Optimization of Distillation Units Using Collocation Models

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Reduced-order models are developed based on orthogonal collocation on finite elements for the steady-state optimization of multicomponent distillation units. The formulation divides the column sections into subdomains (finite elements) to track irregularities in the column profiles accurately and requires that plates with discontinuities in the flows introduced by feedstreams or sidestreams should be treated as discrete equilibrium stages. Application of the model formulation to a number of examples show that reduced-order models converge to the same optimal solution as the full-order, tray-by-tray model. Optimization results show that computational time can be reduced significantly using the more compact model formulation, and it is possible to converge to the optimal solution from a larger region for the initial set of variable values.

Introduction

Equation-based optimization requires the use of process models that accurately describe the underlying physical phenomena. However, the simultaneous optimization of many process units leads to complex mathematical models of large dimensionality. This increases the computational difficulties to obtain the optimal operating conditions. The need for more efficient process models that require less solution effort was the motivation for researchers to develop techniques to simplify and reduce the size of the process models used in the steady-state optimization layer of modern advanced control systems in practice (Prett and García, 1988). However, simplified models must have certain properties in order to be adequate for use in real-time optimization. Specifically, simplified models must contain all the necessary gradient information of the rigorous model in order to guarantee convergence to the optimum of the rigorous model. Failure to satisfy this condition may lead to convergence to a different optimal solution or no convergence at all (Biegler et al., 1985).

Some of the most common methods used for distillation modeling are based on empirical shortcut techniques, such as: the Fenske-Underwood-Eduljee equations (Eduljee, 1975), Smoker's equation, the Smith-Brinkley method (Smith and Brinkley, 1960), and the methods proposed by Glinos and Malone (1984). The degree of simplification of shortcut models does not allow their extended use in multicomponent distillation optimization. The major reason is that even though they may result in reasonable predictions of the steady-state behavior of the process, they do not guarantee that they recognize the true optimum solution of the process, since valuable gradient information has been lost as a result of the simplified assumptions that are made.

Another category of model size reduction is based on compartmental methods (España and Landau, 1978; Benallou et al., 1986) which has been mainly developed for the dynamic behavior of distillation processes. The behavior of a number of stages that cannot be defined rigorously is represented by only one tray, namely the "sensitivity tray." A major disadvantage is that the location of the sensitive tray is not defined explicitly and its location plays an important role in the time required for the simulation (Horton et al., 1991).

Orthogonal collocation techniques were used extensively for the solution and optimization of process systems described by differential and algebraic equations (Renfro, 1986; Cuthrell and Biegler, 1987). Orthogonal collocation was implemented as a model reduction and solution method to the set of partial differential equations resulting from the dynamic model of a distillation process by Wong and Luus (1980). Stewart et al. (1985) and Cho and Joseph (1983) used orthogonal collocation techniques with the number of equilibrium stages a continuous variable. The dynamic material and energy balances and equi-

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librium relations are satisfied exactly at certain points called the collocation points, which are defined as the roots of orthogonal polynomials. Although the collocation points do not necessarily have any physical meaning in the model, since their locations need not correspond to the location of any stage, the nature of the full-order, tray-by-tray, model is preserved.

Stewart et al. (1985) proposed that the collocation points be located at the roots of the Hahn family of orthogonal polynomials, which are superior to Jacobi polynomials (Cho and Joseph, 1983, 1984).

Discontinuities in the composition and temperature profiles due to feed streams and sidestreams were treated by applying different interpolating polynomials above and below the point of discontinuity (Stewart et al., 1985; Srivastava and Joseph, 1987a). This formulation is similar to orthogonal collocation on finite elements (OCFE) method with the breakpoints of the finite elements at the points of discontinuities. Swartz and Stewart (1987) discussed the use of finite elements in the simulation of multiphase distillation. The element breakpoints were located at the moving miscibility front of the two liquid phases.

Srivastava and Joseph (1987b) described a formulation that uses collocation schemes with fewer collocation points for components that appear in small concentrations (nonkey components) that do not change significantly in large sections of the column. Information regarding the composition of the nonkey components was transferred by interpolation between the different collocation schemes.

Swartz and Stewart (1986) used orthogonal collocation methods for the optimal design of distillation columns by transforming the discrete problem into a continuous one that can be solved by standard nonlinear programming (NLP) methods.

In this article, the method described by Stewart et al. (1985) is extended and used to identify a steady-state optimal solution as compared to a full-order (tray-by-tray) model.

Full-Order Model Formulation

The full-order model used for the steady-state simulation and optimization of a stagewise distillation column is a tray-by-tray model applying mass and energy balances and equilibrium relations at each tray in the column.

Similar to Stewart et al. (1985), the major assumptions made are:

(*a*) Complete mixing of each phase at each stage

(*b*) Constant holdups of liquid and no vapor phase holdup on each stage

(*c*) No entrainment from stage to stage

(*d*) Adiabatic stages

(*e*) Thermal equilibrium between the leaving liquid and vapor stream from each stage.

The total number of equations in the model is further reduced by eliminating the component vapor molar flows using the equilibrium relations (Holland, 1981). This formulation evaluates the equilibrium relations only once for every iteration, and the component vapor molar flow rates do not participate in the set of nonlinear variables. The advantage of this elimination is that the total number of nonlinear constraints and variables is reduced and hence the efficiency and the speed of the NLP solver is improved, even though the Jacobian matrix becomes denser. For a typical case involving a four component distillation column, the solution time is reduced by a factor of 2 as a direct result of this formulation.

On every tray, i, mass and energy balances are applied as:

$$l_{m,i-1}+K_{m,i+1}V_{i+1}\frac{l_{m,i+1}}{L_{i+1}}-l_{m,i}-K_{m,i}V_i\frac{l_{m,i}}{L_i}+f_{m,i}=0 \qquad m=1,\ldots,C \tag{1}$$

$$L_{i-1}h_{i-1}+V_{i+1}H_{i+1}-L_ih_i-V_iH_i+F_iH_{Fi}+Q_i=0 \tag{2}$$

where

$$L_i=\sum_{m=1}^{C} l_{m,i} \tag{3}$$

$$V_i=\sum_{m=1}^{C} K_{m,i}V_i\frac{l_{m,i}}{L_i} \tag{4}$$

$$K_{m,i}=f(T_i,\ P_i) \qquad m=1,\ldots,C \tag{5}$$

$$h_i=\sum_{m=1}^{C}\frac{l_{m,i}}{L_i}\,h_{m,i}(T_i) \tag{6}$$

$$H_i=\sum_{m=1}^{C}\frac{v_{m,i}}{V_i}\,H_{m,i}(v_{m,i},\ T_i,\ P_i) \tag{7}$$

Index i denotes the tray number, and m denotes the component.

A Murphree stage efficiency may be used for each stage, but in this work all stages are assumed to be ideal.

Equilibrium coefficients, liquid, and vapor stream enthalpies are evaluated on each tray using regression equations. Thermodynamic data were determined for ideal solutions at the operating conditions of the columns used in the examples and regression equations were fit to these data (Bailey, 1991). K values were determined using regression equations of the form:

$$K_{m,i}=\exp(a_{m,1}+a_{m,2}T_i+a_{m,3}T_i^2+a_{m,4}P_i) \quad m=1,\ldots,C \tag{8}$$

The specific molar liquid enthalpy for each component is given by the following regression equation:

$$h_{m,i}=b_{m,1}+b_{m,2}T'_{\text{corr},m,i}+b_{m,3}T'^{2}_{\text{corr},m,i}+b_{m,4}T'^{3}_{\text{corr},m,i} \qquad m=1,\ldots,C \tag{9}$$

where $T'_{\text{corr},m,i}$ is a corrected temperature defined as:

$$T'_{\text{corr},m,i}=T_iT_{c_m}\left(\sum_{k=1}^{C}x_{k,i}V_{c_k}\right)\Bigg/\left(\sum_{k=1}^{C}x_{k,i}V_{c_k}T_{c_k}\right) \qquad m=1,\ldots,C \tag{10}$$

where V_{c_m} and T_{c_m} are the critical volume and temperature of the mth component, respectively, and $x_{m,i}$ are the liquid molar fractions of each component. Finally, liquid molar enthalpy is given by Eq. 6.

