Collocation Methods for Distillation Design I: Model Description and Testing

Robert Huss

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COLLOCATION METHODS FOR DISTILLATION DESIGN I: MODEL DESCRIPTION AND TESTING

Robert S. Huss and Arthur W. Westerberg

Abstract

Fast and accurate distillation design requires a model that significantly reduces the problem size while accurately approximating a full order distillation column model. Variable number of trays and variable feed tray location make optimization possible.

This collocation model builds on the concepts of past collocation models for design of complex real-world separation systems. Two variable transformations make this method unique. Polynomials cannot accurately fit trajectories which flatten out. In columns, flat sections occur in the middle of large column sections, or where concentrations go to zero or one. With an exponential transformation of the tray number which maps zero to an infinite number of trays onto the range zero to one, two collocation trays can accurately simulate a large column section. With a hyperbolic tangent transformation of the mole fractions, the model can simulate columns which reach high purities. Furthermore, this model uses multiple collocation elements for a column section, which is more accurate than a single high order collocation section.

This work has been partially supported by the Engineering Design Research Center, a NSF Engineering Research Center.

Introduction

Several researchers have explored and developed collocation for distillation column modeling. In this paper, we present a collocation model which expands on prior models, addressing the problems specific to steady-state, continuous columns. We describe the formulation of the model in detail and compare it to prior models, using rigorous column simulations as a benchmark.

Motivation

The desire for a method to perform minimum reflux calculations for highly nonideal systems was the original motivation for this collocation method. For a specific separation, the required reflux ratio decreases as the number of trays in the column increases. As one increases the number of trays in a column section to a very large number, a region of constant composition occurs, referred to as a pinch. At a pinch point, the vapor and liquid passing each other are in equilibrium. They are also in material balance with the compositions entering and leaving at the end of that column section.

Consider a separation of a ternary mixture A, B, and C, where we want to separate A from B and C (see Figure 1). Given the products and a specified reflux ratio, Levy et al. [1985] solved this type of problem by starting from the ends of the column and calculating the trajectories inward. When the concentration changes in each section fall below some minimum value, they stop calculating and assume this is the pinch point. If the trajectories intersect, then they have a feasible column profile. If one trajectory just pinches on the other, they have a minimum reflux profile.

For a larger number of species, one cannot completely specify a product for a column. Typically one can ask that component splits satisfy inequalities — e.g., we want at least 99.9% of A and 99% of B and no more than 1% of C and less than 0.01% of D to exit in the distillate. Solving such a problem requires one to discover

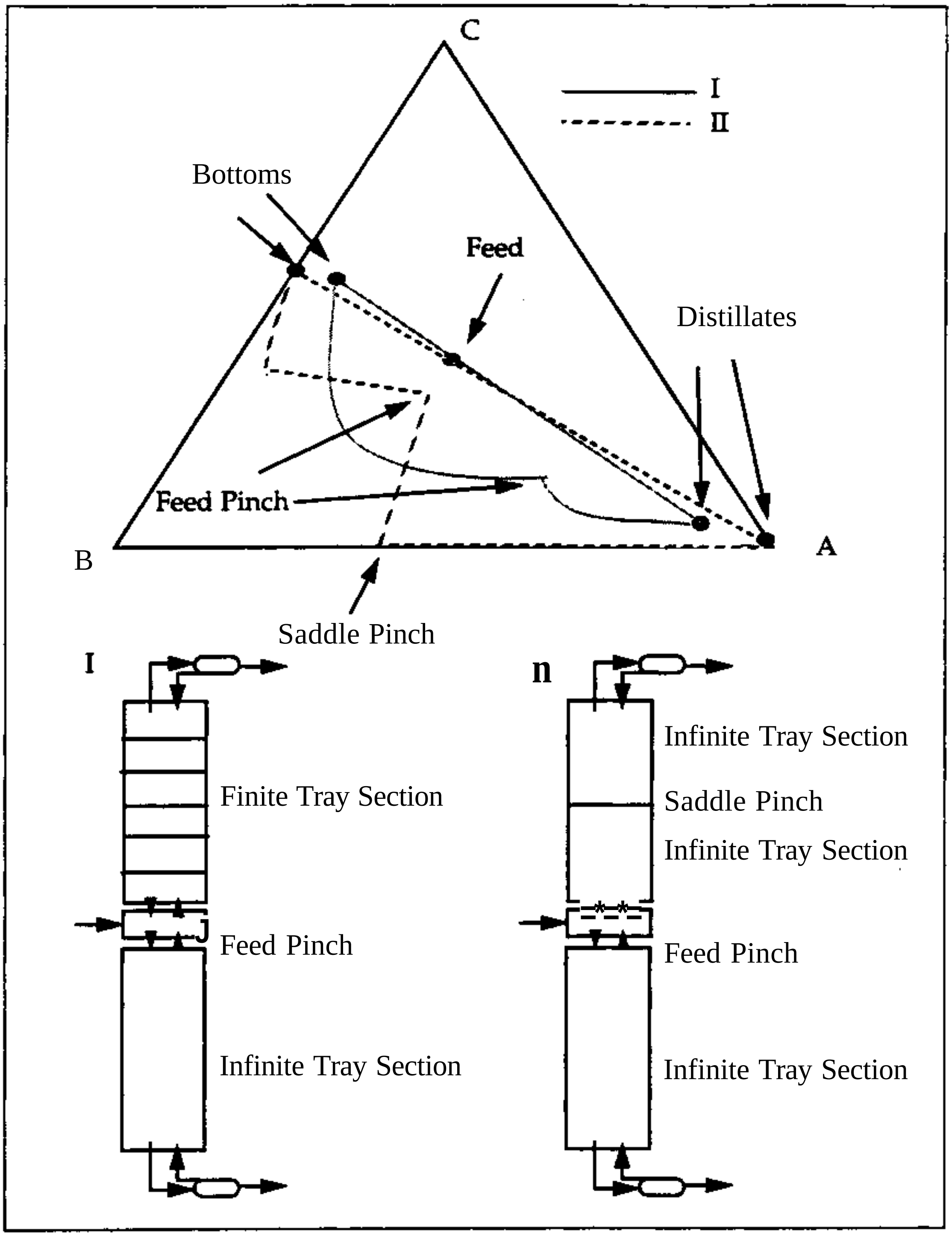

Figure 1. Minimum reflux trajectories and column configurations

which of these constraints are active. We saw that one can still use a pinch strategically located, but we also discovered that one needs a tray by tray column section model in a form which can compute the number of trays it contains. Conventional column models require one to specify the trays as an integer input.

This thinking led us to consider using a collocation model for the parts of the column where Levy et al. [1985] used a tray by tray computation. For such a column section, the number of trays is a continuous variable which the model can compute.

Returning to the three component example, Levy et al. [1985] showed that, as they decreased the concentration of C in the distillate, the minimum reflux decreased. Therefore, for a specific separation between the key components, A and B, the minimum reflux occurs when they allow no C in the distillate. In this case the top section has a saddle pinch point along the A-B edge where the concentration of C goes to zero. Levy et al. [1985] noticed that, as their computations approached this saddle pinch, it, the feed composition, and the feed pinch became colinear. Requiring colinearity of these points gave them a method to determine minimum reflux without the needed tray by tray computation. For a constant relative volatility, constant molar overflow system, they proved this method becomes exactly Underwood's method. They proposed using this colinearity even for nonideal systems. In a similar manner and for multicomponent nonideal systems, Koehler et al. [1991] used a minimum angle criterion between the three points, and Julka and Doherty[1990] revised the colinearity condition to one of having a set of pinch points and the feed composition lie inside a minimum volume in composition space. All these methods assume sharp splits as they are based on computing a saddle pinch point. These geometric techniques do not guarantee a feasible column for nonideal systems, and they do not work for nonsharp splits.

To guarantee the intersection of the column sections for sharp splits, one must prove the existence of a tray by tray calculation linking a saddle pinch point and the feed tray composition, a calculation that passes through an infinite number of trays. This requirement led us to examine extending the collocation model to handle an infinite number of trays. We looked at different transformations to map tray number going from zero to infinity onto a variable z that goes from zero to one. With such a model, we concluded we should be able to compute minimum reflux for any column by computing pinch points and properly located column sections that can have a finite or an infinite number of trays. For case I shown in Figure 1, a finite collocation section simulates the unknown number of trays. For case II, the infinite tray section between the saddle pinch point and the feed tray is modeled by an infinite collocation section.

