x_{i,\text{s}}^* = V_{\text{s}}^*y_{i,\text{s}}^* + B^{\text{rev}}x_{i,\text{B}}^{\text{rev}} \tag{20}$$

$$L_{\text{s}}^*h_{\text{L,s}}^* + Q_{\text{H}}^{\text{rev}} = V_{\text{s}}^*h_{\text{V,s}}^* + B^{\text{rev}}h_{\text{B}} \tag{21}$$

$$\sum_{i=1}^{\text{NC}} x_{i,\text{s}}^* = 1 \qquad \sum_{i=1}^{\text{NC}} y_{i,\text{s}}^* = 1 \tag{22}$$

$$x_{1,\text{s}}^* = 0 \qquad y_{1,\text{s}}^* = 0 \tag{23}$$

$$K_i = K_i(x_{i,\text{s}}, y_{i,\text{s}}, T_{\text{s}}, p_{\text{s}}) \qquad i = 1, ..., \text{NC} \tag{24}$$

$$h_{\text{L,s}} = h_{\text{L,s}}(x_{i,\text{s}}, T_{\text{s}}, p_{\text{s}}) \qquad h_{\text{V}} = h_{\text{V}}(y_{i,\text{s}}, T_{\text{s}}, p_{\text{s}}) \tag{25}$$

$$p_{\text{s}} = p_{\text{C}} \tag{26}$$

This model is formulated to an adiabatic column where the reversible separation task is performed. Equations 14−17 are the mass and energy balances and the mole fraction summations formulated to a portion of the rectifying section comprising the column top and the region where the heaviest component is completely removed. Note that eqs 18 impose the condition of the exhaustion of this component. Analogous expressions

Table 1. Results of the RDSM Simulation for Various Distillations[a]

feed composition	product composition: distillate bottom	$Q_{C,rev}$ (KJ/s)		$Q_{H,rev}$ (KJ/s)		saddle pinch composition: upper lower
		theoretical	our model	theoretical	our model	
nnn[b]	0.9702/0.0296/2.1e-4	254.69	254.25	265.03	264.57	0.8786/0.1213/0
0.8/0.1/0.1	0/0.4309/0.5691					0/0.8539/0.1460
nnn	0.564/0.4395/2.5e-4	153.1	152.28	161.98	161.08	0.2275/0.7724/0
0.2/0.6/0.2	1.6e-3/0.689/0.3109					0/0.7872/0.2127
nnn	0.7837/0.2162/0	101.2	100.73	120.54	119.89	0.2014/0.7986/0
0.1/0.1/0.8	5.8e-4/0.083/0.9163					0/0.1423/0.857
nnn	0.7945/0.2054/0	166.64	166.64	186.38	186.41	0.4097/0.5902/0
0.33/0.33/0.34	0/0.4184/0.5815					0/0.5457/0.4542
nin[c]	0.8826/0.1167/7.3e-4	181.72	181.74	190.10	190.12	0.3811/0.6188/0
0.33/0.33/0.34	6.6e-6/0.4573/0.5426					0/0.5396/0.4604
nin	0.8161/0.1813/2e-3	180.25	179.97	187.04	186.73	0.3235/0.6764/0
0.3/0.5/0.2	2e-4/0.6850/0.3147					0/0.7436/0.2563
nin	0.7116/0.2864/1e-3	164.07	165.17	169.12	170.20	0.2141/0.7858/0
0.2/0.6/0.2	2e-3/0.7212/0.2765					0/0.766/0.2336
nin	0.9581/0.0418/8.2e-5	228.12	228.29	235.98	236.16	0.6724/0.3276/0
0.6/0.2/0.2	0/0.4650/0.5349					0/0.6245/0.3754

[a] Pressure: $p = 101.3$ KPa; feed, boiling liquid; products, saturated liquids; 80 stages; $F = 10$ mol/s. [b] n-Pentane, n-hexane, n-heptane. [c] n-Butane, isopentane, n-pentane.
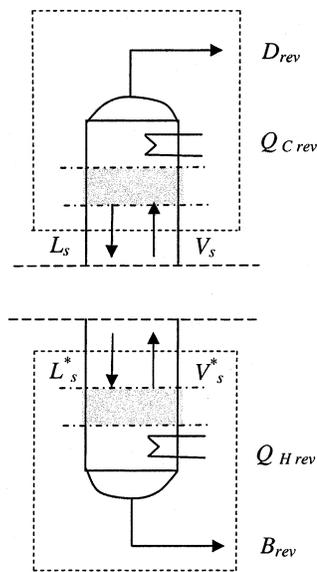
Figure 7. Balance control volume for saddle pinch points calculations.

