Synthesis of Nonequilibrium Reactive Distillation Processes by MINLP Optimization

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A mixed integer nonlinear programming (MINLP) model is presented for synthesizing reactive distillation columns when chemical reaction equilibrium cannot be assured. The MINLP minimizes the total annual cost subject to a rigorous tray-by-tray model. The solution of this MINLP yields the optimal number of trays, the optimal feed rates, and the optimal feed tray locations. The liquid holdup per tray, the reflux ratio, and the temperature and composition profiles within the column are optimized as well. The MINLP is solved using generalized Benders decomposition, and the technique is illustrated with ethylene glycol synthesis.

Introduction

Reactive distillation is an attractive alternative to conventional chemical processing schemes. When reactions are equilibrium limited, reactive distillation continuously removes products from the reaction zone, which dramatically increases the overall conversion. The technique may also increase selectivity in certain competing reaction systems by continuously separating products from reactants. Lastly, reactive distillation may prove economically attractive by reducing the number of processing units and providing direct heat integration between reaction and separation. The total annualized cost of a reactive distillation process can be an order of magnitude smaller than the annualized cost of a conventional chemical manufacturing process (Doherty and Buzad, 1992).

Most of the previous research in reactive distillation has focused upon computing a single steady-state solution to the material balances. Extensions of numerical methods originally developed for nonreactive distillation have been presented by Nelson (1971), Suzuki et al. (1971), Komatsu and Holland (1977), Tierney and Riquelme (1982), and Xu and Chen (1985). More recently, a comprehensive model capable of accounting for mass-transfer effects was presented by Alejski (1991), and automated steady-state calculations using a modified inside-out algorithm have been implemented in ASPEN (Venkataraman et al., 1990).

While it has been relatively easy to extend simulation methods developed for nonreactive distillation, it has not been easy to extend nonreactive distillation design techniques to reactive distillation columns.

There are several reasons for this: in conventional distillation design, the major design variables are the number of trays in the column, the feed tray location, and the reflux ratio; it is reasonable to initially assume constant molar overflow; that the liquid holdup on each tray is a secondary design variable and that a feed stream will be sent to a single tray, rather than distributed to several trays. In contrast, in a reactive distillation column, one cannot assume constant molar overflow unless the reaction is thermally neutral and stoichiometrically balanced. One cannot assume that the holdup volume is a minor parameter, since the reactions usually occur within the liquid holdup, and one cannot assume that the column has a single feed, since an economically optimal column may feature distributed feeds.

In reactive distillation, the volume of the liquid holdup on a tray is a major design parameter that determines the extent of reaction on that tray. The holdup volume cannot be determined *post priori* with a heuristic or a correlation, for it will vary with the chemical reaction system, and may vary from one tray to another. If the reactions are slow or are not equilibrium limited, this critical design parameter must be accounted for during the conceptual design stage (Agreda and Partin, 1984; Agreda et al., 1990).

These critical differences between reactive distillation and conventional distillation make it difficult to derive reactive distillation design methods by modifying techniques originally

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developed for conventional distillation. Barbosa and Doherty (1988c,d) are the only workers to successfully apply design methods developed for conventional distillation to reactive distillation processes.

Barbosa and Doherty (1988a,b) developed a thermodynamically based approach for analyzing equilibrium limited, thermally neutral reactive distillation systems. This work employed a novel composition coordinate system to transform the problem into a form completely analogous to nonreactive distillation. Using residue curve map techniques, Barbosa and Doherty (1988c,d) were able to rapid screen for reactive azeotropes and feasible designs, and to compute the number of trays and the minimum reflux ratio. Recently, Doherty and Buzad (1992) outlined how kinetic effects can be included in this analysis, when the residence time (via the Damköhler number) is fixed.

Barbosa and Doherty's techniques were developed to analyze reactive distillation systems that are near chemical equilibrium, are thermally neutral, and involve only one reaction. When any one of these assumptions are violated, the reaction kinetics, the heat of reaction, the liquid holdup, and the residence times become major design parameters that cannot be accounted for in the modified residue curve map techniques. This is an unfortunate limitation of the only major reactive distillation design technique, for there are a number of potential applications for reactive distillation that cannot be analyzed with the residue curve map techniques of Barbosa and Doherty. These applications include, but are not limited to, hydrolysis reactions (Doherty and Buzad, 1992), ethylene glycol synthesis (Parker, 1958), and cumene production (Shoemaker and Jones, 1987).

Clearly, there is a need for a technique to design reactive distillation columns when there are multiple reactions or when reactive equilibrium or thermal neutrality cannot be assured. This article presents a novel approach for synthesizing reactive distillation units that can accommodate these elements of the synthesis problem. A rigorous tray-by-tray model is combined with kinetic-rate-based expressions to give the basic constraints of an optimization model that minimizes the total annual cost. Solution of this model yields the optimum number of trays, the optimal feed tray location(s), reflux ratio, condenser and reboiler duties, and liquid holdups on each tray. Since the number of trays is an integer variable, the resulting optimization model is a mixed integer nonlinear programming (MINLP) problem that can be solved to local optimality with generalized Benders decomposition (GBD). This model has some similarities to the MINLP presented by Viswanathan and Grossman (1990) for optimizing a conventional distillation column. However, an assumption that there is a single feed tray is interwoven into the Viswanathan and Grossman model; this assumption is quite appropriate for a simple column, but is not appropriate for a reactive distillation column.

The approach is illustrated with a case study demonstrating the production of ethylene glycol via ethylene oxide in a reactive distillation column.