We began developing a collocation method capable of simulating infinite column sections and discovered several other advantages and uses for collocation. Distillation design requires an adaptable column model, with the ability to compute the number of trays in each distillation section, a computation that discovers how many trays one needs and where to place the feed. One can simulate complex column configurations. Optimal design of distillation sequences requires small robust models for each distillation column. Collocation both reduces the size of a column model and provides a continuous variable for the number of trays. Furthermore, the variable transformation required for modeling an infinite tray section improved the accuracy whenever such separation problem requires a relatively large number of trays.

Background of Collocation

Cho and Joseph [1983] developed a reduced-order method for modeling staged separation processes. They used orthogonal collocation to obtain accurate solutions of significantly reduced-order. Their model had a single collocation section for each section of the column. They tested by modeling a simple absorber system, and binary and three component distillation, and used the Antoine equation for the equilibrium relationship. In later papers Srivastava and Joseph [1984,1987a] developed methods for handling multiple feeds and side draws.

They also developed a complex method for handling steep and flat composition profiles by fitting the composition profiles with different polynomials for each component. They developed a complicated approach using two sets of collocation points, global and local, to fit both the key components and non key components [Srivastava and Joseph, 1987b]. They tested these later ideas using constant relative volatility systems.

Stewart, Levien, and Morari [1984] developed a collocation method that stresses selecting gridpoints based on the stagewise nature of distillation. Their method became stage-by-stage at full order, and had errors at least an order of magnitude smaller than Cho and Joseph's default choice of collocation points. They tested for binary and six-component distillation columns with constant relative volatility and for a ternary system using UNIQUAC for equilibrium. Swartz and Stewart [1986] applied the method to design, iteratively passing from the model to an SQP optimization algorithm. Swartz and Stewart [1987] also developed a finite-element method for handling multiphase distillation problems.

Recently, Seferlis and Hrymak [1994] adapted the model of Stewart et al. [1984] by using collocation elements to track irregularities in column profiles for existing columns. They investigated optimal placing of the collocation elements, based on comparison with the actual column. They obtained higher accuracy with multiple collocation sections of lower order than with a single collocation section of higher order.

Table 1 lists the characteristics of each of these collocation methods as well as the characteristics of the model presented in this paper.

Description of Model

Collocation is generally thought of as a method for numerically solving differential equations. The use of collocation for simulation of a distillation column is an extension of this technique. Given a differential equation,

Table 1. Comparison of Collocation Methods

	Elements/ Section	Placement of points	Thermo-dynamics tested	Variable transformations
Choand Joseph 1983	Single	Continuous orthogonal (Jacobi)	Antoine	none
Srivastava and Joseph 1987	Single(global), Multiple(local)	Continuous orthogonal (Jacobi)	Constant relative volatility	none
Stewart et al 1984	Single	Discrete orthogonal (Hahn)	UNIQUAC	none
Swartz and Stewart 1986	Single	Discrete orthogonal (Hahn)	Ideal	none
Swartz and Stewart 1987	Multiple (breakpoints at phase changes)	Discrete orthogonal (Hahn)	Nonideal three phase	none
Seferlis and Hrymak 1994	Multiple	Discrete orthogonal (Hahn)	Regression of data	none
This work	Multiple	Continuous (orthogonal for 2 or 3 points)	UNIFAC/ Pitzer	Transform tray number and mole fractions

$$\frac{dy}{dx} = f(x, y)\ ,\ y(0) = y_0 \tag{1}$$

we want to find y as a function of *x*. We can approximate y as a polynomial in *x*,

$$\hat{y}: \; = \; y<>^{+\ a\backslash x\ +\ a}\ {}_{2}x^{2} + \ldots + a_{n}x^{n} \tag{2}$$

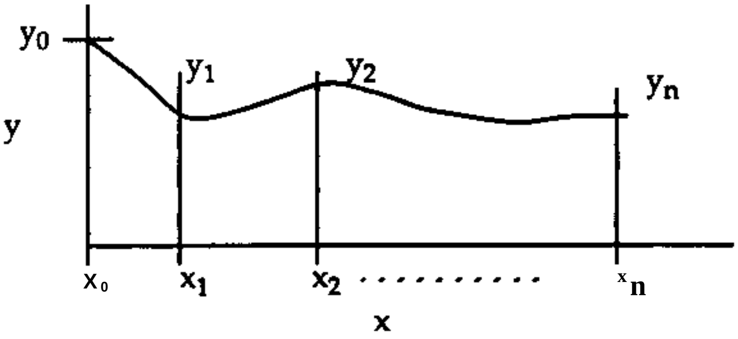

Figure 2. Collocation of a differential equation

We can then approximate y, *dy/dx*, and/as functions of *x*. At any point in *x*, we can define an error for this approximation,

$$error(x) = f(x,y) - \left(a_1 + 2a_2x^1 + \dots + na_nx^{n-1} \right) \qquad (3)$$

At *n* collocation points, $x..x_n$, we say that the error =0 and get *n* equations to solve for *n* coefficients to the polynomial. See Figure 2.

Collocation of a distillation column uses the same concepts. A set of equations defines a distillation column tray, where *x* would be the tray location in the column and y would be mole fractions. Polynomials defined by tray location approximate the mole fractions and, at each collocation point, the set of equations for a distillation column must be satisfied.

There are many equations in a distillation column model, even a reduced order model. Rather than just list the basic equations, we are going to provide a detailed degrees of freedom analysis to demonstrate the reason for using a certain set of equations.

We begin the degrees of freedom analysis with a stream model. Gibbs phase rule gives the number of degrees of freedom for a system in equilibrium.

$$F = 2 + n_c - n_p \qquad (4)$$

F is the number of degrees of freedom for a given number of components, n_c, and a given number of phases, n_p. For a single phase, F is n_c + 1. For a stream we also need a flowrate which adds one more variable, giving n_c + 2 degrees of freedom. The set of variables could be the molar flowrates, temperature, and pressure. Once we know n_c + 2 of these variables and assume the phase, we can compute all other molar properties. We shall assume a stream introduces a net of n_c + 2 new variables and shall assume all other properties are available.

A standard distillation tray has two input streams and two output streams, as shown in Figure 3. The four streams introduce a net of 4(n_c + 2) new variables, which is the first entry on Table 2. By keeping track of the number of variables and equations introduced by each new element of the model, we can determine the degrees of freedom, and how many variables must be fixed to obtain a system with the same number of equations and free variables. We can write the following equations for a single tray.

Component Material Balances:

$$L(out)x_{\{}(out) - L(in)Xi(in) = V(in)y_t<in) - V(out)y_{\{}(out) \qquad (5)$$

Equilibrium:

$$y_i(\mathrm{out}) = \frac{\alpha_i}{\alpha} *_i \{out) \quad , T_L(out) = Ty(out), P_L(out) = Py(out) \qquad (6)$$

Heat balance:

$$L(in)h(in) - L(out)h(out) = V(in)H(in) - V(out)H(out) \qquad (7)$$

L, *V*, *x*, *y*, *h*, *H* are liquid flowrate, vapor flowrate, liquid mole fraction, vapor mole fraction, liquid molar enthalpy, and vapor molar enthalpy, respectively, a; is the relative volatility of species *i*, and $\bar{a}$ is the mole fraction average relative volatility. The liquid and vapor molar enthalpies and the relative volatilities are functions of composition and temperature. We write equations 5 and 6 for each component

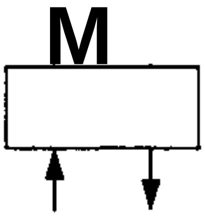

Figure 3. Diagram of tray

and equation 7 once. As shown in Table 2, the component material balances therefore introduce n_c equations. There are $n_c + 2$ equilibrium equations. The equilibrium equation also introduces one new variable, $\bar{a}$. The heat balance, which could be replaced by a constant molar overflow assumption, introduces one equation. Therefore, the degrees of freedom for an isolated tray are $2(n_c+2)+2$. Specifying two input streams, the pressure and $\bar{\mathbf{a}}$ of the tray would be sufficient to solve the tray model.