Figure 8. Adiabatic column structure.

are formulated for the stripping section region from eqs 19 to 23. Physical properties are modeled by (24)−(26).

Once both preliminary problems have been solved, enough information is available for formulating the main synthesis problem.

4.3. Synthesis Model. Given is a feed flow rate Fo with composition and enthalpy zfo_i and hfo, respectively. Consider the adiabatic distillation column superstructure of Figure 8 with NS trays with one condenser and one reboiler. The trays are numbered top downward, so the condenser is in the first tray and the reboiler in the last (NSth) tray.

Let N denote the set of trays n, top and bot the subsets corresponding to the trays where heat exchange occurs, and prods the stages where product emerges:

$$N = \{n/n = 1, 2, ..., NS\}$$

$$top = \{1\}$$

$$bot = \{NS\}$$

$$prods = top + bot$$

Let N_F be the subset that includes the stage located in

the half part of the unit and floc denote candidate tray locations for the feed stream:

$$floc = \{(N_F - 2) \leq n \leq (N_F + 2)\}$$

Let I be the set of components of a multicomponent zeotropic feed, ordered in decreasing volatility:

$$I = \{i/i = 1, 2, ..., NC\}$$

Finally, let col be the subset of trays of the rectifying and stripping sections of the column:

$$col = \{n/n = 2, ..., (N_F - 3), (N_F + 3), ..., NS - 1\}$$

The model is formulated as a MINLP problem, which allows the optimization of the system of nonlinear equations containing both continuous and discrete variables. For the structural optimization, binary variables (0/1) denote the existence or nonexistence of a feed stream entering in a stage.

The formulation is based on the concept of equilibrium stage, which is modeled by the well-known MESH equations.[13] A detailed and rigorous description of ideal liquid−vapor equilibrium as well as material and enthalpy balances is computed. Note that the tray-by-tray formulation does not include any simplifying assump-

tion. Next, the efficient rigorous single column (ERSC) optimization model is detailed:

ERSC:

$$\text{Min } z_{\text{ERSC}} = \sum_{i \in I} (x_{\text{top},i} - x_{i,\text{D}}^{\text{rev}})^2 + (x_{\text{bot},i} - x_{i,\text{B}}^{\text{rev}})^2 \quad (27)$$

subject to

$$\left\{ \begin{array}{l} F_n zf_{n,i} + L_{n-1}x_{n-1,i} + V_{n+1}y_{n+1,i} = L_n x_{n,i} + V_n y_{n,i} \\ zf_{n,i} = zfo_i \quad \forall i \in I \end{array} \right\}$$
$$\forall i \in I \quad n \in \text{floc} \quad (28)$$

$$\sum_{n \in \text{floc}} F_n = Fo \quad (29)$$

$$\sum_{n \in \text{floc}} hf_n = hfo \quad (30)$$

$$L_{n-1}x_{n-1,i} = \text{PL}_n x_{n,i} + V_n y_{n,i} \quad \forall i \in I \quad n \in \text{bot} \quad (31)$$

$$V_{n+1}y_{n+1,i} = (L_n + \text{PL}_n)x_{n,i} + \text{PV}_n y_{n,i} \quad \forall i \in I \quad n \in \text{top} \quad (32)$$

$$L_{n-1}x_{n-1,i} + V_{n+1}y_{n+1,i} = L_n x_{n,i} + V_n y_{n,i} \quad \forall i \in I \quad n \in \text{col} \quad (33)$$

$$F_n hf_n + L_{n-1}hl_{n-1} + V_{n+1}hv_{n+1} = L_n hl_n + V_n hv_n \quad \forall n \in \text{floc} \quad (34)$$

$$Q_n + L_{n-1}hl_{n-1} = \text{PL}_n hl_n + V_n hv_n \quad \forall n \in \text{bot} \quad (35)$$

$$Q_n + V_{n+1}hv_{n+1} = (L_n + \text{PL}_n)hl_n + \text{PV}_n hv_n \quad \forall n \in \text{top} \quad (36)$$

$$L_{n-1}hl_{n-1} + V_{n+1}hv_{n+1} = L_n hl_n + V_n hv_n \quad \forall n \in \text{col} \quad (37)$$