Problem Statement

The synthesis problem for designing a cost optimal reactive distillation column can be stated as follows. One must be *given*:

- A set of chemical species $i = 1 \,..\, I$ in the reactive distillation system
- The subset of desired products $i \in P$ and the production rate P_i of each product
- A set of chemical reactions $j = 1 \,..\, J$, the stoichiometric coefficients for all species ν_{ij} and rate expressions $r_j = f(x_i, T)$
- A maximum number of trays K
- The heat of vaporization and vapor-liquid equilibrium data
- The cost of downstream separations
- The cost c_s and composition x_{is} of all feedstocks $s = 1 \,.\, S$.

The goal is to *determine* the optimal number of trays, holdup per tray, reflux ratio, condenser and reboiler duties, and feed tray location(s).

The following assumptions are made: the vapor and liquid phases are in equilibrium on each tray; no reaction occurs in the vapor phase; the liquid phase is always homogeneous; the enthalpy of liquid streams is negligible; the heat of vaporization is constant; temperature dependence of the reaction rates can be expressed in Arrhenius form; and the cost of separating products downstream is given by an analytical function.

It should be noted that the first five assumptions are basic to the model. The remaining assumptions simplify the model but do not limit it. For example, the seventh assumption could be relaxed by incorporating either shortcut design equations for downstream columns or by including the reactive distillation model presented here in a larger MINLP that synthesizes a large-scale process.

Problem Formulation

The optimal reactive distillation problem is formulated as a MINLP optimization problem, with the total annualized cost taken as the objective. The major variables are the number of trays in the column, the feed tray location(s), the temperature and composition profiles within the column, the reflux ratio, the internal flows within the column, and the column diameter. Constraints are formed from the material balances, vapor-liquid equilibria, mole fraction summations, and enthalpy balance (MESH) equations on each tray, material balances at the top and bottom of the column, kinetic and thermodynamic relationships, and logical relationships between process variables and the number of trays. The resulting MINLP is solved with GBD (Geoffrion, 1974).

Binary representation of column trays

The number of trays in a reactive distillation column is an integer variable. This is accounted for by introducing a set of binary variables Y_k, where $Y_k = 1$ represents the existence of the *k*th tray from the bottom of the column. If there are a total of N trays in the column, then:

$$Y_k = \begin{cases} 1 \text{ if } k \leq N \\ 0 \text{ if } k > N \end{cases}$$

It follows that:

$$Y_k \geq Y_{k+1} \qquad (1)$$

It should be noted that $Y_k - Y_{k+1}$ equals zero everywhere in the column except at the top tray:

$$Y_k - Y_{k+1} = \begin{cases} 1 \text{ if } k=N \\ 0 \text{ otherwise.} \end{cases}$$

As a consequence, the number of trays N in the column is given by:

$$N = \sum_k k(Y_k - Y_{k+1}) \tag{2}$$

These relationships will prove useful later in the model development.

The optimization problem is formulated from two components: an objective function that seeks to minimize the total annualized cost, and a set of constraints modeling the reactive distillation column. These components are described in more detail below.

Objective function

The objective function Z is composed of two basic terms: annual operating costs and the annualized investment. The annual operating cost is determined by the consumption of raw materials, steam, and cooling water. The annualized investment is composed of the cost of the column, its internals, and the reboiler and condenser:

$$Z = \sum_{s,k} c_s F_{sk} + c_H Q_B + c_w Q_c + R(C_{cs} + C_{ci} + C_r + C_c). \tag{3}$$

Here, c_s is the cost of raw material s, F_s is the feed rate of material s, c_H is the cost of steam, Q_B is the reboiler duty, c_w is the cost of cooling water, and Q_c is the condenser duty. R is an annualizing factor; C_{cs}, C_{ci}, C_r, and C_c are the installed costs of the column shell, trays, reboiler, and condenser. The formulae for the column investment costs, given below, are from Douglas (1988):

$$C_{cs} = 0.3639 M\&S D^{1.066} H^{0.802} (2.18 + F_c) \tag{4}$$

$$C_{ci} = \sum_k 0.0168 M\&S D^{1.55} H_k F_c' \tag{5}$$

The exchanger investment costs are modeled as a linear function of the heat duty:

$$C_r = cr_1 + cr_2 Q_R \tag{6}$$

$$C_c = cc_1 + cc_2 Q_C \tag{7}$$

Here, $M\&S$ is the Marshall and Swift Index, D is the column diameter, H is the height of the tower, Q_R and Q_C are the heat duties of the reboiler and condenser, F_c, F_c', and F_c'' are materials of construction factors, and H_k is the height of tray k. The diameter D of the column is readily calculated from the internal vapor flow rate, and the materials of construction factors will be constant for a given system. Note that Eq. 4 is simplified by assuming that $D^{1.066} \approx D$.

The height of the tower is taken as $H = \Sigma_k H_k + H_o$. The minimum tray spacing is set equal to two feet; additional spacing is required to account for the liquid holdup needed for reaction W_k. Thus, the height of a tray can be found from:

$$H_k = 2Y_k + 1.27 \frac{W_k}{D^2} \tag{8}$$

Note that Y_k is the binary variable indicating the existence of tray k. A separate constraint will specify that W_k equals zero when $Y_k = 0$. Consequently, H_k will equal zero if Y_k equals zero.