Table 2. Degrees of Freedom for an Isolated Tray

	New Variables	New Equations
4 streams	$4(n_{c+}2)$	
CMB		n_c
Equilibrium	1	$n_c + 2$
HB		1
totals	$4(n_c+2)+1$	$2n_c+3$
DOF for isolated tray	$2(n_c+2) + 2$	

Figure 4 shows a diagram of a single collocation section. A collocation section has a liquid input and vapor output at the top and a vapor input and liquid output at the bottom. The example shown has two collocation trays which are not connected. In this example, we number from the top of the collocation section downward. Liquid and vapor streams passing each other have the same

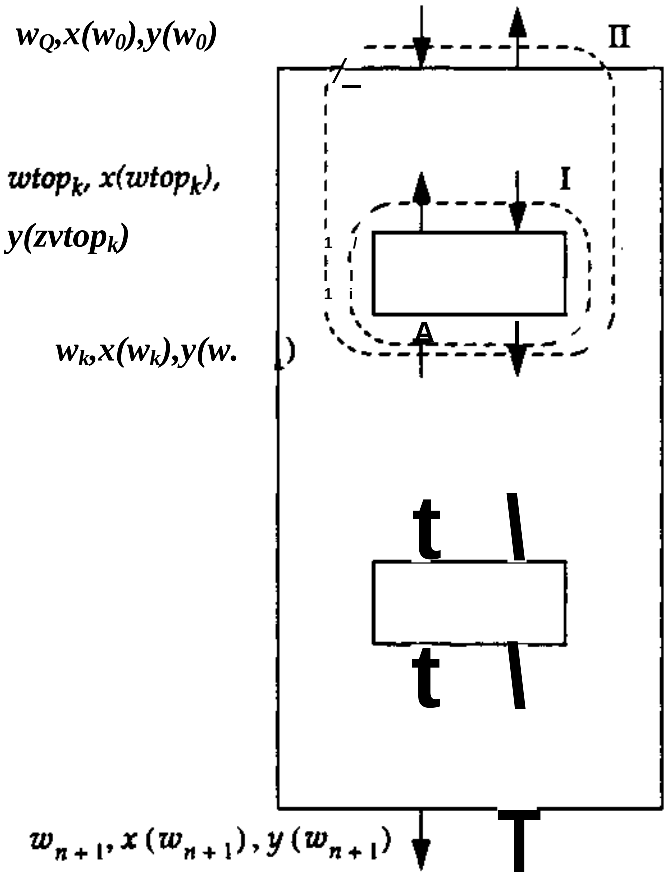

Figure 4. Diagram of collocation section, I and II are material and energy balance envelopes for a tray.

index. We use a general position index, w, which will be either the tray number or a transformation of the tray number which we shall describe later. The index denotes the distance from the top of the collocation section. We index each tray *k* by *wy,* the position of the bottom of the tray. We index the liquid entering and the vapor leaving the top of the tray by $wtop_k$, which in tray location is *w^-1,* but with a transformation on the tray location is more complicated. Equations 5,6, and 7 become the following

$$L(w_k)x_i(w_k) - L(wtop_k)x_i(wtop_k) = V(w_k)y_i(w_k) - V(wtop_k)y_i(wtop_k) \qquad (8)$$

$$y_{\mathfrak{t}}(zvtop_k) = \frac{{}^{a}1^{\cdot}}{\alpha}x_{\{}(w_k) \quad , T_L(w_k) = Ty(wtop_k), Pi(w_k) = Py(wtop_k) \tag{9}$$

$$L(w_k)h(w_k) - L(wtop_k)h(wtop_k) = V(w_k)H(w_k) - V(wtop_k)H(wtop_k) \tag{10}$$

Starting with an isolated tray, Table 3 aids the degrees of freedom analysis for a collocation tray. Collocation of the liquid mole fractions requires the liquid input and output compositions for the tray to be on the polynomial approximations of the liquid mole fraction. Collocating the liquid and vapor mole fractions for n_c-l components creates 4(n_c-l) equations. The number of variables introduced (the polynomial coefficients) will depend on the order of the polynomial, which we shall decide later.

Using a Lagrange polynomial, the following equations:

$$x_{\mathfrak{t}}(w) = \overset{n+1}{\underset{lc=0}{{}^{1}\pounds}} w_k(w)x_i(w_k) \qquad i = l...iic-l \tag{11}$$

$$y_{\mathfrak{t}}(zv) = \overset{rt+1}{\underset{*=o}{\wedge}} W_{fc}(u;)y_{f}.(w_{fc}) \quad i = l...\text{»}c-l \tag{12}$$

are the polynomial approximations of order *n* for the liquid and vapor mole fractions at position *w*. We use a Lagrange form because the coefficients of the polynomials, $Xj(w_k)$ and $\}/j(w_k)$ are also the liquid and vapor mole fraction at position w_k, the location of the k^{th} collocation point. The lc term of a Lagrange polynomial, W_k, is defined by the following equation:**

$$W_k(w) = \underset{j=o}{TT}\frac{\text{"JL?}\,TV-IV.}{*}2-_{;} \tag{13}$$

Table 3. Degrees of Freedom for a Single Tray

	New Variables	New Equations
tray model	$2(n_c+2)+2$	
collocate x, y, for n_c -1	?	$4(n_c-1)$
collocate $\bar{h}$ for liquid and vapor	?	4
CMB around end		n_c
HB around end		1
Fix Pressures		3
Fix $\bar{a}$ at 1		1
totals	$2n_c+6$ + ?	$5n_c+5$
Net equations	??	$3n_c-1$

Collocating the enthalpies of the liquid and vapor entering and leaving introduces 4 equations. Again, the number of polynomial coefficients introduced as new variables will depend on the order of the polynomial. The following equations define the enthalpy polynomials.

$$h(w) = \sum_{k=0}^{n+1} W_k(w)\, h(w_k) \tag{14}$$

$$H(w) = \sum_{k=0}^{n+1} W_k(w)\, H(w_k) \tag{15}$$

Since a single tray is isolated, we can add some overall balance equations between the tray and the end of the collocation section:

Component Mass Balances:

$L(w_k)x_i(w_k)$ - ^ ^ j j ^ w ^ J =

$$V(w_k)\,y_i(w_k) - V\left(w_{n_s+1}\right)y_i\left(w_{n_s+1}\right) \tag{16}$$

Heat balance:

$$L(w_k)h(w_k) \quad - L\left(w_{n_s+1}\right)h\left(w_{n_s+1}\right) =$$

$$V(w_k)\,H(w_k) - V\left(w_{n_s+1}\right)H\left(w_{n_s+1}\right) \tag{17}$$

The component mass balance adds n_c equations, and the heat balance adds 1 equation. Since we are assuming a constant pressure column, we need to fix the pressures of both input streams and one output stream, adding 3 equations. Finally, we specify that $\bar{a}$ for the tray is fixed at 1.0. This leaves a total of $3n_c-1$ excess equations for each collocation tray. The question marks indicate that we have not yet accounted for the polynomial coefficients.

Table 4 aids the degrees of freedom analysis for the entire section. The section has n_s trays, introducing $n_s(3n_c-1)$ net new equations. It also has two input and two output streams, creating $4(M_C+2)$ variables. Specifying the two input streams creates $2(n_c+2)$ equations. We can write the following balances over the entire section:

Component Mass Balances:

$$L(0)\,x_i(0) - L\left(w_{n_s+1}\right)x_i\left(w_{n_s+1}\right) =$$

$$V(0)\,y_i(0) - V\left(w_{n_s+1}\right)y_i\left(w_{n_s+1}\right) \tag{18}$$

Table 4. Degrees of Freedom for Section

	New Variables	New Equations
ns trays		$n_s(3n_c-1)$
4 streams	$4(n_c+2)$	
2 stream specs		$2(n_c+2)$
CMB		n_c
HB		1
Fix Pressures		2
collocate x, y for n_c -1	?	$4(n_c-1)$
collocate $\bar{h}$ for liquid and vapor	?	4
totals	$4n_c+8$ + ?	$7n_c+7+n_s(3n_c-1)$
Net equations		$(n_s+1)(3n_c-1)$

Heat balance:

$$L(0)\,h(0) - L\left(w_{n_s+1}\right)h\left(w_{n_s+1}\right) = V(0)\,H(0) - V\left(w_{n_s+1}\right)H\left(w_{n_s+1}\right) \tag{19}$$

The component mass balance creates n_c equations, and the heat balance creates 1 equation. Fixing the pressures of the two output streams introduces 2 equations. Collocating the liquid and vapor mole fractions introduces $4(n_c$-l) equations. Again, the number of variables introduced depends on the order of the polynomials. Collocating the enthalpies creates 4 equations. The net equations for a collocation section is $(n_s$+l)$(3n_c$-l).