$$y_{n,i} = K_{n,i}x_{n,i} \quad \forall i \in I \quad n \in N \quad (38)$$

$$\sum_{i=1}^{\text{NC}} x_{n,i} = 1 \qquad \sum_{i=1}^{\text{NC}} y_{n,i} = 1 \quad \forall n \in N \quad (39)$$

$$\left\{ \begin{array}{l} \sum_{n \in \text{floc}} F_n zf_{n,i} = \sum_{n \in \text{top}} \text{PL}_n x_{n,i} + \sum_{n \in \text{bot}} \text{PL}_n x_{n,i} \\ \sum_{n \in \text{floc}} F_n hf_n + Q_{\text{C,tot}} + Q_{\text{H,tot}} = \sum_{n \in \text{top}} \text{PL}_n hl_n + \sum_{n \in \text{bot}} \text{PL}_n hl_n \end{array} \right\}$$
$$\forall i \in I \quad (40)$$

$$Q_{\text{C tot}} = \sum_{n \in \text{top}} Q_n \quad (41)$$

$$Q_{\text{H tot}} = \sum_{n \in \text{bot}} Q_n \quad (42)$$

$$F_n \leq bf_n F_{\text{max}} \quad \forall n \in \text{floc} \quad (43)$$

$$\sum_{n \in \text{floc}} bf_n = 1 \quad (44)$$

$$\text{PV}_n = 0 \quad n \in \text{prods} \quad (45)$$

$$L_n = 0 \quad n \in \text{bot} \quad (46)$$

$$V_n = 0 \quad n \in \text{top} \quad (47)$$

The objective function of the model is given by eq 27. The product compositions are specified by minimizing the difference of the product compositions and the
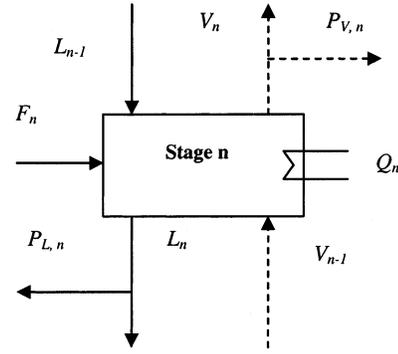
Figure 9. Superstructure of a single stage.

reversible product compositions, computed in section 4.2. The mass balance of the separation is oriented in the reversible direction, and the products are forced to coincide with the maximum reversible ones. This means that the objective function "moves" the solutions toward the mass balance line extremes.

Each stage n of the distillation column that approximates the reversible unit is modeled by the MESH equations (see Figure 9). Mass balances are given from eqs 28 to 33 and the energy balances from eqs 34 to 37. The VLE is rigorously modeled by (38) and the summation of mole fractions are given by eqs 39. Global balances are given by eqs 40 and the heat loads involved in the process are defined by (41) and (42).

Variable feed tray locations are modeled in concordance with Viswanathan and Grossmann.[13] Binary variables bf_n indicate whether a stage from floc is a feed tray, and is described by the eq 43. For this variable only values of zero or one are allowed. The feed stream can only enter in a stage if the corresponding binary variable value is 1. This equation has to be written as an inequality constraint with F_{max} as an upper bound of the feed flow rate. The value of F_{max} (big-M formulation) is estimated in about one and a half times the maximum estimated flow. Equation 44 implicates that only one feed stream can enter the column.

Equation 45 imposes the condition of liquid products and eqs 46 and 47 impose the condition that there is no liquid flow leaving the bottom tray and no vapor flow emerging from the top tray. Note that variable location for the heat exchange was not considered in this model because the objective function does not involve the cost of the process. Thus, the heat exchanger location remains in the column extremes to satisfy the purity specifications.

5. Numerical Examples

We adopted two ternary zeotropic mixtures to test the proposed methodology: n-pentane/n-hexane/n-heptane and n-butane/isopentane/n-pentane.

The models are implemented and solved in GAMS. The following algorithms are used: the outer-approximation equality-relaxation argumented-penalty algorithm DICOPT++,[14,15] a MINLP solver and the generalized reduced gradient algorithm CONOPT as an NLP solver. These algorithms are available as parts of the GAMS modeling system.