The specific molar vapor enthalpy for each component is given by the expression:

$$H_{m,i} = c_{m,1} + c_{m,2} p_{r_{m,i}}^2 + c_{m,3} p_{r_{m,i}} + c_{m,4} T_{r_{m,i}} p_{r_{m,i}} + c_{m,5} T_{r_{m,i}} + c_{m,6} T_{r_{m,i}}^2 \quad m = 1, \ldots, C \qquad (11)$$

where

$$p_{r_{m,i}} = P_{r_{m,i}} \exp(1 - T_{r_{m,i}}) \quad m = 1, \ldots, C \qquad (12)$$

$T_{r_{m,i}}$ and $P_{r_{m,i}}$ are the reduced temperature and pressure of the mth component at the ith tray. The total molar vapor enthalpy is then calculated by Eq. 7.

Reduced Order Model

Collocation on column sections

The development of the reduced order models is based on the same assumptions made for the tray-by-tray model.

Distillation columns are separated into sections, each defined as the group of trays between two sidestreams leaving or entering the column. A column with a single feed stream and no sidestreams is separated into two sections, the rectifying and the stripping sections. The number of stages in each section is considered to be a continuous variable. The condenser, feed tray, and reboiler are treated as discrete equilibrium stages. The formulation of the model can be applied in any column, regardless of the number of sidestreams, by locating the breakpoints of the elements at the trays where the sidestreams enter or leave the column.

Liquid and vapor component molar flows, as well as liquid and vapor enthalpies, are expressed as polynomial functions of position in the given column section. These functions are to be adjusted so that the equations which describe the material, energy, and equilibrium relationships in the column are satisfied exactly at the collocation points. In every section, the number of n interior collocation points is specified, with the restriction that n must be no greater than the number of stages, N, contained in that section. Also, the boundary points of each section $s_o = 0$ and $s_{n+1} = N + 1$ are used as interpolation points for liquid and vapor states, respectively. The approximation functions that are used in the collocation scheme are:

$$\tilde{l}_m(s) = \sum_{j=0}^{n} W_{lj} \tilde{l}_m(s_j) \quad 0 \le s \le N, \quad m = 1, \ldots, C \qquad (13)$$

$$\tilde{v}_m(s) = \sum_{j=1}^{n+1} W_{vj} \tilde{v}_m(s_j) \quad 1 \le s \le N+1, \quad m = 1, \ldots, C \qquad (14)$$

$$\tilde{L}(s)\tilde{h}(s) = \sum_{j=0}^{n} W_{lj} \tilde{L}(s_j)\tilde{h}(s_j) \quad 0 \le s \le N \qquad (15)$$

$$\tilde{V}(s)\tilde{H}(s) = \sum_{j=1}^{n+1} W_{vj} \tilde{V}(s_j)\tilde{H}(s_j) \quad 1 \le s \le N+1 \qquad (16)$$

where

$$\tilde{L}(s) = \sum_{m=1}^{C} \tilde{l}_m(s) \qquad (17)$$

$$\tilde{V}(s) = \sum_{m=1}^{C} \tilde{v}_m(s) \qquad (18)$$

The functions, W_{lj} and W_{vj}, are Lagrange interpolation polynomials of order $n+1$, given by the expressions:

$$W_{lj}(s) = \prod_{\substack{k=0 \\ k \ne j}}^{n} \frac{s - s_k}{s_j - s_k} \quad j = 0, \ldots, n \qquad (19)$$

$$W_{vj}(s) = \prod_{\substack{k=1 \\ k \ne j}}^{n+1} \frac{s - s_k}{s_j - s_k} \quad j = 1, \ldots, n+1 \qquad (20)$$

A set of residual equations is derived by substituting the approximation relations for the variables (Eqs. 13-16) in the mass and energy balance equations at the collocation points. The residuals of these equations are required to be zero at the collocation points, s_j.

Mass Balance Residual Equations:

$$\tilde{l}_m(s_j - 1) + \tilde{v}_m(s_j + 1) - \tilde{l}_m(s_j) - \tilde{v}_m(s_j) = 0 \quad m = 1, \ldots, C \qquad (21)$$

Equilibrium Equations:

$$\frac{\tilde{v}_m(s_j)}{\tilde{V}(s_j)} - K_m[\tilde{T}(s_j), \tilde{P}(s_j)] \frac{\tilde{l}_m(s_j)}{\tilde{L}(s_j)} = 0 \quad m = 1, \ldots, C \qquad (22)$$

Energy Balance Residual Equations:

$$\tilde{L}(s_j - 1)\tilde{h}(s_j - 1) + \tilde{V}(s_j + 1)\tilde{H}(s_j + 1) - \tilde{L}(s_j)\tilde{h}(s_j) - \tilde{V}(s_j)\tilde{H}(s_j) = 0 \qquad (23)$$

Similar to the procedure used in the full-order model, the molar vapor component flows are eliminated from the above set of equations by using the equilibrium equations. Even though the vapor component molar flow rates do not belong in the set of nonlinear variables, the vapor flows are calculated every time the subroutine which evaluates the nonlinear constraints is called, and then the vapor flows are interpolated. This procedure requires the evaluation of the equilibrium parameters only once per collocation point and iteration.

Those points within the column in which discontinuities in the liquid or vapor composition occur (such as the condenser, feed plate, and the reboiler) are treated as discrete equilibrium stages by applying separate mass and energy balances. This approach is similar to that proposed by Stewart et al. (1985) with the exception that in the present work the feed plate is treated as a separate equilibrium stage. Stewart et al. (1985) proposed that the liquid and vapor part of the feed stream must be added to the liquid and vapor streams connecting the two column sections which is correct only in the case of adiabatic columns of constant molar overflow. However, the temperature and composition at the feed plate change in order to satisfy the product quality specifications. In addition, feed stream conditions strongly affect the temperature and the distribution of the feed stream into the liquid and vapor phases. Mass, energy balances, and equilibrium relations are solved at the feed plate given the feed flow rate and enthalpy. Pinto and Biscaia (1988) suggested that a collocation point should be located at the feed plate, but this requires the use of special orthogonal polynomials in order to locate a polynomial root at the feed plate. The discrete equilibrium stage at the feed location allows the use of Hahn polynomials for the placement of the collocation points. Kim et al. (1989) suggested a sequential modular approach on the column sections to deal with the feed tray discontinuity; however, this method requires an iterative procedure to obtain the solution.

The mass balance, equilibrium and energy balance relations for the condenser, the feed plate and the reboiler are:
Condenser:

$$\sum_{j=1}^{n_R+1} W_{vj}^R(1)\tilde{v}_m^R(s_{Rj}) - \tilde{l}_m^R(s_0) - d_m = 0 \quad m=1, \ldots, C \tag{24}$$

$$\sum_{j=1}^{n_R+1} W_{vj}^R(1)\tilde{V}_R(s_{Rj})\tilde{H}_R(s_{Rj}) - \tilde{L}_R(s_0)\tilde{h}_R(s_0) - DH_D + Q_D = 0 \tag{25}$$

$$\frac{d_m}{D} - K_m^D[\tilde{T}_R(s_0), \tilde{P}_R(s_0)] \frac{\tilde{l}_m^R(s_0)}{\tilde{L}_R(s_0)} = 0 \quad m=1, \ldots, C \tag{26}$$