With n_c-\ liquid and vapor polynomials, and 1 polynomial for the liquid and vapor enthalpies, there are a total of $2n_c$ polynomials, so the number of variables introduced by the polynomials will be $2n_c$(n+l), where n is the order of the polynomial. In principle we want to choose n so the number of equations and variables are equal for the section model:

$$2n_c(n + 1) = (n_s + 1)\ (3n_c - 1) \qquad (20)$$

For three components and two stages, n is 3, while for four components and two stages n is 3.25. In most cases, n is not an integer, so something is not right. Previous papers select $n = n_s$. This leaves $(n_\$ + l)(n_c - 1)$ excess equations. We expect the number of trays and the order of the polynomials to be linked, but we must remove the excess equations.

Cho and Joseph[1983] showed that when they assumed constant molar overflow the component material balances between the trays and the end of the collocation section given by equation 16 were held even when not enforced. We have found that the error in the component mass balances is negligible even for heat balanced columns. Rather than enforce the component mass balances between each tray and the end of the collocation section, we can enforce only the overall mass balance for each tray:

$$L(w_k)\ -\ Uw_{ns}\wedge)\ =\ V(w_k)\ -\ ViWns+i) \qquad (21)$$

This removes $(n_c$ -1) equations per tray. Furthermore, if we enforce the component mass balance over the entire section given by equation 18, we do not need to calculate both output streams from the polynomials. Therefore, we can ignore the polynomial equations for the compositions for one output stream, removing the remaining n_c-l equations for the entire collocation section. This removes the $(n_s + l)(n_c - 1)$ extra equations, giving us zero degrees of freedom if we set $n = n_s$. Therefore, for a two tray collocation section, we get a second degree polynomial with three coefficients for each fitted component.

Another option is to add slacks to the ignored equations in the first example. If the slacks are too large, one can add more trays. When the component material balances between the individual trays and the top of the collocation section are ignored, the components can be out of balance on individual trays even though they will be in mass balance over the entire section. Our tests have shown that even with nonideal systems with constant molar overflow, the component mass balances are satisfied. Also the polynomial equations for the one output stream that we ignored in the first case is satisfied. When we use heat balances rather than constant molar overflow, the component mass balances have very small errors, and the polynomial equations have slightly more significant errors. However, even when the trajectories of the collocation section are inaccurate, the residuals of these equations are not good indicators of the error.

A third alternative is to minimize the residuals of all the equations and solve for a best set of n_s+1 coefficients for each polynomial:

$$\begin{aligned} &\min(\|\varepsilon\|) \\ &eqn_j = \varepsilon_j \end{aligned} \tag{22}$$

However, the arguments just given show that the additional equations did not have significant error terms. Therefore, the optimization would probably only yield a minor improvement on the first option.

We have used the first option in this work. The order of the polynomial will be the same as the number of stages used as collocation points.

Point Placement

The most difficult decision in collocation is the placement of the collocation points. Carnahan et al [69] showed that, for integration of differential equations, collocation points placed at the zeros of an orthogonal polynomial were best. However, this is not necessarily true for collocation of a distillation column. Cho and Joseph [1983] placed their points at the zeros of Jacobi polynomials defined by,

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Motivation

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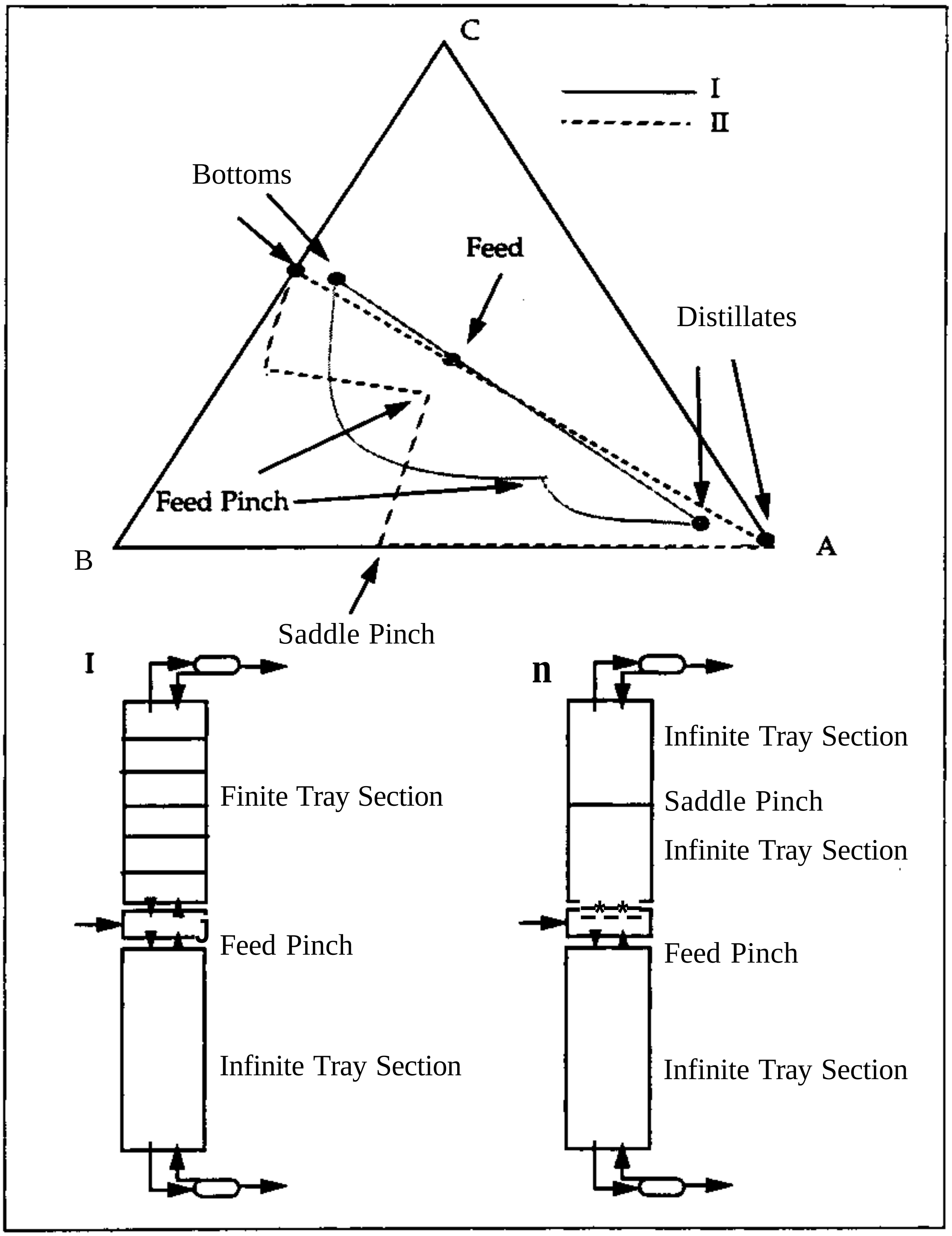

Figure 1. Minimum reflux trajectories and column configurations

which of these constraints are active. We saw that one can still use a pinch strategically located, but we also discovered that one needs a tray by tray column section model in a form which can compute the number of trays it contains. Conventional column models require one to specify the trays as an integer input.

This thinking led us to consider using a collocation model for the parts of the column where Levy et al. [1985] used a tray by tray computation. For such a column section, the number of trays is a continuous variable which the model can compute.