Some results are presented in Table 1. Note that for the different feed compositions, the composition of the reversible distillate and bottom products are presented as well as the energy demands and the saddle pinch point compositions. The theoretical values for the heat

Mole Fraction
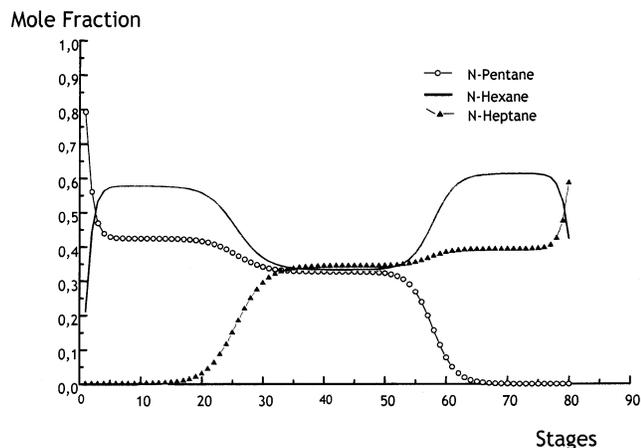
Figure 10. Concentration profiles of the algebraic approach to the RDSM.

Table 2. Auxiliary Problems Sizes

problem	no. of variables	no. of equations	no. of nonzero nonlinear elements
reversible product model	88	74	109
saddle pinch points model	45	39	94

Table 3. Single Column Problem Size

no. of variables	no. of equations	no. of nonzero nonlinear elements	time[a] (s) min	max
1957	1548	5253	1.2	1.5

[a] Times reported are in CPU seconds on a Pentium III, 640 K, 500 MHz.

loads are the ones for the reversible separation computed in the preprocessing phase. Note that in all cases, the values obtained by the model are very close to the theoretical values. In Figure 10, the concentration profiles for a mixture of composition (0.33/0.33/0.34) of *n*-pentane, *n*-hexane, and *n*-heptane are shown. The three pinch point zones are well defined: from stage 5 to 15 and from 65 to 75 the saddle pinches are developed, and around the feed tray a double pinch point with composition similar to that of the feed stream occurs from stage 35 to 50, approximately.

The sizes of the preprocessing problems are presented in Table 2. Note that the computational time for solving the models is low: 0.75 s for solving the reversible products model (including a previous feed flash calculation) and 0.32 s to compute saddle pinch point calculations in a subsequent step. For the rigorous single column model with 1957 variables and 1548 equations, 1.5 s is needed for solving (see Table 3). Note that the average time for solving the complete synthesis model including its preprocessing phase is about 2.4 s.

In all cases, the reversible distillate composition, flow rates, and heat loads Q_C^{rev} and Q_H^{rev} computed in the preprocessing phase were used to initialize and bound the variables involved in the MINLP model. We found that this procedure improves the model convergence and considerably reduces the solution times. The convergence to the desired separation task is guaranteed for any given zeotropic mixture.

It should be noted that the solutions obtained by solving the model with the proposed methodology do not necessarily involve minimum energy demand. Many alternatives were evaluated to approach a RDC at minimum energy demand. According to our experience, the best alternative involves setting bounds on the heat loads. Therefore, upper and lower bounds around the

Mole Fraction
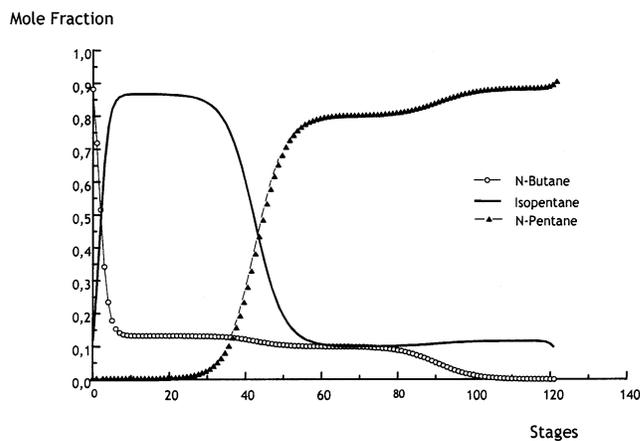
Figure 11. Composition profiles with the HYSYS simulator.

reversible values Q_C^{rev} and Q_H^{rev} were introduced. Different fractions were tried above and bellow the reversible levels for the upper and lower bounds of the separation energy demand, respectively. The convergence is assured to the desired solution even employing small percents, like 0.01%. Thus, the heat loads bounds were defined as fractions of Q_C^{rev} and Q_H^{rev} defining the feasible region for these variables.

Other alternatives involve the optimization of a multiple objective function, which comes up from the linear combination of (27) with the addition of the summation of the total heat loads involved in the separation. According to our experience, the disadvantage of this choice is that the heat loads weight factor has a strong dependence on the composition and nature of the problem mixture. Therefore, a value arbitrarily selected does not guarantee the convergence of the MINLP model.