Substituting this expression into Eq. 4 provides an equation that has binary variables appearing in nonlinear terms:

$$C_{cs} = 0.3639 M\&S (F_c + 2.18) D \times \left(H_o + \sum_k 2Y_k + 1.27 \frac{W_k}{D^2}\right)^{0.802} \tag{9}$$

This expression can be simplified by noting that $Y_k - Y_{k+1}$ equals zero everywhere except at the top of the column. This enables us to transform Eq. 9 to:

$$C_{cs} = 0.3639 M\&S (F_c + 2.18) D \times \sum_k \left(H_o + \sum_{k' \le k} 2 + 1.27 \frac{W_{k'}}{D^2}\right)^{0.802} (Y_k - Y_{k+1}) \tag{10}$$

The cost of the trays in terms of the design variables is more straightforward:

$$c_{ci} = 0.0168 M\&S F_c' D^{1.55} \sum_k \left(2Y_k + 1.27 \frac{W_k}{D^2}\right) \tag{11}$$

The overall objective function becomes:

$$\begin{aligned} Z = \sum_{s,k} c_s F_{s,k} + c_H Q_B + c_w Q_C + R[0.3639 M\&S (F_c + 2.18) D \\ \times \sum_k \left(H_o + \sum_{k' \le k} 2 + 1.27 \frac{W_{k'}}{D^2}\right)^{0.802} (Y_k - Y_{k+1}) \\ + 0.0168 M\&S F_c' D^{1.55} \sum_k \left(2Y_k + 1.27 \frac{W_k}{D^2}\right) \\ \times cr_1 + cr_2 Q_B + cc_1 + cc_2 Q_c] \end{aligned}$$

By lumping constants, the objective simplifies to:

$$\begin{aligned} Z = c_o + \sum_{s,k} c_s F_{s,k} + c_R Q_B + c_C Q_C + c_T D^{1.55} \sum_k \left(2Y_k + 1.27 \frac{W_k}{D^2}\right) \\ + c_{SH} D \sum_k \left(H_o + \sum_{k' \le k} 2 + 1.27 \frac{W_{k'}}{D^2}\right)^{0.802} (Y_k - Y_{k+1}) \end{aligned}$$

Constraint set

The constraint set is composed of material and energy balances at each tray, material balances at the top and bottom of the column, thermodynamic relationships, and logical relationships.

Material and Energy Balances.

$$\sum_s x_{is}F_{s1} - L_1x_{i1}(1-\beta) + L_2x_{i,2} - V_1K_{i1}x_{i1} + \sum_j \nu_{ij}\xi_{1j} = 0 \quad (12)$$

$$\left[\sum_s x_{is}F_{sk} + V_{k-1}K_{i,k-1}x_{ik-1} + L_{k+1}x_{i,k+1} - L_kx_{ik} - V_kK_{ik}x_{ik} + \sum_j \nu_{ij}\xi_{ik}\right]Y_k = 0 \quad k = 2\,..\,K \quad (13)$$

$$\left[\sum_i x_{ik} - 1\right][Y_k + Y_{k-1}] = 0 \quad (14)$$

$$\left[\sum_i K_{ik}x_{ik} - 1\right]Y_k = 0 \quad (15)$$

$$\left[\lambda V_{k-1} - \lambda V_k - \sum_j \Delta H_j\xi_{jk}\right]Y_k = 0 \quad (16)$$

$$B_i = (1-\beta)L_1x_{i1} \quad (17)$$

$$xd_i\cdot \text{Dist} + B_i = P_i \quad i \in P \quad (18)$$

Equation 12 is the material balance over the bottom tray, and Eq. 13 is the material balances over all other trays. Here, F_{sk} is the flow rate of stream s onto tray k, x_{is} is the mole fraction of component i in feedstream s, V_k is the vapor flow rate off tray k, K_{ik} is the vapor-liquid partition coefficient for component i on tray k, x_{ik} is the mole fraction of component i on tray k, L_k is the liquid flow rate off tray k, ν_{ij} is the stoichiometric coefficient of component i in reaction j, and ξ_{jk} is the extent of reaction j on tray k.

Equations 14 and 15 specify that the sum of the mole fractions in both the liquid and vapor phases equals one, and Eq. 16 is an overall energy balance. Equation 17 computes molar flow of component i in the bottoms stream from the boil-up ratio, the liquid flow off the bottom tray, and the composition of the bottom tray. Equation 18 specifies the production rate.

Notice that a number of these equations are multiplied by an integer term. We will solve this model with a master-subproblem decomposition solution approach that selects integer variables (the number of trays) in a master program, and optimizes a column with a fixed number of trays in the primal problem. Multiplying these equations by an integer term insures that constraints associated with nonexistent trays will not appear in the primal subproblem, which reduces the size of the primal subproblem.

Notice that the integer term in Eq. 14 will insure that the summation equation will appear for one extra tray. This is necessary for computing the composition of the liquid reflux, and will be discussed in more detail below.