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To guarantee the intersection of the column sections for sharp splits, one must prove the existence of a tray by tray calculation linking a saddle pinch point and the feed tray composition, a calculation that passes through an infinite number of trays. This requirement led us to examine extending the collocation model to handle an infinite number of trays. We looked at different transformations to map tray number going from zero to infinity onto a variable z that goes from zero to one. With such a model, we concluded we should be able to compute minimum reflux for any column by computing pinch points and properly located column sections that can have a finite or an infinite number of trays. For case I shown in Figure 1, a finite collocation section simulates the unknown number of trays. For case II, the infinite tray section between the saddle pinch point and the feed tray is modeled by an infinite collocation section.

We began developing a collocation method capable of simulating infinite column sections and discovered several other advantages and uses for collocation. Distillation design requires an adaptable column model, with the ability to compute the number of trays in each distillation section, a computation that discovers how many trays one needs and where to place the feed. One can simulate complex column configurations. Optimal design of distillation sequences requires small robust models for each distillation column. Collocation both reduces the size of a column model and provides a continuous variable for the number of trays. Furthermore, the variable transformation required for modeling an infinite tray section improved the accuracy whenever such separation problem requires a relatively large number of trays.

Background of Collocation

Cho and Joseph [1983] developed a reduced-order method for modeling staged separation processes. They used orthogonal collocation to obtain accurate solutions of significantly reduced-order. Their model had a single collocation section for each section of the column. They tested by modeling a simple absorber system, and binary and three component distillation, and used the Antoine equation for the equilibrium relationship. In later papers Srivastava and Joseph [1984,1987a] developed methods for handling multiple feeds and side draws.

They also developed a complex method for handling steep and flat composition profiles by fitting the composition profiles with different polynomials for each component. They developed a complicated approach using two sets of collocation points, global and local, to fit both the key components and non key components [Srivastava and Joseph, 1987b]. They tested these later ideas using constant relative volatility systems.

Stewart, Levien, and Morari [1984] developed a collocation method that stresses selecting gridpoints based on the stagewise nature of distillation. Their method became stage-by-stage at full order, and had errors at least an order of magnitude smaller than Cho and Joseph's default choice of collocation points. They tested for binary and six-component distillation columns with constant relative volatility and for a ternary system using UNIQUAC for equilibrium. Swartz and Stewart [1986] applied the method to design, iteratively passing from the model to an SQP optimization algorithm. Swartz and Stewart [1987] also developed a finite-element method for handling multiphase distillation problems.

Recently, Seferlis and Hrymak [1994] adapted the model of Stewart et al. [1984] by using collocation elements to track irregularities in column profiles for existing columns. They investigated optimal placing of the collocation elements, based on comparison with the actual column. They obtained higher accuracy with multiple collocation sections of lower order than with a single collocation section of higher order.

Table 1 lists the characteristics of each of these collocation methods as well as the characteristics of the model presented in this paper.

Description of Model

Collocation is generally thought of as a method for numerically solving differential equations. The use of collocation for simulation of a distillation column is an extension of this technique. Given a differential equation,

Table 1. Comparison of Collocation Methods

	Elements/ Section	Placement of points	Thermo-dynamics tested	Variable transformations
Choand Joseph 1983	Single	Continuous orthogonal (Jacobi)	Antoine	none
Srivastava and Joseph 1987	Single(global), Multiple(local)	Continuous orthogonal (Jacobi)	Constant relative volatility	none
Stewart et al 1984	Single	Discrete orthogonal (Hahn)	UNIQUAC	none
Swartz and Stewart 1986	Single	Discrete orthogonal (Hahn)	Ideal	none
Swartz and Stewart 1987	Multiple (breakpoints at phase changes)	Discrete orthogonal (Hahn)	Nonideal three phase	none
Seferlis and Hrymak 1994	Multiple	Discrete orthogonal (Hahn)	Regression of data	none
This work	Multiple	Continuous (orthogonal for 2 or 3 points)	UNIFAC/ Pitzer	Transform tray number and mole fractions

$$\frac{dy}{dx} = f(x, y)\ ,\ y(0) = y_0 \tag{1}$$

we want to find y as a function of *x*. We can approximate y as a polynomial in *x*,

$$\hat{y}: \; = \; y<>^{+}\ a_{\backslash}x + a\ {}_{2}x^{2} + \ldots + a_{n}x^{n} \tag{2}$$

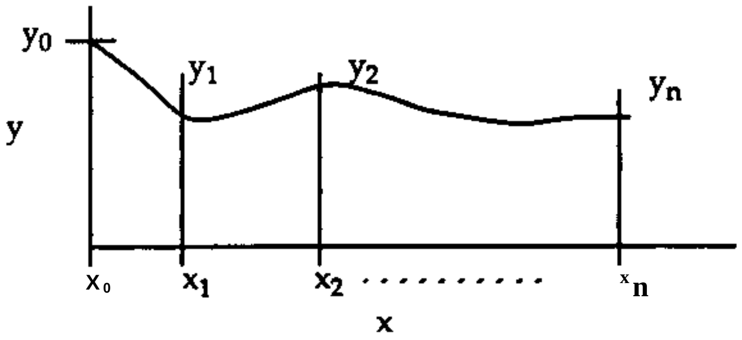

Figure 2. Collocation of a differential equation

We can then approximate y, *dy/dx*, and/as functions of *x*. At any point in *x*, we can define an error for this approximation,

$$error(x) = f(x,y) - \left(a_1 + 2a_2x^1 + \ldots + na_nx^{n-1} \right) \qquad (3)$$

At *n* collocation points, $x..x_n$, we say that the error =0 and get *n* equations to solve for *n* coefficients to the polynomial. See Figure 2.

Collocation of a distillation column uses the same concepts. A set of equations defines a distillation column tray, where *x* would be the tray location in the column and y would be mole fractions. Polynomials defined by tray location approximate the mole fractions and, at each collocation point, the set of equations for a distillation column must be satisfied.

There are many equations in a distillation column model, even a reduced order model. Rather than just list the basic equations, we are going to provide a detailed degrees of freedom analysis to demonstrate the reason for using a certain set of equations.

We begin the degrees of freedom analysis with a stream model. Gibbs phase rule gives the number of degrees of freedom for a system in equilibrium.

$$F = 2 + n_c - n_p \qquad (4)$$

F is the number of degrees of freedom for a given number of components, n_c, and a given number of phases, n_p. For a single phase, F is $n_c + 1$. For a stream we also need a flowrate which adds one more variable, giving $n_c + 2$ degrees of freedom. The set of variables could be the molar flowrates, temperature, and pressure. Once we know $n_c + 2$ of these variables and assume the phase, we can compute all other molar properties. We shall assume a stream introduces a net of $n_c + 2$ new variables and shall assume all other properties are available.

A standard distillation tray has two input streams and two output streams, as shown in Figure 3. The four streams introduce a net of $4(n_c + 2)$ new variables, which is the first entry on Table 2. By keeping track of the number of variables and equations introduced by each new element of the model, we can determine the degrees of freedom, and how many variables must be fixed to obtain a system with the same number of equations and free variables. We can write the following equations for a single tray.

Component Material Balances:

$$L(out)x_{\{}(out) - L(in)Xi(in) = V(in)y_t{<}in) - V(out)y_{\{}(out) \qquad (5)$$

Equilibrium:

$$y_{i}\,(\text{out}) = \frac{\alpha_i}{\alpha} *_{i} \{out) \quad , T_L(out) = Ty(out), P_L(out) = Py(out) \qquad (6)$$

Heat balance:

$$L(in)h(in) - L(out)h(out) = V(in)H(in) - V(out)H(out) \qquad (7)$$

L, *V, x, y, h, H* are liquid flowrate, vapor flowrate, liquid mole fraction, vapor mole fraction, liquid molar enthalpy, and vapor molar enthalpy, respectively, a; is the relative volatility of species *i*, and $\bar{a}$ is the mole fraction average relative volatility. The liquid and vapor molar enthalpies and the relative volatilities are functions of

composition and temperature. We write equations 5 and 6 for each component

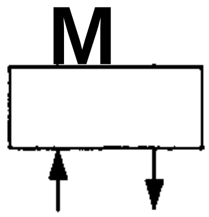

Figure 3. Diagram of tray

and equation 7 once. As shown in Table 2, the component material balances therefore introduce n_c equations. There are $n_c + 2$ equilibrium equations. The equilibrium equation also introduces one new variable, $\bar{a}$. The heat balance, which could be replaced by a constant molar overflow assumption, introduces one equation. Therefore, the degrees of freedom for an isolated tray are $2(n_c+2)+2$. Specifying two input streams, the pressure and $\bar{\mathbf{a}}$ of the tray would be sufficient to solve the tray model.