It should be noted that in all cases studied, global optimal solutions are achieved with the proposed methodology. The optimal globality of the solutions is tested by simply comparing the values obtained by solving the rigorous model with the theoretical values computed in the preprocessing phase. It is well-known that a RDC is the most efficient distillation column because no entropy is created. Therefore, if the solutions achieved with the model we present coincide with the theoretical values relative to the RDC, global solutions are achieved.

The reversible separation was simulated in the commercial simulator HYSYS plant 2.1. The number of trays of the column and two additional variables has to be specified, then the degree of freedom is three. The number of stages employed for each problem mixture was computed using the algorithmic procedure presented in section 4.1. Once the "infinite" adiabatic was defined, the degrees of freedom are two, as those of a reversible column. Thus, two extra variables have to be fixed to start the simulation. For a detailed description of the RDSM degrees of freedom, see Koehler et al.[4]

According to our experience, these two specifications cannot be selected arbitrarily. Only specifying a product flow rate and the mole fraction of component 3 (1) in the distillate (bottom), the simulation converges to the reversible solution. In the case of fixing any other pair of variables, a solution is not assured. The product compositions obtained with the proposed methodology are very similar to those obtained in the simulation. In Figure 11, the concentration profiles obtained by the HYSYS simulation are shown.

It is worth noting that the vapor−liquid equilibrium model included in the simulator is not the same as the

one employed in our model; for that reason, the specifications provided to the simulator were calculated with its own liquid−vapor equilibrium data, according to eqs 1−13.

7. Extensions of the Work

Considering the synthesis scheme presented in this paper, the approximation to the reversible separation is a well-defined problem. However, the reversible single column design is not realistic from the economic point of view. Distillation columns keeping some of the reversible solution elements but involving a smaller number of trays are usually desired. In addition, a certain product composition needs to be specified in practical applications. Then, departing from the solutions presented in this work, a cost-based objective function can be minimized. Note that the advantage of solving first the approximation of the reversible separation is that a good initial guess for the economic problem is available.

8. Conclusions

This paper has presented a methodology for designing multicomponent single distillation columns that closely approximate reversible conditions. The methodology involves two solution phases. A model preprocessing phase is first considered, where relevant information relative to the RDSM is computed by solving fairly easy NLP problems. This phase provides initial values and bounds for the variables involved in the rigorous tray-by-tray MINLP model, which is solved in a second step.

The RDC-based superstructure can be globally solved by using proper objective functions and constraints. In spite of this, the problem is modeled through a tray-by-tray nonconvex MINLP; the proposed methodology guarantees global optimality because the solutions obtained closely approximate reversible conditions. The globality of the solutions is tested by simply comparing the model solutions with the theoretical values computed in the preprocessing phase. The methodology is general and automatic because no external parameters have to be tuned. Many cases studied were presented to confirm that the procedure is also robust.

The solutions obtained with the model presented were compared with the ones of the single adiabatic column simulated in HYSYS. The composition profiles obtained in both cases are similar to the ones obtained with the model presented.

The relationship between the reversible model and its adiabatic approximation was presented. The occurrence of pinch point zones was used as a sufficient criterion of minimum reflux and degree of sharpness of the operation. With the RDC algebraic approximation, the same product composition and heat loads as in the ideal rectification model were achieved, because saddle pinches zones as well as a double pinch around the feed stage occur in all the cases studied.

Finally, an alternative method for constructing pinch point curves for multicomponent systems was introduced. By solving the optimization model proposed, we could easily calculate the reversible energy profiles. These diagrams are useful tools to deal with sequence design. Relevant separations due to large flows, small volatility differences, or extreme temperatures can be indicated a priori.

Nomenclature

B = binary variable
Card = cardinal
D = distillate flow (mol/s)
h = enthalpie
k = set relative to a pinch point
K = equilibrium coefficient
L = liquid flow (mol/s)
n = stage number
ord = ordinal
PL = liquid product flow (mol/s)
PV = vapor product flow (mol/s)
p = pressure (Pa)
p^o = vapor pressure (Pa)
q = vapor fraction
Q = heat duty
T = temperature (K)
V = vapor flow (mol/s)
x = liquid mole fraction (mol/mol)
y = vapor mole fraction (mol/mol)
z_f = feed mole fraction (mol/mol)
z = objective function value