Feed Tray:

$$\sum_{j=1}^{n_S+1} W_{vj}^S(1)\tilde{v}_m^S(s_{Sj}) + \sum_{j=0}^{n_R} W_{lj}^R(N_R)\tilde{l}_m^R(s_{Rj}) - \tilde{v}_m^R(s_{n_R+1}) - \tilde{l}_m^S(s_0) + f_m = 0 \quad m=1, \ldots, C \tag{27}$$

$$\sum_{j=1}^{n_S+1} W_{vj}^S(1)\tilde{V}_S(s_{Sj})\tilde{H}_S(s_{Sj}) + \sum_{j=0}^{n_R} W_{lj}^R(N_R)\tilde{L}_R(s_{Rj})\tilde{h}_R(s_{Rj}) - \tilde{V}_R(s_{n_R+1})\tilde{H}_R(s_{n_R+1}) - \tilde{L}_S(s_0)\tilde{h}_S(s_0) + FH_F = 0 \tag{28}$$

$$\frac{\tilde{v}_m^R(s_{n_R+1})}{\tilde{V}_R(s_{n_R+1})} - K_m^F[\tilde{T}_S(s_0), \tilde{P}_S(s_0)] \frac{\tilde{l}_m^S(s_0)}{\tilde{L}_S(s_0)} = 0 \quad m=1, \ldots, C \tag{29}$$

Reboiler:

$$\sum_{j=0}^{n_S} W_{lj}^S(N_S)\tilde{l}_m^S(s_{Sj}) - \tilde{v}_m^S(s_{n_S+1}) - b_m = 0 \quad m=1, \ldots, C \tag{30}$$

$$\sum_{j=0}^{n_S} W_{lj}^S(N_S)\tilde{L}_S(s_{Sj})\tilde{h}_S(s_{Sj}) - \tilde{V}_S(s_{n_S+1})\tilde{H}_S(s_{n_S+1}) - Bh_B + Q_B = 0 \tag{31}$$

$$\frac{\tilde{v}_m^S(s_{n_S+1})}{\tilde{V}_S(s_{n_S+1})} - K_m^B[\tilde{T}_S(s_{n_S+1}), \tilde{P}_S(s_{n_S+1})] \frac{b_m}{B} = 0 \quad m=1, \ldots, C \tag{32}$$

Index R is used for the rectifying section, and index S is used for the stripping section of the column. Figure 1 shows the formulation of the feed stage. The composition and the enthalpy of the vapor stream entering the condenser, the liquid stream entering the reboiler, and the liquid and vapor streams entering the feed plate are determined by extrapolation using the Lagrange polynomial of the section in which each stream is located. For the liquid state, component molar flow rates and total enthalpy are evaluated by extrapolation at points $s=N_R$ and $s=N_S$ for the rectifying and stripping sections respectively, which correspond to the endpoints of each column section for the liquid states, and for the vapor state at point $s=1$ for both column sections.

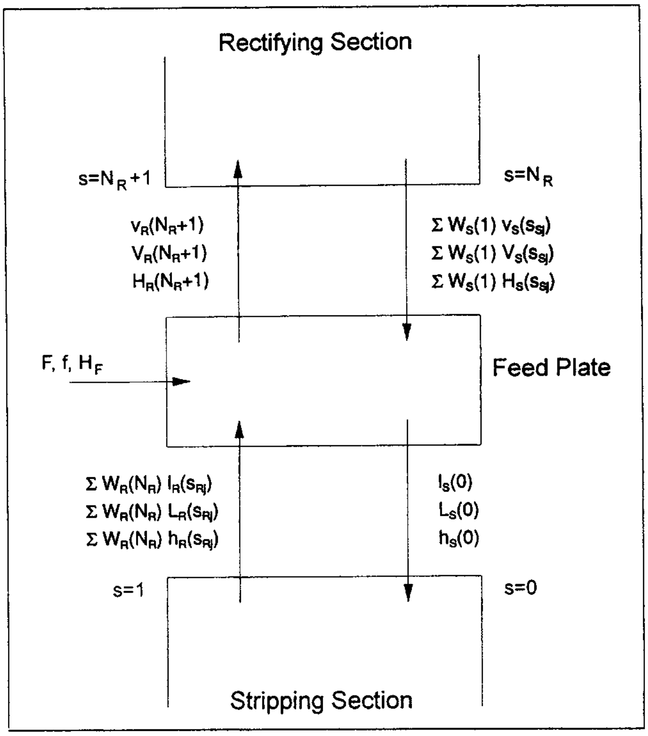

Figure 1. Feed tray formulation in the OCFE model.

Equilibrium coefficients and stream enthalpies are calculated using the regression Eqs. 8, 9, and 11.

Stewart et al. (1985) investigated approximation error using different families of orthogonal polynomials for the selection of collocation points and showed that the roots of the Hahn orthogonal polynomials are the best selection. Hahn polynomials $Q_n(x;\ \alpha,\beta,M)$ obey the weighted orthogonality condition:

$$\sum_{x=0}^{M} w(x;\ \alpha,\beta,M)Q_m(x;\ \alpha,\beta,M)Q_n(x;\ \alpha,\beta,M) = 0 \quad (m \neq n) \tag{33}$$

where

$$w(x;\ \alpha,\beta,M) = \frac{(\alpha+1)_x(\beta+1)_{M-x}}{x!\,(M-x)!} \tag{34}$$

Stewart et al. (1985) reported that when both parameters α and β have the value zero, which results in a uniform weighting to the residuals, then the approximation error becomes significantly small. The collocation points are the roots of a Hahn orthogonal polynomial with $x=s-1$ and $M=N-1$.

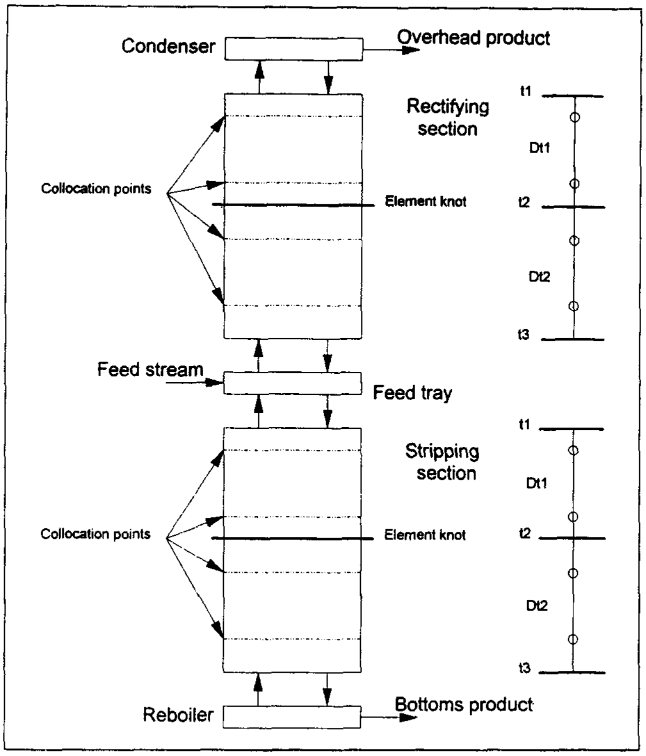

Figure 2. OCFE model for a conventional distillation column.

Another useful property of the Hahn polynomials is that whenever the number of interior collocation points is equal to the number of stages in this section then the roots of the polynomials coincide with the discrete stages, and thus the full model is recovered. The collocation model retains the stagewise structure of the full order model and approximates it with fewer equations. For more details about the properties of Hahn polynomials such as analytical expressions for the roots of up to fourth-order polynomials, the reader is referred to Stewart et al. (1985) and Askey (1975).