Table 2. Degrees of Freedom for an Isolated Tray

	New Variables	New Equations
4 streams	$4(n_{c+}2)$	
CMB		n_c
Equilibrium	1	$n_c + 2$
HB		1
totals	$4(n_c+2)+1$	$2n_c+3$
DOF for isolated tray	$2(n_c+2) + 2$	

Figure 4 shows a diagram of a single collocation section. A collocation section has a liquid input and vapor output at the top and a vapor input and liquid output at the bottom. The example shown has two collocation trays which are not connected. In this example, we number from the top of the collocation section downward. Liquid and vapor streams passing each other have the same

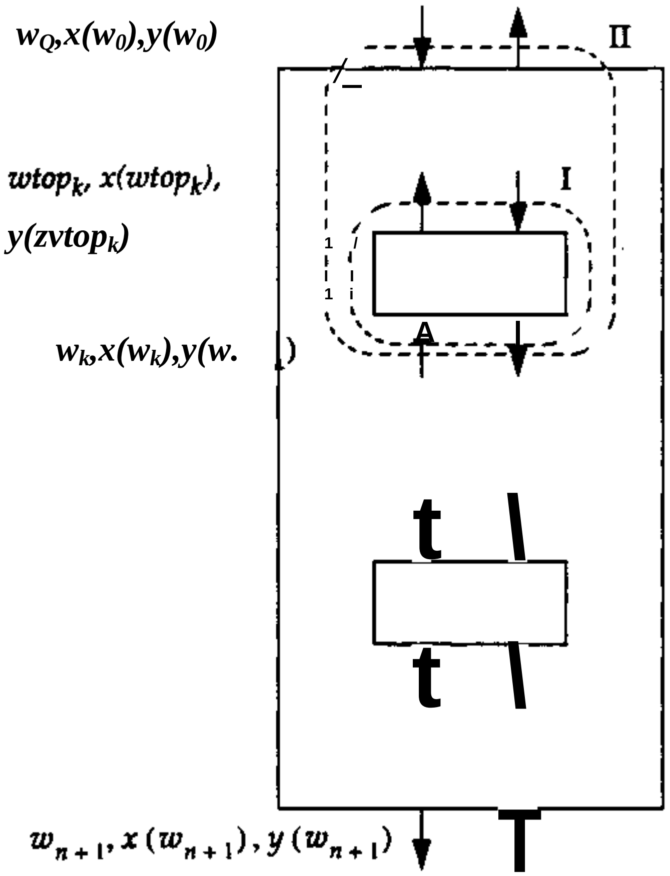

Figure 4. Diagram of collocation section, I and II are material and energy balance envelopes for a tray.

index. We use a general position index, w, which will be either the tray number or a transformation of the tray number which we shall describe later. The index denotes the distance from the top of the collocation section. We index each tray *k* by *wy,* the position of the bottom of the tray. We index the liquid entering and the vapor leaving the top of the tray by *wtop*$_k$, which in tray location is *w^-1,* but with a transformation on the tray location is more complicated. Equations 5,6, and 7 become the following

$$L(w_k)x_i(w_k) - L(wtop_k)xi(wtop_k) = V(w_k)y_i(w_k) - V(wtop_k)y_i(wtop_k) \qquad (8)$$

$$y_i(wtop_k) = \frac{\alpha_i}{\bar{\alpha}} x_i(w_k) \quad , \; T_L(w_k) = T_V(wtop_k), \; P_L(w_k) = P_V(wtop_k) \tag{9}$$

$$L(w_k)h(w_k) - L(wtop_k)h(wtop_k) = V(w_k)H(w_k) - V(wtop_k)H(wtop_k) \tag{10}$$

Starting with an isolated tray, Table 3 aids the degrees of freedom analysis for a collocation tray. Collocation of the liquid mole fractions requires the liquid input and output compositions for the tray to be on the polynomial approximations of the liquid mole fraction. Collocating the liquid and vapor mole fractions for n_c-1 components creates 4(n_c-1) equations. The number of variables introduced (the polynomial coefficients) will depend on the order of the polynomial, which we shall decide later.

Using a Lagrange polynomial, the following equations:

$$x_i(w) = \sum_{k=0}^{n+1} W_k(w) x_i(w_k) \qquad i = 1 \ldots n_c - 1 \tag{11}$$

$$y_i(w) = \sum_{k=0}^{n+1} W_k(w) y_i(w_k) \qquad i = 1 \ldots n_c - 1 \tag{12}$$

are the polynomial approximations of order *n* for the liquid and vapor mole fractions at position *w*. We use a Lagrange form because the coefficients of the polynomials, $x_i(w_k)$ and $y_i(w_k)$ are also the liquid and vapor mole fraction at position w_k, the location of the k^{th} collocation point. The k^{th} term of a Lagrange polynomial, W_k, is defined by the following equation:

$$W_k(w) = \prod_{\substack{j=0 \\ j \neq k}}^{n+1} \frac{w - w_j}{w_k - w_j} \tag{13}$$

Table 3. Degrees of Freedom for a Single Tray

	New Variables	New Equations
tray model	$2(n_c+2) +2$	
collocate x, y, for n_c -1	?	$4(n_c-1)$
collocate $\bar{h}$ for liquid and vapor	?	4
CMB around end		n_c
HB around end		1
Fix Pressures		3
Fix $\bar{a}$ at 1		1
totals	$2n_c+6$ + ?	$5n_c+5$
Net equations	??	$3n_c-1$

Collocating the enthalpies of the liquid and vapor entering and leaving introduces 4 equations. Again, the number of polynomial coefficients introduced as new variables will depend on the order of the polynomial. The following equations define the enthalpy polynomials.

$$h(w) = \sum_{k=0}^{n+1} W_k(w)\, h(w_k) \tag{14}$$

$$H(w) = \sum_{k=0}^{n+1} W_k(w)\, H(w_k) \tag{15}$$

Since a single tray is isolated, we can add some overall balance equations between the tray and the end of the collocation section:

Component Mass Balances:

$$L(w_k)_{Xi}(w_k)\ -\ \wedge\ \wedge\ \mathrm{j}\ \mathrm{j}\ \wedge\ \mathrm{w}\ \wedge\ \mathrm{J}\ =$$

$$V(w_k)\,y_i(w_k) - V\left(w_{n_s+1}\right)y_i\left(w_{n_s+1}\right) \qquad (16)$$

Heat balance:

$$L(w_k)h(w_k) \quad -L\left(w_{n_s+1}\right)h\left(w_{n_s+1}\right) =$$

$$V(w_k)\,H(w_k) - V\left(w_{n_s+1}\right)H\left(w_{n_s+1}\right) \qquad (17)$$

The component mass balance adds n_c equations, and the heat balance adds 1 equation. Since we are assuming a constant pressure column, we need to fix the pressures of both input streams and one output stream, adding 3 equations. Finally, we specify that $\bar{a}$ for the tray is fixed at 1.0. This leaves a total of $3n_c$-l excess equations for each collocation tray. The question marks indicate that we have not yet accounted for the polynomial coefficients.

Table 4 aids the degrees of freedom analysis for the entire section. The section has n_s trays, introducing $n_s(3n_c-1)$ net new equations. It also has two input and two output streams, creating $4(M_C+2)$ variables. Specifying the two input streams creates $2(n_c+2)$ equations. We can write the following balances over the entire section:

Component Mass Balances:

$$L(0)\,x_i(0) - L\left(w_{n_s+1}\right)x_i\left(w_{n_s+1}\right) =$$

$$V(0)\,y_i(0) - V\left(w_{n_s+1}\right)y_i\left(w_{n_s+1}\right) \qquad (18)$$

Table 4. Degrees of Freedom for Section

	New Variables	New Equations
ns trays		$n_s(3n_c-1)$
4 streams	$4(n_c+2)$	
2 stream specs		$2(n_c+2)$
CMB		n_c
HB		1
Fix Pressures		2
collocate x, y for n_c -1	?	$4(n_c-1)$
collocate $\bar{h}$ for liquid and vapor	?	4
totals	$4n_c+8$ + ?	$7n_c+7+n_s(3n_c-1)$
Net equations		$(n_s+1)(3n_c-1)$

Heat balance:

$$L(0)\,h(0) - L\left(w_{n_s+1}\right)h\left(w_{n_s+1}\right) = V(0)\,H(0) - V\left(w_{n_s+1}\right)H\left(w_{n_s+1}\right) \tag{19}$$

The component mass balance creates n_c equations, and the heat balance creates 1 equation. Fixing the pressures of the two output streams introduces 2 equations. Collocating the liquid and vapor mole fractions introduces 4(n_c-l) equations. Again, the number of variables introduced depends on the order of the polynomials. Collocating the enthalpies creates 4 equations. The net equations for a collocation section is (n_s+l)(3n_c-l).