Subscripts and Superscripts

A = most volatile component
B = bottom product
C = least volatile component
c = condenser
col = column
D = distillate product
F = feed
H = reboiler
i = component
k = set relative to a pinch point
L = liquid
l = lower
max = maximum
min = minimum
n = stage
NC = heaviest component of the mixture
P = product
p = relative to a pinch point
rev = reversible
s = saddle point
t = transposed
u = upper
V = vapor
° = equilibrium
* = striping section

Greek Letters

λ = sep-length
φ = angle cosine
α = angle between two adjacent segments
ϵ = tolerance

Appendix A: Pinch Point Curves Calculations

The pinch point curve calculation was considered by several authors. It is a very useful tool for determining the feasible regions for azeotropic distillation of the product[8,9,16] as well as for minimum reflux calcula-

tions.[4−6,17] Many relevant contributions to construct product pinch point curves have been done.[8,9,16,18,19] Aguirre and Espinosa[20] presented a rigorous algorithm based on imbedding homotopic continuation methods. The algorithm was developed without the use of derivative calculations making modifications on the classical homotopic continuation procedure. Instead of using unit tangent vectors in the prediction step, we defined a secant vector on the mole fraction space. The original problem variables were considered as homotopy parameters. Then, a variable that increases or decreases monotonically between the column end and the pinch is chosen, such as the component mole fraction to be eliminated in a section. On the basis of our previous work[20] we focus the problem with a different approach. An optimization problem is formulated to construct the homotopy path. The pinch points describing the solution curve are calculated simultaneously by maximizing a proper objective function.

The pinch point curve can be constructed by solving an NLP optimization problem where relevant elements of imbedding homotopy continuation methods are applied.[21,22] For an arbitrary product, we are interested in computing the entire pinch point curve. Hence, one of the original problem variables is considered as the imbedded parameter. The component mole fraction is selected as the homotopy parameter. The model is formulated for constructing a distillate pinch point curve; however, analogous expressions can be formulated for the reversible stripping section.

Let k be the set of points of the curve. The control volume is defined as a zone of the rectifying section involving the column top and an arbitrary column section k, from where a vapor flow Vp_k enters and a liquid Lp_k emerges from it, with compositions $y_{i,k}$ and $x_{i,k}$, respectively. The energy demand for obtaining D_{rev} with composition $x_{i,rev}$ departing from the fictitious current $(Vp_k - Lp_k)$ is Q_{Ck}.

The NLP model for constructing the distillate product pinch point curve is presented next (see Figure 12):

$$\max z = \sum_k \text{norm}_k \qquad (A1)$$

subject to

$$Lp_k + D^{rev} = Vp_k \qquad (A2)$$

$$Lp_k x_{i,k} + D^{rev} x_{i,D} = Vp_k y_{i,k} \qquad (A3)$$

$$Lp_k hl_k + D^{rev} h_D + Q_{Ck}^{rev} = Vp_k hv_k \qquad (A4)$$

$$\text{dif}_{i,k} = x_{i,k} - x_{i,k-1} \qquad (A5)$$

$$\text{norm}_k = ||x_{i,k} - x_{i,k-1}|| \qquad (A6)$$

$$\text{sec}_k \, \text{norm}_k = \text{dif}_k \qquad (A7)$$

$$\text{norm}_{k-1} \, \lambda_k = \text{norm}_k \, \varphi_k \qquad (A8)$$

$$\sum_i (\text{sec}_{i,k} \, \text{sec}_{i,k-1}) - \varphi_k = 0 \qquad (A9)$$

$$\text{dif}_k - \lambda_k \, \text{dif}_{k-1} \leq \epsilon \qquad (A10)$$

The model is solved in two steps to guarantee the convergence to the optimal solution. The model involving (A2)−(A10) is first solved. The distillate (bottom) pinch point curve can be approached by a straight line
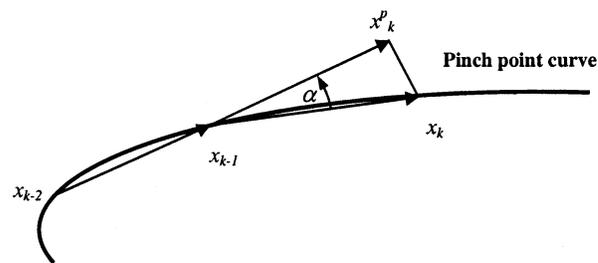
Figure 12. Pinch point calculation algorithm.
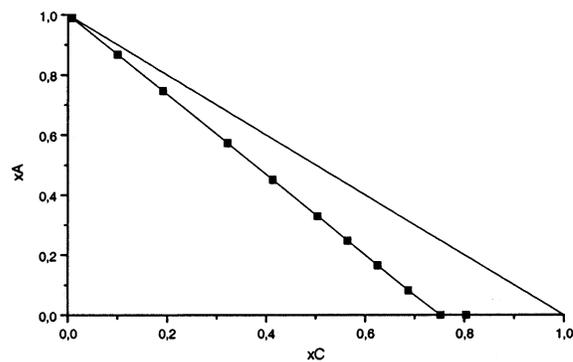
Figure 13. Stripping reversible distillation profile.