The distillate flow is calculated from the difference between the vapor flow off the top tray and the liquid flow onto it:

$$D_{ist} = \sum_k (V_k - L_{k+1})(Y_k - Y_{k+1}) \quad (19)$$

For a column with N trays, the term $Y_k - Y_{k-1}$ will equal zero except when $k = N$. Consequently, Eq. 19 leads to:

$$D_{ist} = V_N - L_{N+1}.$$

Here, L_{N+1} can be interpreted as the liquid reflux onto the top tray. The composition of the distillate and the liquid reflux is set equal to the composition of the vapor leaving tray N through Eq. 14 and the additional relationships:

$$xd_i - K_{ik}x_{ik} - 1 + Y_k - Y_{k+1} \leq 0 \quad (20)$$

$$x_{i,k+1} - xd_i - 1 + Y_k - Y_{k+1} \leq 0 \quad (21)$$

$$\sum_i xd_i = 1 \quad (22)$$

Notice that when $Y_k - Y_{k+1}$ equals zero, Eqs. 21 and 22 simplify to $xd_i \leq 1 + K_{ik}x_{ik}$ and $x_{i,k+1} \leq 1 + xd_i$. Since xd_i and $x_{i,k+1}$ are less than one, these constraints will never be active for $k \neq N$. For $k = N$, $Y_k - Y_{k+1}$ equals 1, Eqs. 21 and 22 simplify to $xd_i \leq K_{ik}x_{ik}$ and $x_{i,k+1} \leq xd_i$. It is easy to show that the only solution to these bounds and the summation equations one are $xd_i = K_{ik}x_{ik}$ and $x_{i,k+1} = xd_i$.

Kinetics and Thermodynamic Relationships. The extent of reaction is computed from the liquid holdup and the kinetic relationships, while the vapor-liquid equilibria and partition coefficients are computed from thermodynamic relations:

$$\xi_{jk} = W_kf_j(x_{ik}, T_k) \quad (23)$$

$$K_{ik} = K_{ik}(x_{ik}, T_k) \quad (24)$$

Here, W_k is the liquid holdup on tray k, T_k is the temperature of tray k, f_j is a function describing the kinetic rate of reaction j, and K_{ik} is the vapor-liquid equilibrium partition coefficient for component i.

Logical Constraints. Logical constraints are needed to link flow onto and off of a tray with the existence of the tray:

$$V_k - F_{\max}Y_k \leq 0 \quad (25)$$

$$\sum_s F_{sk} - F_{\max}Y_k \leq 0 \quad (26)$$

$$L_{k+1} - F_{\max}Y_k \leq 0 \quad (27)$$

$$W_k - W_{\max}Y_k \leq 0 \quad (28)$$

Notice that if k is the top tray, then L_{k+1} is the liquid reflux. L_{k+1} must be zero if tray k is above the top tray: hence, the logical relationship controlling L_{k+1} is given in terms of Y_k, not Y_{k+1}.

Equation 1 must also be included as a logical constraint:

$$Y_{k+1} \leq Y_k$$

Reboiler and Condenser Duties. The reboiler and condenser duties are computed with the following relationships:

$$Q_B=\beta\lambda L_1 \tag{29}$$

$$Q_C=\sum_k \lambda V_k(Y_k-Y_{k+1}) \tag{30}$$

Here, Q_B is the reboiler duty and Q_C is the condenser duty. Notice that Q_B is a simple function of the boil-up ratio, the liquid flowing off the bottom tray, and the composition on the bottom tray.

Q_C is calculated from the energy required to completely condense the vapor flow rate off the top of the top tray of the column. If there are N trays in the column, then Q_C is found from the V_N vapor flow rate off tray N, and the heat of vaporization. Since the number of trays is an optimization variable, Q_C is computed as a sum over all trays k, with an integer term (Y_k-Y_{k+1}) used as a weight. This term equals zero except for the top tray; consequently, when the integer variables are fixed, Eq. 30 computes Q_C for the vapor flowing off the top tray only.

Column Diameter. The minimum column diameter can be computed from Douglas (1988):

$$D\geq c\sqrt{V}\left[379M_G\frac{T_b}{520}\frac{14.7}{P}\right]^{1/4} \tag{31}$$

Here, c is a constant, V is the vapor flow rate, M_G is the molecular weight of the gas, T_b is the boiling point of the gas, and P is the column pressure. This relationship is simplified by assuming that the column diameter will be computed at the bottom of the column, and T_b, P, and M_G are approximately constant for every design. In addition, it should be noted that the vapor flow rate V at the bottom of the column equals βL_1, where β is the boil-up ratio, and L_1 is the liquid flow rate off the bottom tray.

Lumping constants together allows Eq. 31 to be simplified to:

$$D^4\geq C_D\beta^2L_1^2.$$

An additional numerical bound on the minimum diameter, $D_{\min}$, is also specified, giving two equations for the column diameter:

$$D^4\geq C_D\beta^2L_1^2 \tag{32}$$

$$D\geq D_{\min} \tag{33}$$

MINLP Optimization Model

The optimization model used to identify the optimal reactive distillation column is summarized below:

$$\min Z=c_o+\sum_{sk}c_sF_{sk}+c_RQ_B+c_CQ_C+c_TD^{1.55}$$
$$\times\sum_k\left(2Y_k+1.27\frac{W_k}{D^2}\right)$$
$$+c_{SH}D\sum_k\left(H_o+\sum_{k'\leq k}2+1.27\frac{W_k{}'}{D^2}\right)^{0.802}(Y_k-Y_{k+1})$$

subject to (R)

$$\sum_s x_{is}F_{s1}-L_1x_{i1}(1-\beta)+L_2x_{i,2}-V_1K_{i1}x_{i1}+\sum_j \nu_{ij}\xi_{1j}=0$$

$$\left[\sum_s x_{is}F_{sk}+V_{k-1}K_{i,k-1}x_{ik-1}+L_{k+1}x_{i,k+1}-L_kx_{ik}-V_kK_{ik}x_{ik}\right.$$
$$\left.+\sum_j \nu_{ij}\xi_{ik}\right]Y_k=0\quad k=2\,..\,K$$