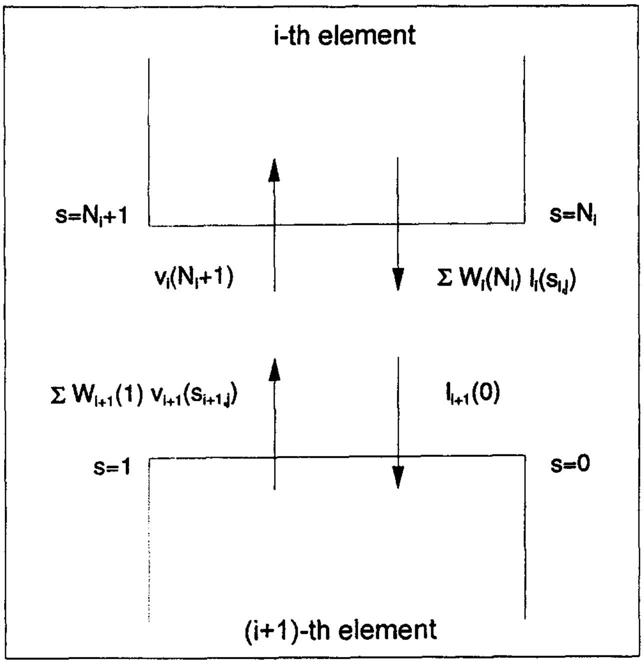

Figure 3. Boundary conditions between elements.

Collocation on subdomains of column sections

The collocation method on the column sections described in the previous section uses $(n+1)$th-order approximation polynomials for each column section where n is the total number of collocation points in each column section. When the composition profiles in the column are steep or change rapidly, then a large number of collocation points would be required to track the steep fronts in the solution and obtain an accurate approximation. Thus, each section is divided into smaller parts, named finite elements.

A more accurate representation will be achieved if the division of each column section into smaller subdomains is made such that the density of collocation points is greater in those regions where significant changes in the composition or temperature occur. Fewer collocation points can be used where the profiles in the column follow a smooth behavior. A (k_i+1)th-order polynomial is defined on every element, where k_i is the number of collocation points in the element and a set of piecewise continuous polynomials (Eqs. 19 and 20) is used for the approximation. This results in the use of more low order Lagrange interpolation polynomials compared with collocation schemes of the same total number of collocation points and only one element per column section. Each finite element is bounded by two endpoints (breakpoints). At the breakpoints of each element, continuity of the polynomials is required, so that the approximation piecewise function is continuous throughout the entire column section. Polynomials of lower order and more collocation points can be used for regions in the column where composition and temperature profiles change rapidly. The formulation of this technique for a conventional distillation column with two finite elements on each section is shown in Figure 2.

Similar to the method described in the preceding section, k_i interior collocation points, which are the roots of Hahn orthogonal polynomials, are selected for every finite element. Also $s_{i,o}=0$ and $s_{i,k_i+1}=N_i+1$, where N_i is the number of stages in the ith element, are interpolation points for liquid and vapor phase respectively.

The boundary conditions between finite elements obey zero-order continuity and are given by:

Liquid Phase:

$$\sum_{j=0}^{k_i} W_{l,i,j}(N_i)\tilde{l}_{m,i}(s_{i,j})=\tilde{l}_{m,i+1}(s_{i+1,0}) \quad m=1,\ldots,C \tag{35}$$

Vapor Phase:

$$\tilde{v}_{m,i}(s_{i,k_i+1})=\sum_{j=1}^{k_{i+1}+1} W_{v,i+1,j}(1)\tilde{v}_{m,i+1}(s_{i+1,j}) \quad m=1,\ldots,C \tag{36}$$

where index i denotes the element. Similar relations are used for the total liquid and vapor stream enthalpy. Detailed rep-

Table 1. Column Specifications

	Case 1 C_3-Splitter	Case 2 DIB	Case 3 C_3-C_4 Splitter
Feed			
Total flow (Mmols/d)	1.0734	6.4240	7.4544
Temperature (°C)	46.11	94.80	69.88
Pressure (kPa)	1,860.60	1,730.40	1,741.00
Composition (% mol)			
ethane	—	—	0.09
propylene	89.73	—	—
propane	10.27	3.83	22.11
isobutane	—	63.76	52.47
n-butane	—	28.22	23.09
isopentane	—	4.19	2.07
pentane	—	—	0.17
Condenser type	equilibrium	equilibrium	equilibrium
Reboiler type	equilibrium	equilibrium	equilibrium
Ideal Stages			
Rectifying section	115	14	9
Stripping section	60	19	11
Product Specifications			
Overhead product (% mol)	propane ≤ 0.25	*n*-butane ≤ 3.0	isobutane ≤ 0.6
Bottoms product (% mol)	propylene ≤ 0.50	isobutane ≤ 5.0	propane ≤ 4.0

resentation of the boundary conditions of the elements is shown in Figure 3. Liquid molar flow rates and enthalpy of the stream leaving the ith element are evaluated by extrapolation at point N_i using the Lagrange polynomial for ith element. An analogous procedure is used for the vapor molar flow rates and enthalpy of the stream entering the $(i+1)$th element. They are calculated by extrapolation at point $s=1$ using the Lagrange polynomial for the $(i+1)$th element.

The size of each finite element can be determined such that the total approximation error in every column section is minimized. Hahn polynomials can be applied not only for integer values but also for real values of N; the length of every finite element can be any real number. The only requirement is that the sum of all the finite-element lengths in each column section is equal to the integer number of equilibrium stages in that section. In addition, the order of the interpolation polynomial used to approximate the behavior of the variables in a given element cannot exceed the number of equilibrium stages included in the element.

An alternative method for approximating composition and temperature profiles in the column is to use cubic splines instead of Lagrange polynomials. Cubic splines may allow the second derivative of the piecewise cubic interpolation functions to be continuous at the knots connecting the elements of each section, which implies continuity of curvature (de Boor, 1985). However, since derivative information is not available regarding the approximated functions of component composition and temperature, due to the discrete nature of the full-order model, the properties of splines are not helpful. Although the models using cubic spline interpolation polynomials approached the optimum solution, the measure of the infeasibilities in the solution could not be reduced below the specified tolerance. The set of equations becomes more complicated because the derivatives of the approximated function need to be estimated, thus making the optimization problem more difficult to solve. Cubic spline methods were not explored any further in this work.

Optimization Results

The performance of the OCFE models in steady-state optimization was tested with three distillation columns. Two different NLP solvers have been used to determine the optimal solution for the distillation columns are: MINOS 5.3, an augmented projected Lagrangian algorithm (Murtagh and Saunders, 1982), and a reduced sequential quadratic programming (R-SQP) algorithm developed for large-scale problems (Schmid and Biegler, 1992).

Case I: C_3-splitter

This example involves the optimization of a propylene-propane splitter. The main characteristics of this type of distillation column are: high reflux ratios (which increases the operating costs) and a larger number of equilibrium stages (because of the low relative volatility of the two components). The conditions of the feed stream as well as other characteristics and specifications of the column are shown in Table 1. The regression Eqs. 8, 9, and 11 are used for the evaluation of the thermodynamic properties of the liquid and vapor phases except that absolute temperatures were used for the calculation of the liquid enthalpy. The values of the parameters that are used in the regression equations are given in Tables 2, 3, and 4. The assumption of ideal solutions was made for the evaluation of the thermodynamic properties, and the present method requires modification as suggested by Swartz and Stewart (1987) when applied to multiphase distillation. Pressure is fixed for every tray at the values given by a simulation case. The pressure at each collocation point is calculated by a linear interpolation of the pressure values at the two neighboring trays. The initial point for the optimization was the solution of a simulation case using HYSIM 1.51 (Hyprotech, 1991) and interpolating linearly between the equilibrium stages to obtain the values of the variables at the collocation points. The total number of nonlinear constraints for a OCFE model with n

Table 2. Regression Coefficients for K-Values

	a_1	a_2	a_3	a_4
Used in the C_3-Splitter				
propylene	8.020373e-1	-1.775595e-2	5.587970e-3	-4.647275e-4
propane	6.854639e+1	-4.326426e-1	6.837252e-4	-1.058095e-4
Used in the Deisobutanizer (DIB)				
propane	-9.85809	0.545316e-1	-0.579078e-4	-0.139112e-2
isobutane	-8.67675	0.365983e-1	-0.208579e-4	-0.146493e-2
n-butane	-15.41127	0.780988e-1	-0.889839e-4	-0.117645e-2
isopentane	-19.12111	0.946910e-1	-0.112866e-4	-0.997234e-3
Used in the C_3-C_4 Splitter				
ethane	-5.420597	0.348876e-1	-0.388490e-4	-0.509808e-3
propane	-13.133830	0.691381e-1	-0.813411e-4	-0.412676e-3
isobutane	-14.462916	0.688440e-1	-0.754950e-4	-0.341044e-3
n-butane	-17.345122	0.825619e-1	-0.932420e-4	-0.317356e-3
isopentane	-20.023894	0.912537e-1	-0.101955e-3	-0.239818e-3
pentane	-22.205646	0.101407e+0	-0.114963e-3	-0.220114e-3

collocation points is calculated as: mass balances: $[n+3]C$; energy balances: $[n+3]$; equilibrium relations: $[n+3]$; summation equations: $[n+3]$; molar fractions at the overhead and bottoms products: $2C$; and reflux ratio relation.