when the concentration of the least (most) volatile component approaches unity. This is the assumption made in this solution phase. For computing the distillate pinch point curve, we considered a composition interval within the region rich in the heaviest component. This portion of the complete path, which is considered as a straight line, is divided in k points. The mole fraction of the heavy component is chosen as the homotopy variable. Thus, the heaviest component compositions of the k points are fixed in this first solution phase in the following values:

$$x_{NC,k} = x_{NC}^U - \text{ord}(k)\frac{x_{NC}^U - x_{NC}^L}{\text{card}(k)} \qquad (A11)$$

where x_c^u and x_c^l are the heaviest component upper and lower concentration extremes of the interval considered, respectively. All the other variables involved in the problem are initialized lengthwise in the interval. The values used were obtained as flash calculation solutions of the mixture involved with compositions x^u and x^l.

A second solution phase is considered, where the optimization model defined by eqs A1−A10 is solved.

Summarizing, k points are calculated in the first solution phase. These points describe a small and straight portion of the complete reversible path. This branch of the distillate (bottom) curve is located in a heaviest (lightest) component rich zone. To construct the complete curve, a subsequent solution phase is considered. The objective function of the problem, given by (A1), is maximized to force the k points previously calculated to separate one from the other.

In Figure 13, the pinch point curve for the reversible bottom product obtained from a ternary feed with composition (0.2, 0.2, 0.6) is shown. The reversible path for a distillate product is presented in Figure 14, where the effect of the presence of the heavy component traces is shown.

It is worth noting that the computation of the reversible profiles also provides the minimum energy profiles as a function of the column internal temperature for the
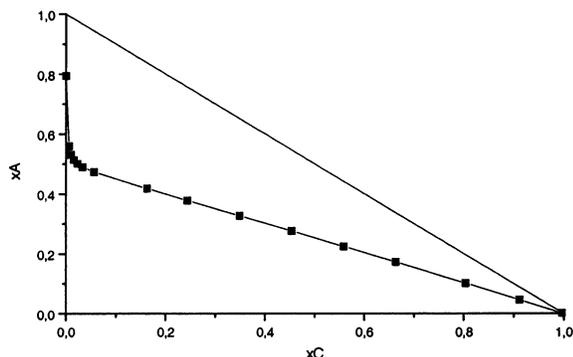
Figure 14. Distillate pinch point curve.
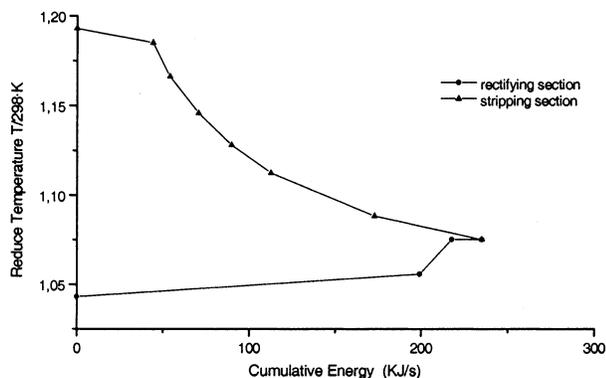
Figure 15. RDSM cumulative energy profiles for an ideal three-component mixture.

separation task involved. The energy profiles of both sections of a reversible column are shown in Figure 15 for a three-component mixture, assuming saturated liquid products. Each value of $Q(T)$ is the cumulative amount of energy that has to be introduced in the stripping section or withdrawn from the rectifying section.

Finally, it should be noted that the assumption that the energy values are set to zero at the column ends was made. Then, the discontinuities (jumps) in the energy profiles at the feeds location will reflect the respective overall column balance. The stripping energy profile can be expressed as a function of the rectifying one as $Q_s(T) = Q_r(T) + \Delta H$, with $\Delta H = H_D + H_B - H_F$.