$$\left[\lambda V_{k-1}-\lambda V_k-\sum_j \Delta H_j\xi_{jk}\right]Y_k=0$$

$$D_{ist}=\sum_k(V_k-L_{k+1})(Y_k-Y_{k+1})$$

$$B_i=(1-\beta)L_1x_{i1}$$

$$B_i=P_i\quad i\in P$$

$$\left[\sum_i x_{ik}-1\right][Y_k+Y_{k-1}]=0$$

$$\left[\sum_i K_{ik}x_{ik}-1\right]Y_k=0$$

$$xd_i-K_{ik}x_{ik}-1+y_k-y_{k+1}\leq 0$$

$$x_{i,k+1}-xd_i-1+y_k-y_{k+1}\leq 0$$

$$\sum_i xd_i=1\qquad \xi_{jk}=W_kf_j(x_{ik},T_k)$$

$$K_{ik}=K_{ik}(x_{ik},T_k)\qquad V_k-F_{\max}Y_k\leq 0$$

$$\sum_s F_{sk}-F_{\max}Y_k\leq 0\qquad L_{k+1}-F_{\max}Y_k\leq 0$$

$$W_k-W_{\max}Y_k\leq 0\qquad Q_B=\beta\lambda L_1$$

$$Q_C=\sum_k \lambda V_k(Y_k-Y_{k+1})\qquad D^4\geq C_D\beta^2L_1^2$$

$$D\geq D_{\min}\qquad Y_{k+1}\leq Y_k$$

Solution Procedure

Problem R contains both continuous variables (for example, temperature, composition, flow rates, and so on) and integer variables (that is, number of trays). In addition, the objective and a number of the constraints are nonlinear. Thus, problem R is a MINLP optimization problem.

Note that the objective and Eqs. 13-16 and Eqs. 19 and 30 contain terms of the form $f(x)*Y$. These terms are nonlinear but become linear when the continuous variables are fixed. Consequently, a solution of this model can be found by applying GBD (Geoffrion, 1974), with integer variables selected as the complicating variable set.

The GBD solution procedure for mixed integer nonlinear programming problems involves solving a series of *primal* and *master* subproblems. The *primal* subproblem is obtained by fixing the integer variables. The solution of a primal subproblem gives the locally optimal solution for a particular combination of integer variables, the values of the variables and the Lagrange multipliers of each constraint, and an upper bound on the final optimum. The variables and Lagrange multipliers are used to construct a Lagrange function in which the integer variables appear linearly. The *master* subproblem is constructed from the purely integer constraints of problem R and the Lagrange function generated from each primal subproblem. The solution of this master subproblem yields a new combination of integer variables, and a lower bound upon the final solution. The algorithm progresses by iterating between primal and master subproblems until the lower bound provided by the master subproblem equals the upper bound provided by the primal subproblem.

It should be noted that the GBD algorithm only requires selecting an initial value of the integer combinations. The approach does not require initializing continuous variables or Lagrange multipliers, although an initially feasible set of continuous variables is quite helpful for solving the nonlinear primal problems.

The *primal* subproblem is obtained from problem R by fixing the integer variables. In other words, the primal subproblem is simply an optimization problem that minimizes the net cost of a reactive distillation column with a fixed number of trays. The master subproblem is constructed from Lagrange functions generated for each primal and from the integer constraints in the original MINLP. The formulation of this master problem is given in Appendix A.

Nonexistent trays

The primal subproblem optimizes a column with a fixed number of trays, N. If N is less than the maximum number of trays, then there are a number of "shadow" or nonexistent trays that are modeled in the MINLP yet do not appear within the column. Clearly, the primal subproblem would be smaller and easier to solve if the MESH equations associated with these shadow trays are removed. This is accomplished in problem R by writing the material and energy balances (Eqs. 13 and 16) and the vapor and liquid composition constraints (Eqs. 14 and 15) in the form $f(x) * Y = 0$. When $Y = 0$, the constraints are trivially satisfied and can be removed from the primal subproblem. This reduces the size of the primal and makes it significantly faster to solve.

What effect do these terms have on the master subproblem? For existing trays (that is, $k \leq N$), the continuous terms of Eqs. 13 through 16 equal zero; consequently, when $k \leq N$, the associated terms in the Lagrangian will always equal zero.

For shadow trays above the condenser ($k > N+1$) Eqs. 25–28 specify that if $Y_k = 0$, then V_k, F_{sk}, L_{k+1}, and W_k also equal zero. Consequently, the continuous nonlinear terms of Eqs. 13 and 16 equal zero. Moreover, it is easy to select nominal values of x_{ik} and K_{ik}, such that the continuous nonlinear terms of Eqs. 14 and 15 are nominally zero. A few nonzero terms associated with the condenser tray remain: these terms are set to zero in the master problem. This assumption functions as a relaxation that reduces the tightness of the lower bound provided by the master subproblem.

Initializing the primal variables

It is not easy to solve the primal subproblem, for it is nonconvex and can be difficult to scale. The material balances contain bi- and tri-linear terms, and the reaction rate terms and vapor-liquid equilibria calculations are highly nonlinear. This difficulty is accounted for by modifying the basic GBD algorithm. Rather than solve a single NLP per primal subproblem, one NLP was solved for each additional tray added to the column relative to the previous primal subproblem. Each of these NLPs gives data for generating a Lagrange function, which can be used in the master subproblem.

This procedure is most efficient when the overall procedure starts with a single tray column; the procedure is least efficient when the overall procedure starts with a large column.