With n_c-\ liquid and vapor polynomials, and 1 polynomial for the liquid and vapor enthalpies, there are a total of $2n_c$ polynomials, so the number of variables introduced by the polynomials will be 2n_c(n+l), where *n* is the order of the polynomial. In principle we want to choose n so the number of equations and

variables are equal for the section model:

$$2n_c(n + 1) = (n_s + 1)\ (3n_c - 1) \tag{20}$$

For three components and two stages, *n* is 3, while for four components and two stages *n* is 3.25. In most cases, *n* is not an integer, so something is not right. Previous papers select $n = n_s$. This leaves $(n_\$ + l)(n_c - 1)$ excess equations. We expect the number of trays and the order of the polynomials to be linked, but we must remove the excess equations.

Cho and Joseph[1983] showed that when they assumed constant molar overflow the component material balances between the trays and the end of the collocation section given by equation 16 were held even when not enforced. We have found that the error in the component mass balances is negligible even for heat balanced columns. Rather than enforce the component mass balances between each tray and the end of the collocation section, we can enforce only the overall mass balance for each tray:

$$L(w_k) - Uw_{ns}\hat{}) = V(w_k) - ViWns{+}i) \tag{21}$$

This removes $(n_c - 1)$ equations per tray. Furthermore, if we enforce the component mass balance over the entire section given by equation 18, we do not need to calculate both output streams from the polynomials. Therefore, we can ignore the polynomial equations for the compositions for one output stream, removing the remaining n_c-l equations for the entire collocation section. This removes the $(n_s + l)(n_c - 1)$ extra equations, giving us zero degrees of freedom if we set $n = n_s$. Therefore, for a two tray collocation section, we get a second degree polynomial with three coefficients for each fitted component.

Another option is to add slacks to the ignored equations in the first example. If the slacks are too large, one can add more trays. When the component material balances between the individual trays and the top of the collocation section are ignored, the components can be out of balance on individual trays

even though they will be in mass balance over the entire section. Our tests have shown that even with nonideal systems with constant molar overflow, the component mass balances are satisfied. Also the polynomial equations for the one output stream that we ignored in the first case is satisfied. When we use heat balances rather than constant molar overflow, the component mass balances have very small errors, and the polynomial equations have slightly more significant errors. However, even when the trajectories of the collocation section are inaccurate, the residuals of these equations are not good indicators of the error.

A third alternative is to minimize the residuals of all the equations and solve for a best set of n_s+1 coefficients for each polynomial:

$$\begin{aligned} &\min(\|\varepsilon\|) \\ &eqn_j = \varepsilon_j \end{aligned} \tag{22}$$

However, the arguments just given show that the additional equations did not have significant error terms. Therefore, the optimization would probably only yield a minor improvement on the first option.

We have used the first option in this work. The order of the polynomial will be the same as the number of stages used as collocation points.

Point Placement

The most difficult decision in collocation is the placement of the collocation points. Carnahan et al [69] showed that, for integration of differential equations, collocation points placed at the zeros of an orthogonal polynomial were best. However, this is not necessarily true for collocation of a distillation column. Cho and Joseph [1983] placed their points at the zeros of Jacobi polynomials defined by,

$$\int_0^1 z^{\beta} (1-z) z^{\alpha} P_n^{(\alpha,\beta)} (z)\, dz = 0 \qquad (23)$$

$$j = 0,\ 1,\ \ldots n-1$$

where a and p are parameters. Their default choice of the parameters for the Jacobi polynomial (a = 1, P = 1) resulted in evenly spaced points. They could have moved the points toward either end of the collocation section by adjusting the parameters and still have been using an orthogonal polynomial. Stewart et al. [1984] showed that placing the collocation points at the zeros of the Hahn polynomial created smaller errors than placing the points by the Jacobi polynomial, using the default values for a and p. They argued that the Hahn polynomial was a better choice because it maintained the stagewise nature of the column and did not require manipulating parameters for best placement of the collocation points. For full order, the collocation points would be placed exactly at the tray locations.

However, the benefit of the Hahn polynomial appears to be due largely to the fact that it spreads out the collocation points more than the default Jacobi selection. As one spreads the collocation points out from being evenly spaced to being all at the ends of the collocation section, the error will go through a minimum. The Hahn placement is closer to this minimum than the default Jacobi, but it is not the optimum. The following experiment demonstrates this. Three different collocation models were used to approximate a three component, constant relative volatility, constant molar overflow column with 15 trays above and below the feed. Figure 5 shows the column trajectories for the three different reflux ratios, generated by a tray-by-tray model. Two collocation sections were used to model the column, one above and one below the feed. We did several simulations with each collocation model with different spreads of the collocation points. For any number of collocation trays, the following equation defined the midpoint of the trays.

w_{mid} = *U>0 +fmid(Wns+l ' ™0>* **(24)**

where/$_m$# is 0.5 to have w_{mid} at the actual center of the collocation section. For the two tray model, the placement of the two collocation trays is defined by,

^{w}l = ^{w}mid + fint<^{w}mid ' ^{w}0> (25)

™2 = ™mid -fint^ns+l ' ^{w}mid> (26)

where *fj$_{nt}$* is 03333 for evenly spaced points.

For the three tray model, zv_2 is at w_{mid}, and we define *Wi* and w_3 as we defined w_1 and w_2 for a two tray model. For the three tray model, an^$_n$j of 0.5 gives evenly spaced points.

For the four tray model, we define *Wj* and zv_4 as we defined *Wi* and *Wi* for a two tray model. We place the interior points, *Wi* and *w$*, one third of the distance

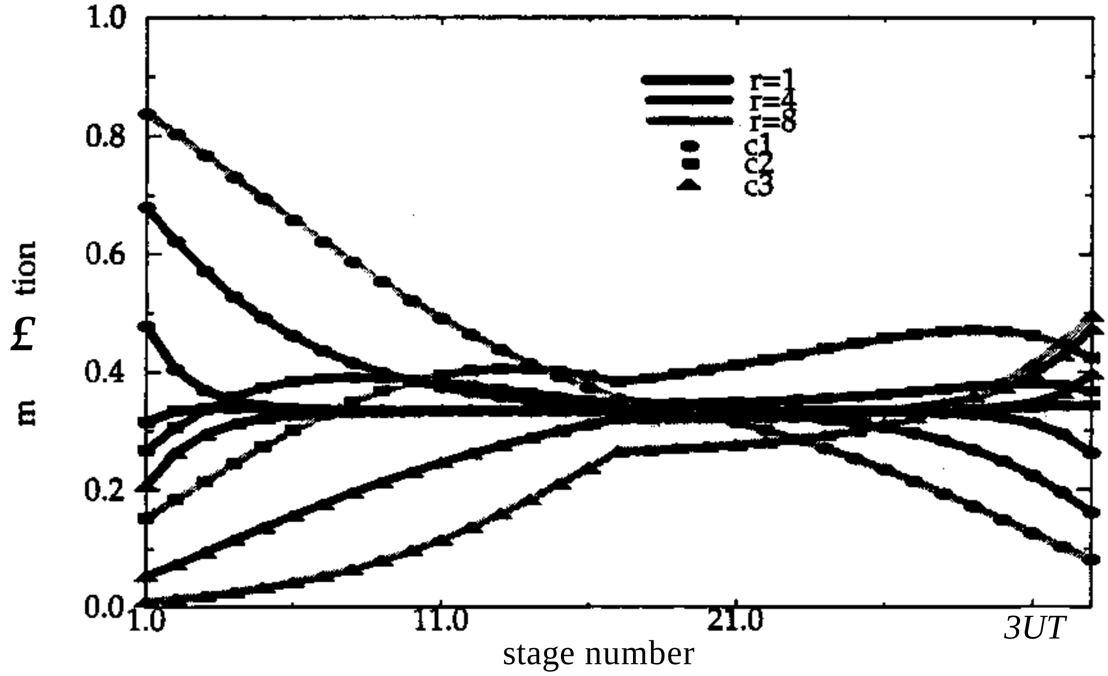

Figure 5. Column trajectories for components cl, c2, and c3 for a range of reflux ratios, r.

from w_{mid} to w_1 and w_4 respectively. For the four tray model, $anfi_{nt}$ of 0.6 gives evenly spaced points. For the two and three tray models, the Hahn placement is at a spread factor of 0.53748 and 0.71864.