In the mass and energy balances, the equations for the three discrete equilibrium stages in the model (condenser, feed plate, and reboiler) are included. There are two degrees of freedom for the column because pressure and feed conditions are specified.

Optimization results for the C_3-splitter are shown in Table 5. The objective function is the minimization of the utility costs required for the separation:

$$\text{Cost} = 2.4Q_B - 0.4Q_D \tag{37}$$

Both tray-by-tray and OCFE models converge to the same optimal solution and the same set of constraints is active at the optimum. The Lagrange multipliers (marginal values) of the active product specification constraints are nearly identical for both models. The Lagrange multiplier of an active constraint indicates the magnitude of change in the objective function per unit increase or decrease in the righthand side term of the constraint and show the sensitivity of the optimal solution to the relaxation or tightening of the given constraint. Optimization results show that a shortcut model based on the Fenske-Underwood-Eduljee equations failed to predict the same optimal solution as the tray-by-tray model (Table 5).

The OCFE model consisted of three elements in every section and three collocation points were used in every element leading to fourth-order Lagrange interpolation polynomials. The model size was reduced by a factor of 8, and as a consequence, the computational time to obtain the solution was reduced significantly. The CPU time to obtain the solution on a VAX 3500, using MINOS 5.3 as the NLP solver, was decreased by a factor of 11 for the OCFE model. The OCFE model was about 3.6 times faster than tray-by-tray when the R-SQP code was used for the optimization. The reflux ratio and the bottoms product flow rate were selected as the independent variables in the R-SQP for the decomposition of the Hessian matrix. The large model size reduction in the OCFE formulation is mainly because of the large flat regions in the component profiles of the column. These flat regions allow the use of only a few collocation points for an accurate representation of the tray-by-tray solution.

The optimal temperature and liquid composition profiles for both models are shown in Figures 4 and 5, respectively. Clearly, OCFE models performed well in predicting the optimal profile of the C_3-splitter.

Cases II and III deisobutanizer and C_3-C_4 splitter

These cases involve the optimization of two complex distillation columns. A four component deisobutanizer (DIB) and a six component C_3-C_4 splitter. The column specifications are shown in Table 1 and Tables 6 and 7 show the optimization results for the DIB and the C_3-C_4 splitter, respectively. The OCFE model for the DIB consisted of three elements for every column section and two and three collocation points per element for the rectifying and stripping sections, respectively.

Table 3. Regression Coefficients for Liquid Enthalpy

	b_1	b_2	b_3	b_4
Used in C_3 Splitter				
propylene	-5.507860e+5	5.180234e+3	-1.673919e+1	1.845696e-2
propane	-2.336810e+5	2.168266e+3	-7.086567e+0	8.169412e-3
Used in the DIB and the C_3-C_4 Splitter				
propane	-4.114596e+5	3.948232e+3	-1.250259e+1	1.363845e-2
isobutane	-2.013476e+5	1.838203e+3	-5.425727e+0	5.811588e-3
n-butane	-1.674945e+5	1.494509e+3	-4.259655e+0	4.503788e-3
isopentane	-9.877590e+4	8.301663e+2	-2.136380e+0	2.317351e-3
pentane	-1.041395e+5	8.668001e+2	-2.195377e+0	2.332018e-3

Table 4. Regression Coefficients for Vapor Enthalpy

	c_1	c_2	c_3	c_4	c_5	c_6
Used in the C_3 Splitter						
propylene	−5.72554e+3	−5.10174e+3	−2.00812e+4	2.08929e+4	2.09357e+4	−1.15250e+3
propane	−7.38623e+3	−7.98970e+3	−3.17627e+4	3.67828e+4	3.86803e+4	−1.26688e+4
Used in the DIB and the C_3-C_4 Splitter						
ethane	3.41889e+3	−1.13518e+4	1.24400e+4	−2.53216e+3	1.20954e+4	4.12111e+3
propane	1.87050e+4	−5.40087e+3	−5.92078e+3	5.58299e+3	5.24836e+3	1.30895e+4
isobutane	2.34751e+4	−6.88974e+3	−7.34538e+3	8.12559e+3	2.86715e+3	2.32235e+4
n-butane	2.75293e+4	−9.09605e+3	−6.53993e+3	9.38289e+3	−9.33633e+2	2.68593e+4
isopentane	2.65374e+4	−7.98028e+3	−9.44774e+3	1.00612e+4	7.00015e+3	3.49152e+4
pentane	2.71551e+4	−7.97346e+3	−1.05076e+4	1.07723e+4	1.08482e+4	3.44538e+4

Both models converge to the same solution, but OCFE required about half of the tray-by-tray CPU time using MINOS 5.3 as the optimization algorithm. OCFE models converge with difficulty when the R-SQP algorithm is used. The minimal OCFE model size for which a feasible solution is obtained using R-SQP is greater than the one achieved with MINOS. The isobutane and n-butane liquid molar flow rates at the optimal solution for both models are shown in Figure 6 and verify the agreement of the optimal solution obtained by the two different process models. The liquid composition profiles for the nonkey components propane and isopentane are shown in Figure 7. The figure shows that OCFE models predict the composition of nonkey components accurately.

The model size reduction is smaller in the case of the C_3-C_4 splitter and as a consequence only a 20% decrease in the total solution time is achieved using the OCFE model. The main reason for this behavior is attributed to the increased complexity of the C_3-C_4 splitter compared to the previous two examples. The C_3-C_4 splitter has six components and the separation requires only 20 equilibrium stages and a larger number of collocation points is needed to track changes in composition and temperature in the column.

The treatment of the feed plate discontinuity as discussed by Stewart et al. (1985) was applied to the example cases I and II. For the C_3-splitter the optimal solution obtained was not very different from the tray-by-tray solution but worse than the solution of the proposed approach (Table 2). However, for the case of the DIB no feasible optimal solution was obtained with the Stewart et al. formulation since the assumption of constant molar overflows is not valid.

Initial point dependence

The dependence of the initial set of variable values for both the full-order and the OCFE models on the performance and computational effort required to converge to the optimal solution is investigated. The initial points tested are constructed by specifying poor estimates for the component molar flow rates and temperature at the two endpoints of the column and then calculating the values for the variables in the interior of the column by linear interpolation. For the OCFE models the values of the variables at the collocation points are evaluated by linear interpolation of the tray-by-tray initial variable values for the same starting point at the adjacent trays.