This solution algorithm was implemented in GAMS (Brooke et al., 1988), producing a computational tool for synthesizing cost optimal reactive distillation columns. This method is used to design a reactive distillation column producing ethylene glycol described below.

Example: Production of Ethylene Glycol

Ethylene glycol ($C_2H_6O_2$) is typically produced from ethylene oxide and water:

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2$$

Ethylene oxide will react further with ethylene glycol to produce the unwanted byproduct diethylene glycol (DEG):

$$C_2H_4O + C_2H_6O_2 \rightarrow C_4H_{10}O_3$$

Both reactions are highly exothermic, and the reaction conditions are mild enough to allow production via reactive distillation (Parker, 1958). Reaction kinetics are taken from Twigg and Lichtenstein (1947) and from Corrigan and Miller (1968). Reaction data are summarized in Table 1, and physical property data for the reacting components are summarized in Table 2. Ideal vapor-liquid equilibria has been assumed.

There are two reasons for producing ethylene glycol via reactive distillation. First, the large volatility difference between ethylene oxide and ethylene glycol will lead to rapid separation of oxide from glycol in the column, improving the overall selectivity. Secondly, reactive distillation can directly absorb the heat of reaction into the heat required for separation, achieving a natural heat integration that may reduce operating costs.

Distributed feed column

Problem R was first solved without any specifications on the number of feed trays or their locations. The MINLP model was formulated using the reaction data in Table 1, physical property data in Table 2, and cost data in Table 3, and by assuming a production rate of 25 kg·mol/h of ethylene glycol. A single tray column was taken as the starting point of the MINLP, and the GBD algorithm converged in 11 iterations.

Table 1. Ethylene Glycol System: Reaction Data

Reaction	Rate (mol/cm^3·s)	ΔH (kJ/mol)
1	$3.15\times 10^9\exp[-9{,}547/T(\mathrm{K})]x_{EO}x_{H_2O}$	−80
2	$6.3\times 10^9\exp[-9{,}547/T(\mathrm{K})]x_{EO}x_{EG}$	−13.1

The problem was solved with GAMS (Brooke et al., 1988) on a Sun Sparc 1+ workstation computer. Each primal subproblem required approximately 550 CPU s of operating time; the master problems required a negligible amount of CPU.

The optimal column contains 10 trays and has a total annualized cost of 15.69×10^6 \$/yr. Column specifications are given in Table 4.

The column is shown in Figure 1. The column has two distinct sections: a reaction zone above tray 4, and a distillation zone below tray 5. All of the water is fed to the top tray of the column, and the ethylene oxide has a small feed to each tray in the reaction zone. The bottoms composition and flow rate are also shown in the figure. The bottoms stream is nearly 95% monoethylene glycol. Most of the remaining material is diethylene glycol; less than 0.2% of the bottoms stream is unreacted water. Using the correlation in Huchette and Ciric (1993), we estimate an excess of 43 moles of water would be required to achieve the same selectivity in a plug-flow reactor.

The composition and temperature profiles are shown in Figures 3 and 4. Clearly, unreacted water is recycled internally by the distillation zone below tray 5. These figures also illustrate that the ratio of oxide to water *within the column* exceeds 200/1. This occurs even though the oxide and water are fed to the column in nearly a 1/1 ratio.

Double feed column

What is the effect of the distributed oxide feed? This question was answered by solving a modified formulation of problem R. Integer variables Y^F_{sk} were introduced to denote the existence of feed stream s to tray k. Three additional sets of constraints were added to problem R:

$$F_{sk} - UY^F_{sk} \le 0 \tag{34}$$

$$\sum_k Y^F_{sk} = 1 \tag{35}$$

$$Y^F_{sk} \le Y_k \tag{36}$$

Here, Eqs. 34 and 35 insure that feed stream s is fed to only one tray in the column. Equation 36 is an integer cut specifying that the feed trays must be assigned to existing trays.

Table 2. Ethylene Glycol System: Physical Property Data

Component	K
EO	$71.9\exp\{5.72[(T-469)/(T-35.9)]\}$
H_2O	$221.2\exp\{6.31[(T-647)/(T-52.9)]\}$
EG	$77\exp\{9.94[(T-645)/(T-71.4)]\}$
DEG	$47\exp\{10.42[(T-681)/T-80.6)]\}$

Data for $P=1$ atm; $T=[\mathrm{K}]$; $c_D=0.01331$.

Table 3. Ethylene Glycol System: Cost Data

- Ethylene Oxide Feedstock: \$43.7/kmol
- Water Feedstock: \$21.9/kmol
- Downstream Separation: \$0.15/kmol H_2O in effluent
- C_{sh} = \$222/yr
- C_T = \$15.7/yr
- C_R = \$146.8/kW·yr
- C_C = \$24.5/kW·yr
- C_0 = \$10,000/yr

This modified MINLP converged after 14 iterations of the modified GBD algorithm. The optimal column is shown in Figure 2. The column has 10 trays, with a reaction zone between trays 4 and 10, water fed to tray 10, and ethylene oxide fed to tray 4. The performance specifications are given in Table 5. Notice that the two feed column achieves the same selectivity as the distributed feed column, but requires slightly more

Table 4. Column Specifications for Distributed-Feed Ethylene Glycol Column*

Tray	Reaction Vol. ft^3 (L)	Vapor Flow Rate kmol/h	Liquid Flow Rate kmol/h
1		605.49	631.8
2		605.49	631.8
3		605.49	631.8
4		605.49	631.8
5	19.46 (551)	613.4	631.8
6	17.03 (482)	622.1	639.1
7	15.84 (448)	630.9	647.6
8	13.10 (371)	639.9	656.3
9	51.82 (1,467)	649.0	665.0
10	0.411 (12)	658.4	678.5

*Column diameter = 4.3 ft (1.3 m); column height = 38 ft (12 m); boil-up ratio = 0.958; reboiler duty = 6.7 MW; condenser duty = 7.31 MW.