Literature Cited

(1) Petlyuk, F. B.; Platonov, V. M.; Slavinskii, D. M. Thermodynamically Optimal Method for Separating Multicomponent Mixtures. *Int. Chem. Eng.* **1965**, *5* (3), 555.

(2) Fonyó, Z. Thermodynamic Analysis of Rectification I. Reversible Model of Rectification. *Int. Chem. Eng.* **1974**, *14* (1), 18.

(3) Stilchmair, J. G.; Fair, J. R. *Distillation. Principles and Practice;* Wiley-VCH: New York, 1998.

(4) Koehler, J.; Aguirre, P. A.; Blass, E. Minimum Reflux Calculations for Nonideal Mixtures Using the Reversible Distillation Model. *Chem. Eng. Sci.* **1991**, *46* (12), 3007.

(5) Koehler, J.; Blass, E. A Review on Minimum Energy Calculations for Ideal and Nonideal Distillations. *Ind. Eng. Chem. Res.* **1995**, *34*, 1003.

(6) Koehler, J.; Kuen, T.; Blass, E. Minimum Energy Demand for Distillations with Distributed Components and Side-Product Withdrawals. *Chem. Eng. Sci.,* **1994**, *49* (19), 3325.

(7) Bausa, J.; Watzdorf, R. V.; Marquardt, W. Minimum Energy Demand for Nonideal Multicomponent Distillation in Complex Columns. *Comput. Chem. Eng.* **1996**, *20*, supp, S55.

(8) Wahnschafft, O. M.; Koehler, J. W.; Blass, E.; Westerberg, A. W. The Product composition Regions of Single-Feed Azeotropic Distillation Columns. *Ind. Chem. Eng. Res.* **1992**, *31*, 2345.

(9) Poellmann, P.; Blass, E. Best Products of Homogeneous Azeotropic Distillations. *Gas Sep. Purif.* **1994**, *8* (4), 194.

(10) Aguirre, P. A.; Corsano, G.; Barttfeld, M. Un Método Híbrido para la Síntesis Optima de Procesos de Destilación Multicomponente. *CIT (Información Tecnológica)* **2001**, *12* (1), 119.

(11) Reid, R. C.; Prausnitz, M. P.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.

(12) Brooke, A.; Kendrick, D.; Meeraus, A.; Raman, R. GAMS, A User Guide. 1998.

(13) Viswanathan, J.; Grossmann, I. E. An Alternative MINLP Model for Finding the Number of Trays Required for a Specified Separation Objective. *Comput. Chem. Eng.* **1993**, *17* (9), 949.

(14) Kocis, G. R.; Grossmann, I. E. Computational Experience with DICOPT Solving MINLP Problems in Process Systems Engineering. *Comput. Chem. Eng.* **1989**, *13* (3), 307.

(15) Viswanathan, J.; Grossmann, I. E. A Combined Penalty Function and Outer Approximation Method for MINLP Optimization. *Comput. Chem. Eng.* **1990**, *14* (7), 769.

(16) Castillo, F. J.; Thong, D. Y.; Towler, G. P. Homogeneous Azeotropic Distillation. 1. Design Procedure for Single-Feed Columns at Nontotal Reflux. *Ind. Chem. Eng. Res.* **1998**, *37*, 987.

(17) Bruggemann, S.; Marquardt, W. Shortcut Methods for Nonideal Multicomponent Distillation: Providing Initials and Bounds for Rigorous Optimization. Internal Report; BUSINESS: LOCATION, May 20, 2001.

(18) Terranova, B. E.; Westerberg, A. W. Temperatureheat Diagrams for Complex Columns. 1. Intercooled/Interheated Distillation Columns. *Ind. Chem. Eng. Res.* **1989**, *28,* 1374.

(19) Fidkowsky, Z. T.; Malone, M. F.; Dohety, M. F. Nonideal Multicomponent Distillations: Use of Bifurcation Theory for Design. *AIChE J.* **1991**, *37* (12), 1761.

(20) Aguirre, P. A.; Espinosa, J. A Robust Method to Solve Mass Balances in Reversible Column Sections. *Ind. Eng. Chem. Res.* **1996**, *35*, 559.

(21) Rion, W. L.; Van Brunt, V. Differential Geometry Based Homotopy Continuation. *Comput. Chem. Eng.* **1990**, *14* (8), 889.

(22) Koehler, J.; Aguirre, P. A.; Blass, E. Evolutionary Thermodynamic Synthesis of Zeotropic Distillation Sequences. *Gas Sep. Purif.* **1992**, *6* (3), 153.