The initial profiles for the isobutane molar flow rates are shown in Figure 8. In Table 8, the optimization results using MINOS 5.3 for different initial points for the DIB are shown. OCFE models are more robust than tray-by-tray models to

Table 5. Propylene-Propane Splitter Optimization Results

	Tray-by-Tray	OCFE	Stewart et al. (1985) Approach	Shortcut
Reflux ratio	19.708	19.701	19.835	17.785
Condenser duty (GJ/d)	−239.056	−238.972	−240.595	−210.955
Reboiler duty (GJ/d)	237.743	237.659	239.282	222.815
Overhead product:				
mol % propylene	99.75	99.75	99.75	99.75
Lagrange multiplier for propane = 0.25% mol ($/mol frac.)	−61,004	−60,949	−62,235	−41,788
Flow (Mmol/d)	0.965	0.965	0.965	0.965
Bottoms product:				
mol % propane	99.50	99.50	99.50	99.50
Lagrange multiplier for propylene = 0.50% mol ($/mol frac.)	−10,358	−10,317	−10,543	−12,209
Flow (Mmol/d)	0.108	0.108	0.108	0.108
VAX 3500 CPU time (s)				
R-SQP	49.5	13.7	—	—
MINOS 5.3	326.0	18.0	17.8	1.3
Number of equations	880	110	110	7
Number of variables	882	112	112	9
Objective function value ($/d)	666.205	665.971	670.515	623.883

OCFE model: 3 elements/section (equispaced), 3 collocation points/element.
Shortcut model: Fenske-Underwood-Eduljee equations.

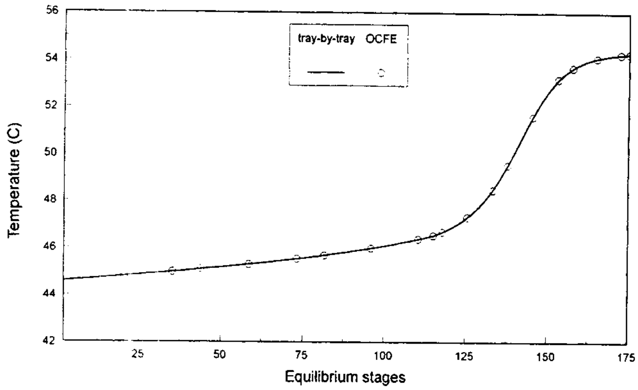

Figure 4. Comparison of optimal temperature profiles for the C_3-splitter between tray-by-tray and OCFE models

poor initial variable values. This can be mainly attributed to the fact that OCFE models have fewer variables. Another reason may be that the OCFE model diminishes near numerical singularities from the Jacobian matrix. As the initial point moves further from a feasible initial point, the ratio of the CPU time required for the tray-by-tray solution to that for the OCFE model increases. For some initial sets of variable values the tray-by-tray model fails to converge to the optimal solution.

For the C_3-splitter, the tray-by-tray model fails to converge whenever the initial temperature profile is assumed to be linear. The reason for this behavior is that the temperature profile for this particular column has a large flat region in the rectifying section and exhibits a steep behavior in the stripping section (Figure 4). The discrepancy between the final solution profile and the initial linear profile is significant. However, the OCFE model converged to the optimal solution when a linear temperature profile was provided as an initial estimate of the temperature variation in the column.

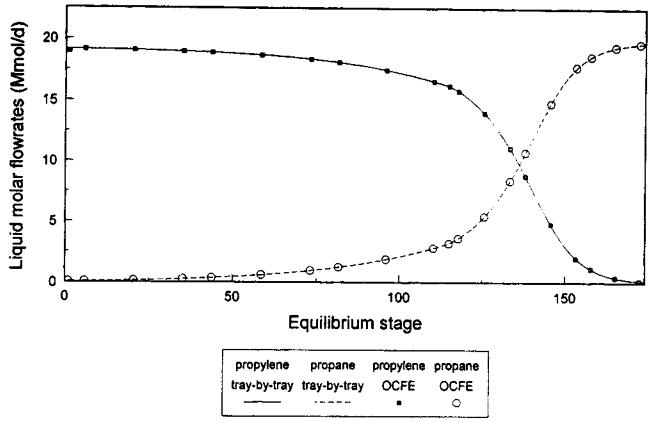

Figure 5. Comparison of optimal liquid composition profiles for the C_3-splitter between the tray-by-tray and OCFE models.

The improved ability of the OCFE models to converge to the optimal solution with a poor initial guess for the variables may be a very useful advantage, when OCFE models are used under a real-time (on-line) optimization framework. Disturbances in the real plant may result in the optimal operating conditions' moving far away from the initial estimate, and then it is very important that the process model converges to the new optimal solution.

Approximation Error Analysis

An important issue with regards to the use of OCFE models for distillation optimization is the selection of the proper combination of number of elements for every column section and the number of collocation points for every element. As the total number of collocation points in the column increases the approximation error defined as the difference of the tray-by-

Table 6. Deisobutanizer (DIB) Optimization Results

	Tray-by-Tray	Tray-by-Tray	OCFE A	OCFE B	Shortcut
	R-SQP	MINOS 5.3	R-SQP	MINOS 5.3	MINOS 5.3
Reflux ratio	7.043	7.043	7.043	7.043	7.358
Condenser duty (GJ/d)	−565.206	−565.206	−565.205	−565.205	−671.317
Reboiler duty (GJ/d)	584.191	584.191	584.190	584.190	694.694
Overhead product:					
mol % propane	5.63	5.63	5.63	5.63	5.63
mol % isobutane	91.37	91.37	91.37	91.37	91.37
Lagrange multiplier for *n*-butane = 3.0% mol ($/mol frac.)	−25,737	−25,741	−25,737	−25,737	−21,218
Flow (Mmol/d)	4.370	4.370	4.370	4.370	4.370
Bottoms product:					
mol % *n*-butane	81.89	81.89	81.89	81.89	81.89
mol % pentane	13.11	13.11	13.11	13.11	13.11
Lagrange multiplier for isobutane = 5.0% mol ($/mol frac.)	−7,195	−7,196	−7,195	−7,194	−11,621
Flow (Mmol/d)	2.054	2.054	2.054	2.054	2.054
VAX 3500 CPU time (s)	29.3	55.5	40.1	29.0	3.5
Number of equations	240	240	177	110	14
Number of variables	242	242	179	112	16
Objective function value ($/d)	1,628.14	1,628.14	1,628.14	1,628.12	1,903.66

OCFE A model: 3 elements/section (equispaced); 3 collocation points/element in rectifying section; and 4 collocation points/element in stripping section.
OCFE B model: 3 elements/section; 2 collocation points/element in rectifying section; and 3 collocation points/element in stripping section.
Element lengths: rectifying section: 3.805, 3.740, 4.455; stripping section: 5.784, 4.927, 7.289.
Shortcut model: Fenske-Underwood-Eduljee equations.
(*) variable at its upper or lower bound.

Table 7. C_3-C_4 Splitter Optimization Results

	Tray-by-Tray	Tray-by-Tray	OCFE
	R-SQP	MINOS 5.3	MINOS 5.3
Reflux ratio	7.043	7.043	7.043
Condenser duty (GJ/d)	− 565.206	− 565.206	− 565.205
Reboiler duty (GJ/d)	584.191	584.191	584.190
Overhead product:			
mol % ethane	0.47	0.47	0.47
mol % propane	98.91	98.91	98.91
mol % *n*-butane	0.02	0.02	0.02
Lagrange multiplier for isobutane = 0.6% mol ($/mol frac.)	− 29,460	− 29,460	− 29,451
Flow (Mmol/d)	1.422	1.422	1.422
Bottoms product:			
mol % *i*-butane	64.70	64.70	64.70
mol % *n*-butane	28.53	28.53	28.53
mol % *i*-pentane	2.56	2.56	2.56
mol % pentane	0.21	0.21	0.21
Lagrange multiplier for propane = 4.0% mol ($/mol frac.)	− 3,760	− 3,760	− 3,760
Flow (Mmol/d)	6.032	6.032	6.032
VAX 3500 CPU time (s)	28.5	37.7	31.4
Number of equations	193	193	139
Number of variables	195	195	141
Objective function value ($/d)	611.99	611.99	611.92

OCFE model: 2 elements/section; 3 collocation points/elements in rectifying section; and 3-2 collocation points/elements in stripping section.
Element lengths: rectifying section: 3.500, 3.500; stripping section: 5.400, 4.600.

tray solution from the OCFE solution, reduces asymptotically. This is expected since the use of the Hahn polynomials guarantee that the full-order model is recovered when the number of collocation points equals the number of equilibrium stages in the column section.