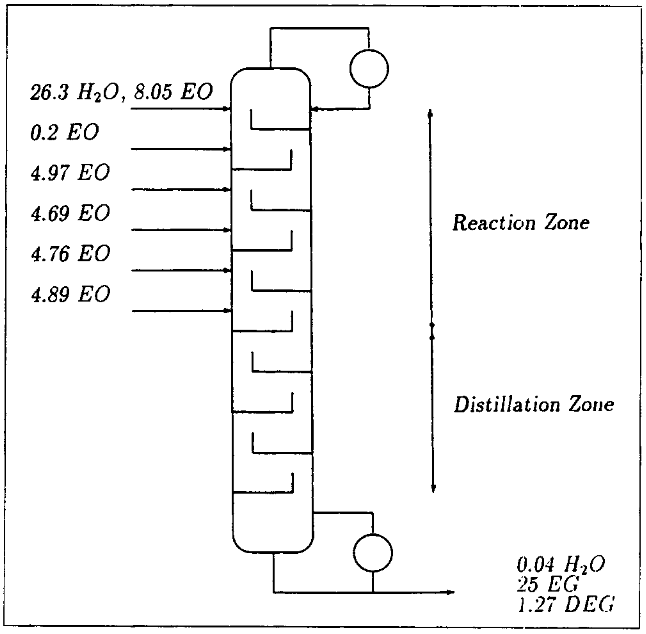

Figure 1. Optimal distributed feed reactive distillation column for ethylene glycol synthesis.

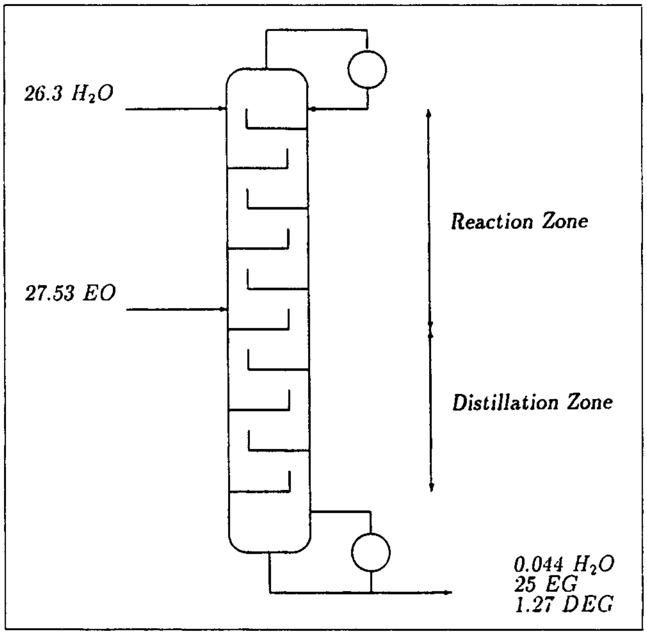

Figure 2. Optimal two-feed reactive distillation column for ethylene glycol synthesis.

holdup volumes, vapor flows, and reboiler and condenser duties. The total annualized cost of this two feed column is $\$15.73 \times 10^6$/yr.

Conclusions

A mixed integer nonlinear programming problem was presented for the optimum design of a reactive distillation column when chemical equilibrium cannot be assured. The model explicitly incorporates reaction kinetics, heats of reaction, and liquid holdup volumes. Solving this model optimizes the number of trays, the feed tray locations, and the internal composition and temperature profiles within a reactive distillation column. The MINLP was solved with a modified form of the GBD algorithm that generated and solved a number of nonlinear programming problems per iteration. The method was illustrated with a case study involving the production of ethylene glycol.

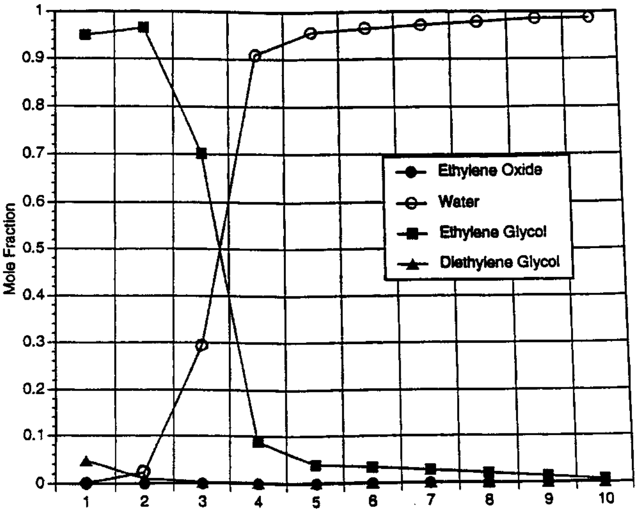

Figure 3. Composition profile within the distributed feed reactive distillation column.

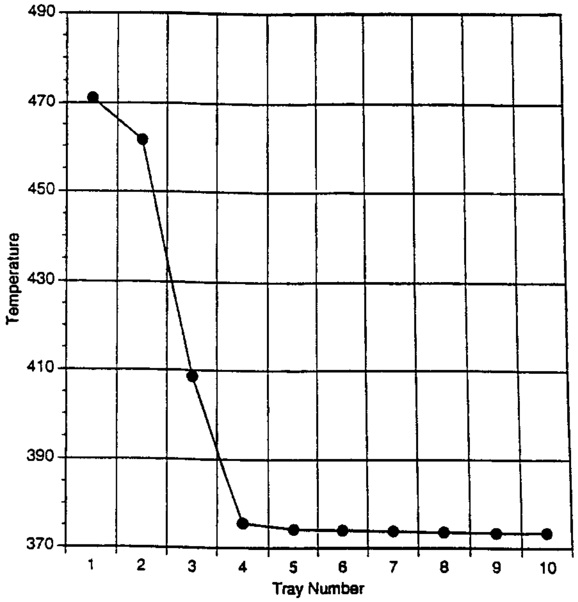

Figure 4. Temperature profile within the distributed feed reactive distillation column.

Notation

B_i = bottoms flow rate of species i
c_s, c_w, c_H, cr_1, cr_2, cc_1, cc_2, c_T = cost parameters
C_c = condenser cost
C_{ct} = cost of column trays
C_{cs} = cost of column shell
C_r = reboiler cost
C_D = constant parameter for computing D
D = column diameter
D_{ist} = distillate flow rate
$D_{\min}$ = minimum column diameter
F_c, F_c', F_c'' = materials of construction factors

Table 5. Column Specifications for Two-Feed Ethylene Glycol Column

Tray	Reaction Vol. ft^3 (L)	Vapor Flow Rate kmol/h	Liquid Flow Rate kmol/h
1		627.7	654.0
2		627.7	654.0
3		627.7	654.0
4		627.7	654.0
5	5.83 (165)	635.5	626.5
6	8.09 (229)	644.0	638.4
7	11.13 (315)	652.8	651.5
8	17.33 (490)	661.8	664.9
9	36.61 (1,036)	671.3	678.6
10	53.68 (1,519)	680.7	692.9

*Column diameter = 4.4 ft (1.3 m); column height = 39 ft (12 m); boil-up ratio = 0.96; reboiler duty = 6.9 MW; condenser duty = 7.5 MW.

$F_{\max}$ = upper bound on flow rates
F_s = feed rate of stream s
H = column height
H_k = height of tray k
H_o = extra column height
i = $1 \ldots I$ index of chemical species
j = $1 \ldots J$ index of chemical reactions
k = $1 \ldots K$ index of trays
K_{ik} = vapor-liquid equilibrium partition coefficient on tray k
l = $1 \ldots L$ iterate counter
L_k = liquid flow rate off tray k
$M \& S$ = Marshall and Swift Index
N = number of trays
$i \in P$ = set of product species
P_i = production rate of species i
Q_B, Q_C = reboiler and condenser duties
R = annualizing factor
s = $1 \ldots S$ index of feed streams
V_k = vapor flow rate off tray k
W_k = holdup volume on tray k
$W_{\max}$ = upper bound on holdup volume
xd_i = distillate composition
x_{ik} = mole fraction of component i on tray k
x_{is} = feedstock composition
Y_k = binary variable denoting tray k
Z = total annualized cost

Greek letters

β = boilup fraction
ΔH_j = heat of reaction j
λ = heat of vaporization
$\lambda 1_{il}$, $\lambda 2_{ikl}$, $\lambda 3_{kl}$, $\lambda 4_{il}$, $\lambda 5_{il}$, $\lambda 6_{kl}$, $\lambda 7_{kl}$ = Lagrange multipliers
μ = objective in master subproblem
ν_{ij} = stoichiometric coefficient of component i in reaction j
ξ_{jk} = extent of reaction j on tray k

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Appendix: Master Problem Formulation

$$\min \mu$$

subject to

$$\begin{aligned}
\mu \geq\ & \Sigma c_s F_{sl} + c_H Q_{Bl} + c_w Q_{cl} \\
& + c_{SH} D_l \Sigma_k \left(H_o + \Sigma_{k' \leq k} 2 + 1.27 \frac{W_{k'l}}{D_l^2} \right)^{0.802} (Y_k - Y_{k+1}) \\
& + c_T D_l^{1.55} \Sigma_k \left(2Y_k + 1.27 \frac{W_{kl}}{D_l^2} \right) + cr_1 + cr_2 QR_l + cc_1 + cc_2 QC_l \\
& + \Sigma_i \lambda 1_{il} [xd_{il} - K_{ikl} x_{ikl} - 1 + y_k - y_{k+1}] \\
& + \Sigma_{ik} \lambda 2_{ikl} [x_{i,k+1l} - xd_{il} - 1 + y_k - y_{k+1}] \\
& + \Sigma_k \lambda 3_{kl} [V_{kl} - F_{\max} Y_k] + \Sigma_k [\lambda 4_{il} \Sigma_i F_{ik} - F_{\max} Y_k] \\
& + \Sigma_k [\lambda 5_{il} L_{k+1l} - F_{\max} Y_k] + \Sigma_k \lambda 6_{kl} [W_k - W_{\max} Y_k] \\
& + \lambda 7_l [QC_l - \Sigma_k \lambda V_{kl} (Y_k - Y_{k+1})] \quad l = 1 \ldots L \\
& Y_k \leq Y_{k+1}
\end{aligned}$$

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