Since the main goal is to achieve the minimum possible size of the OCFE model for which the tray-by-tray solution is obtained, it must be determined how many equilibrium stages can be represented within a given element length for a given polynomial order. The answer to that depends mainly on the shape of the composition and temperature profiles in the given column section. This can be solved by adaptively varying the length of the finite elements so that an optimal distribution of the collocation points in the column is achieved, under the condition that the total number of collocation points is constant (Seferlis and Hrymak, 1994).

The objective in this work is to determine a combination of number of elements per column section and number of collocation points per element that minimizes the approximation error for a given number of total collocation points. However, this optimal combination is difficult to determine a priori. In order to investigate the dependence of the accuracy of the OCFE model on different collocation schemes the approximation error for the temperature and composition is calculated for the C_3-splitter. The approximation error is the sum of squares of the differences of the variables (temperature or composition) obtained by the tray-by-tray model from the values of the same variables evaluated at the location of the equilibrium stages using the OCFE solution and the Lagrange interpolation polynomials. The error for a single tray is given by the following relations:

$$e_{\text{Temp}} = T - \sum_{j=0}^{k_i} W_{l,i,j}(s_l)\,\tilde{T}_i(s_{ij}) \tag{38}$$

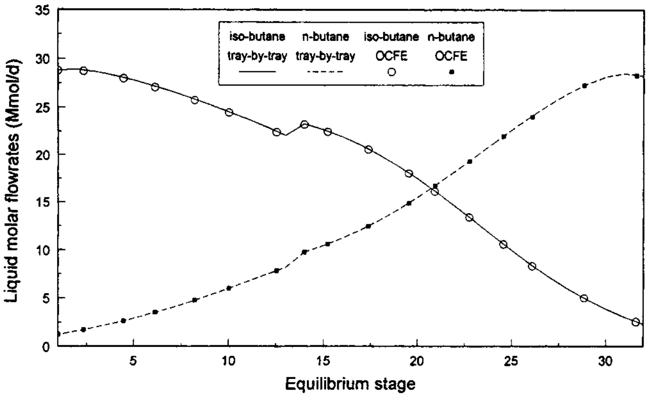

Figure 6. Comparison of optimal key liquid composition profiles for the DIB between the tray-by-tray and the OCFE models.

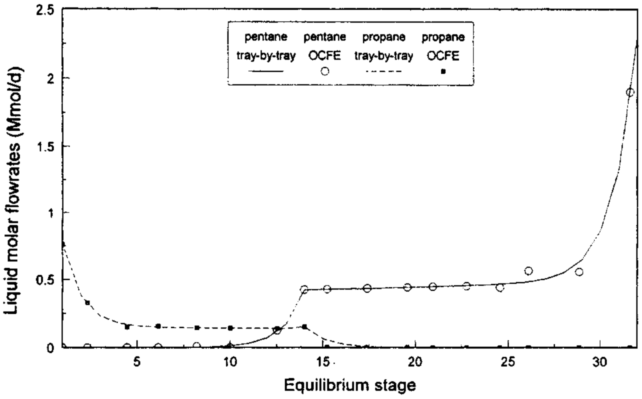

Figure 7. Comparison of optimal nonkey liquid composition profiles for the DIB between the tray-by-tray and the OCFE models.

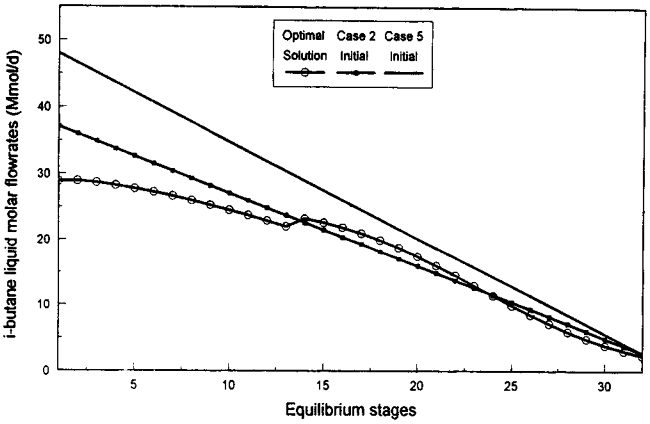

Figure 8. Comparison between the initial and the optimal isobutane liquid composition profiles in the DIB.

$$e_{m,\text{flow}} = l_m - \sum_{j=0}^{k_i} W_{l,i,j}(s_l)\tilde{l}_{m,i}(s_{ij}) \quad m=1,\ldots,C \quad (39)$$

where s_t is the location of the actual tray inside the ith element and $\tilde{T}_i(s_{ij})$, $\tilde{l}_{m,i}(s_{ij})$ are the temperatures and the component liquid molar flow rates at the collocation points in the ith element respectively.

Table 9 shows the error behavior for different collocation schemes. For the cases of two and three elements per column section, with two collocation points per element, convergence to the optimal solution was not possible, which implies that third-order Lagrange polynomials are not very effective in predicting the true solution. In addition, one can assess the performance of different collocation schemes, with equal total number of collocation points, in identifying the optimal full-order solution. For instance, the approximation error is smaller when three elements per section with four collocation points per element are used compared with a scheme that uses four elements per section with three collocation points per element.

Table 8. Optimization Results for the DIB for Different Initial Variable Value Sets

MINOS 5.3		Tray-by-Tray	OCFE
<u>Case 1</u>			
i-butane: 37.1–2.7 Mmol/d	CPU (s)	55.8	33.5
n-butane: 0.9–38.0 Mmol/d	CPU ratio	1.67	1.00
Temperature: 35–60°C	Major itns	8	7
Simulation solution (HYSIM)	Minor itns	110	103
<u>Case 2</u>			
i-butane: 37.1–2.7 Mmol/d	CPU (s)	55.3	29.0
n-butane: 0.9–34.1 Mmol/d	CPU ratio	1.90	1.00
Temperature: 35–60°C	Major itns	8	6
Linear interpolation	Minor itns	116	84
<u>Case 3</u>			
i-butane: 40.0–2.7 Mmol/d	CPU (s)	104.1	42.4
n-butane: 0.9–38.0 Mmol/d	CPU ratio	2.45	1.00
Temperature: 30–65°C	Major itns	10	8
Linear interpolation	Minor itns	59	200
<u>Case 4</u>			
i-butane: 45.0–2.7 Mmol/d	CPU (s)	232.6	60.0
n-butane: 1.0–42.0 Mmol/d	CPU ratio	3.88	1.00
Temperature: 30–65°C	Major itns	11	10
Linear interpolation	Minor itns	601	323
<u>Case 5</u>			
i-butane: 48.0–2.7 Mmol/d	CPU (s)	No convergence	74.6
n-butane: 1.0–45.0 Mmol/d	Major itns	—	10
Temperature: 30–65°C	Minor itns	—	483
Linear interpolation			

Table 9. Approximation Error in Temperature for the C_3-splitter*

	2 Elements/Section	3 Elements/Section	4 Elements/Section
2 collocation points per element	No convergence	No convergence	1.483
			1.696
			2.934
3 collocation points per element	1.794	0.491	0.374
	2.160	0.163	0.044
	3.043	2.394	1.879
4 collocation points per element	0.460	0.340	0.252
	0.117	0.025	0.007
	2.306	1.715	1.262

*Table entries are sum of squares of errors for propylene and propane molar flow rates and temperature.

Conclusions

Orthogonal collocation on finite-elements techniques are used for the model size reduction of distillation units. Each column section is divided into subdomains in which orthogonal collocation is applied. The number of equilibrium stages as well as the component molar flow rates, and the total enthalpies are treated as continuous variables of position in the column. The collocation points are chosen to be the roots of the Hahn orthogonal polynomials. The condenser, the reboiler, and the feed plates are treated as discrete equilibrium stages. This new formulation allows the accurate representation of the column behavior under the presence of discontinuities in column variable profiles due to feed streams and sidestreams.

OCFE models are used for steady-state optimization and the optimal solutions are compared to those obtained by the tray-by-tray model. Both models converge to the same optimal solution, but OCFE models required less computational effort. OCFE formulations are advantageous for columns that have a large number of equilibrium stages since the reduction in model size and solution time is substantial. As the complexity of the distillation column increases, due to the addition of more components or the use of more rigorous thermodynamic models, the minimum number of collocation points for a feasible optimal solution increases.

OCFE models show improved robustness in converging to the optimal solution when a poor initial point is provided, mainly because of their compact size. For a constant number of collocation points there is an optimal combination of number of elements per column section and number of collocation points per element for which a measure of the approximation error is minimized. At present, the minimum number of elements and collocation points, which provide the least approximation error, cannot be determined without a previous solution of the column available.

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Notation

b = component bottoms product molar flow rate, kmol/d
B = bottoms product molar flow rate, kmol/d
C = total number of components in the column
d = component overhead product molar flow rate, kmol/d
D = overhead product flow rate, kmol/d
e = error between full and OCFE models
f = component feed molar flow rate, kmol/d
F = feed flow rate, kmol/d
h = mixture molar liquid enthalpy, kJ/kmol
H = mixture molar vapor enthalpy, kJ/kmol
K = K values
l = component liquid molar flow rate, kmol/d
L = total liquid molar flow rate, kmol/d
M = parameter
n = number of collocation points
N = total number of equilibrium stages
P = pressure, kPa
$Q_n(x;\alpha,\beta,M)$ = nth degree Hahn polynomial
Q = thermal duty, kJ/d
s = continuous stage variable which varies from $s=0$ to $N+1$ within an element
s_j = collocation point
T = tray temperature, K
v = component molar flow rate, kmol/d
V = total vapor molar flow rate, kmol/d
$W_{lj}(s)$ = Lagrange polynomials for liquid states
$W_{vj}(s)$ = Lagrange polynomials for vapor states
$w(x;\alpha,\beta,M)$ = weighting function
x = liquid molar fraction

Greek letters

α = parameter for Hahn polynomials
β = parameter for Hahn polynomials

Subscripts

B = bottoms product
c = critical component data
D = overhead product
F = feed stream
i = ith equilibrium stage in tray-by-tray model or finite-element index in OCFE model
j = jth collocation point
l = liquid state
m = component
r = reduced component data
R = rectifying section
S = stripping section
t = tray location
v = vapor state

Superscripts

R = rectifying section
S = stripping section

Operation

$(a)_k = (a)(a+1)\ldots(a+k-1)$ if $k>0$
$(a)_k = 1$ if $k=0$

Literature Cited

Askey, R., "Continuous Hahn Polynomials," *J. Phys. A.: Math. Gen.*, **18**, L1017 (1985).

Bailey, J. K., "Nonlinear Optimization of a Hydrocracker Fractionation Plant," M. Eng. Thesis, McMaster Univ., Canada (1991).

Benallou, A., D. E. Seborg, and D. A. Mellichamp, "Dynamic Compartmental Models for Separation Processes," *AIChE J.*, **32**(7), 1067 (1986).

Biegler, L. T., I. E. Grossmann, and A. W. Westerberg, "A Note on Approximation Techniques Used for Process Optimization," *Comput. Chem. Eng.*, **9**(2), 201 (1985).

Cho, Y. S., and B. Joseph, "Reduced Order Models for Separation Columns—III. Application to Columns with Multiple Feeds and Sidestreams," *Comput. Chem. Eng.*, **8**(2), 81 (1984).

Cho, Y. S., and B. Joseph, "Reduced Order Steady-State and Dynamic Models for Separation Processes. Part II. Application to Nonlinear Multicomponent Systems," *AIChE J.*, **29**(2), 270 (1983).

Cuthrell, J. E., and L. T. Biegler, "On the Optimization of Differential-Algebraic Process Systems," *AIChE J.*, **33**(8), 1257 (1987).

de Boor, C., *Practical Guide to Splines*, Springer-Verlag, New York (1978).

Eduljee, H. E., "Equations Replace Gilliland Plot," *Hydrocar. Proc.*, **54**(9), 120 (1975).

España, M., and I. D. Landau, "Reduced Order Bilinear Models for Distillation Columns," *Automatica*, **14**, 345 (1978).

Glinos, K., and M. F. Malone, "Maximum Reflux, Product Distribution and Lumping Rules for Multicomponent Distillation," *Ind. Eng. Chem. Process Des. Dev.*, **23**, 764 (1984).

Holland, C. D., *Fundamentals of Multicomponent Distillation*, McGraw-Hill, New York (1981).

Horton, R. R., B. W. Bequette, and T. F. Edgar, "Improvements in Dynamic Compartmental Modelling for Distillation," *Comput. Chem. Eng.*, **15**(3), 197 (1991).

Hyprotech, *HYSIM User's Guide*, Version 1.51, Hyprotech Ltd., Calgary, Alberta, Canada (1991).

Kim, H. S., K. S. Lee, K. P. Yoo, W. H. Lee, and H. S. Park, "Two-Part Modular Reduced-Order Model for Multicomponent Multistage Distillation Columns," *J. Chem. Eng. Japan*, **22**(1), 41 (1989).

Murtagh, B. A., and M. A. Saunders, "A Projected Lagrangian Algorithm and its Implementation for Sparse Nonlinear Constraints," *Math. Program Study*, **16**, 84 (1982).

Pinto, J. C., and E. C. Biscaia, Jr., "Order Reduction Strategies for Models of Staged Separation Systems," *Comput. Chem. Eng.*, **12**(8), 821 (1988).

Prett, D. M., and C. E. García, *Fundamental Process Control*, Butterworths, Boston (1988).

Renfro, J. G., "Computational Studies in the Optimization of Systems Described by Differential/Algebraic Equations," PhD Thesis, Univ. of Houston, TX (1986).

Schmid, C., and L. T. Biegler, "Quadratic Programming Methods for Tailored Reduced Hessian SQP," AIChE Annual Meeting, Miami (1992).

Seferlis, P., and A. N. Hrymak, "Adaptive Collocation on Finite Elements Models for the Optimization of Multi-Stage Distillation Units," *Chem. Eng. Sci.*, in press (1994).

Smith, B. D., and W. K. Brinkley, "General Short-cut Equation for Equilibrium Stage Processes," *AIChE J.*, **6**(3), 446 (1960).

Srivastava, R. K. and B. Joseph, "Reduced Order Models for Separation Columns: V. Selection of Collocation Points," *Comput. Chem. Eng.*, **9**(6), 601 (1985).

Srivastava, R. K. and B. Joseph, "Reduced Order Models for Separation Columns: IV. Treatment of Columns with Multiple Feeds and Sidestreams via Spline Fitting," *Comput. Chem. Eng.*, **11**(2), 159 (1987a).

Srivastava, R. K. and B. Joseph, "Reduced Order Models for Staged Separation Columns: IV. Columns with Steep and Flat Composition Profiles," *Comput. Chem. Eng.*, **11**(2), 165 (1987b).

Stewart, W. E., K. L. Levien, and M. Morari, "Simulation of Fractionation by Orthogonal Collocation," *Chem. Eng. Sci.*, **40**(3), 409 (1985).

Swartz, C. L. E., and W. E. Stewart, "A Collocation Approach to Distillation Column Design," *AIChE J.*, **32**(11), 1832 (1986).

Swartz, C. L. E., and W. E. Stewart, "Finite-Elements Steady State Simulation of Multiphase Distillation," *AIChE J.*, **33**(12), 1977 (1987).

Wong, K. T., and R. Luus, "Model Reduction of High-Order Multistage Systems by the Method of Orthogonal Collocation," *Can. J. Chem. Eng.*, **58**, 382 (1980).

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