For the four tray model, the Hahn placement of the outer points corresponds to a spread factor of 0.79244, but our placement of the inner points does not correspond to the Hahn placement. Figure 6 shows the average error in the mole fractions of the distillate over varying spread factors for each model at the three reflux ratios. Each plot is on a different scale, shown by the labels on the x axis, and the maximum error on the y axis. The Hahn placement points are shown with a larger data point. The standard Jacobi placement is evenly spaced points, which is atf_{int} of 0.333,0.5, and 0.6 for the two, three, and four tray collocations respectively. So, for each case, the Hahn placement has a smaller error than the default Jacobi placement, but not the minimum error possible. This figure also shows that the optimal spread of the collocation points is different for different reflux ratios.

For a low reflux ratio, the trajectories are very flat, and the minimum error occurs with a very wide spread of the collocation points, to get the nonlinear polynomial as flat as possible over the collocation section. As the reflux increases, the trajectories become less flat and then even linear with a fairly large slope. For these cases, there is an optimal spread of the collocation points. In the next section, we will show how variable transformations are more significant than point placement for increasing accuracy.

Variable Transformations

We use two variable transformations in this model to alleviate the problem of flattened trajectories. When the mole fraction of a component is not changing over part of a tray section, we call that a flattened trajectory. Flattened trajectories

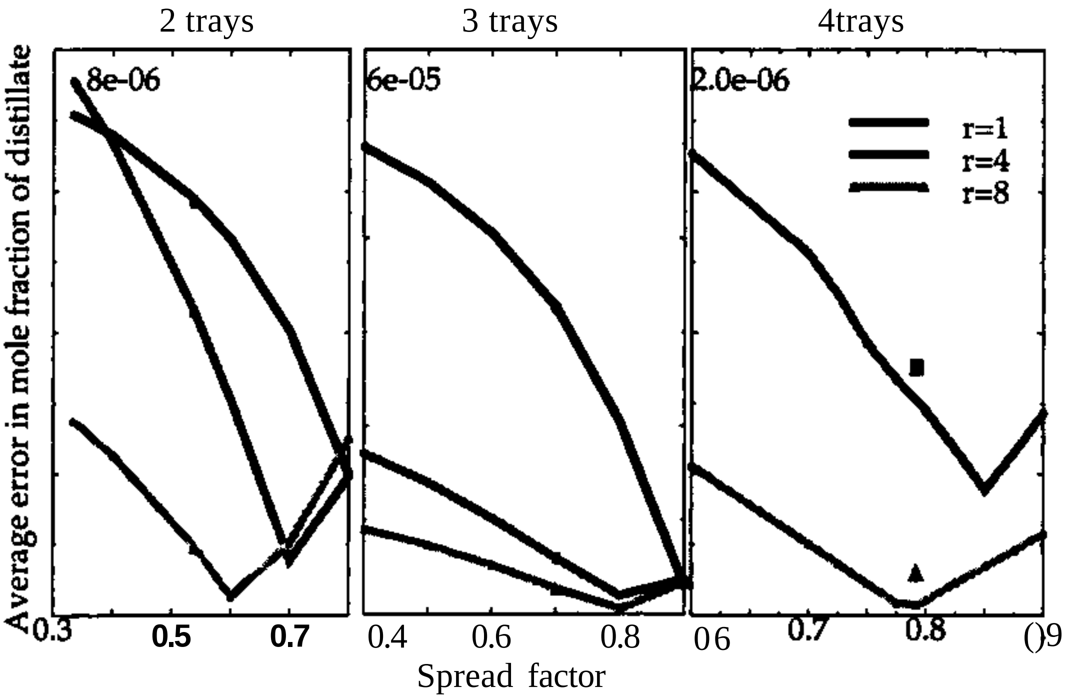

Figure 6. Effect of point placement on error

cannot be fit well with polynomials, so we perform variable transformations to alter the shape.

The first is a transformation of the tray number. To simulate a large number of trays, or an infinite number of trays, we want an index that goes to a finite value as the tray number goes to infinity. Even for finite columns with a large number of trays, the trajectories flatten out as the number of trays increases. Some possible transformations are:

$$z = 1 - e^{(-as)} \tag{27}$$

$$z = \frac{s}{s+a} \tag{28}$$

In both these equations, *s* is stage number, z is the transform variable, and a is a parameter. In both cases, z=0 when s=0, and z tends to 1 as *s* tends to infinity. To discover the better form of the transformation, we first investigated fitting results from the Kremser approximation:

$$y_s = \frac{1-A^S}{1-A} y_1 - \frac{A-A^S}{1-A} \hat{y}_0 \tag{29}$$

A T_U

[illegible]

Figure 7 shows that the variable transformation given by equation 27 did the best at straightening out the trajectory. In the Appendix, we show that, with the exponential variable transformation, the Kremser approximation can be exactly straightened out for the correct choice of *a*. Figure 8 shows how the choice of *a* affects the shape of the trajectories. At the proper selection of *a*, the data can be fitwith a linear function. Therefore, we use the variable transformation in equation 27.

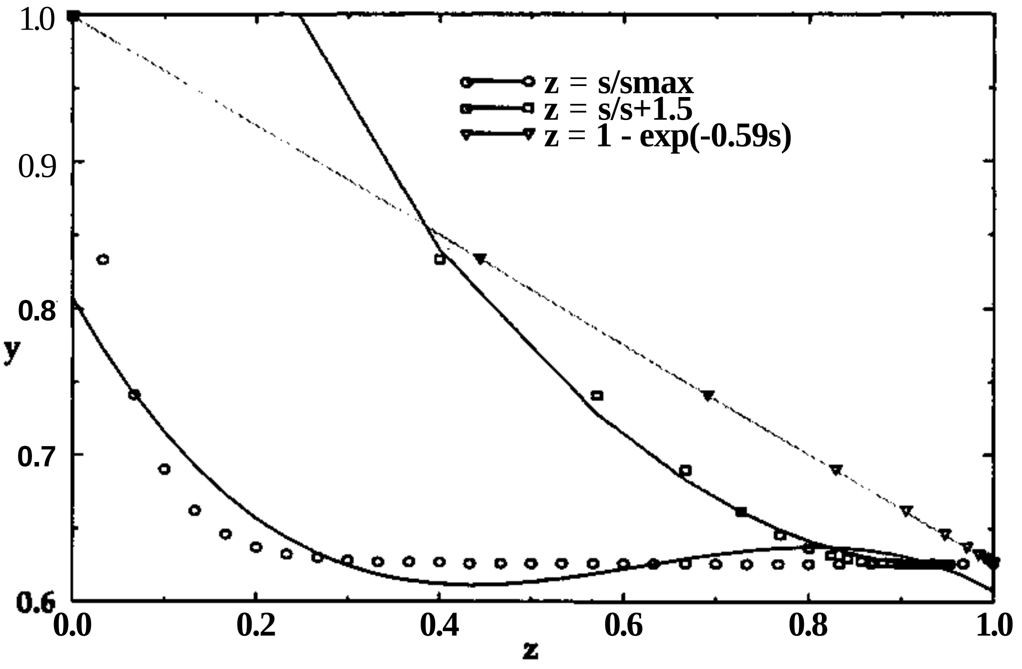

Figure 7. Comparison of variable transformations on *s*

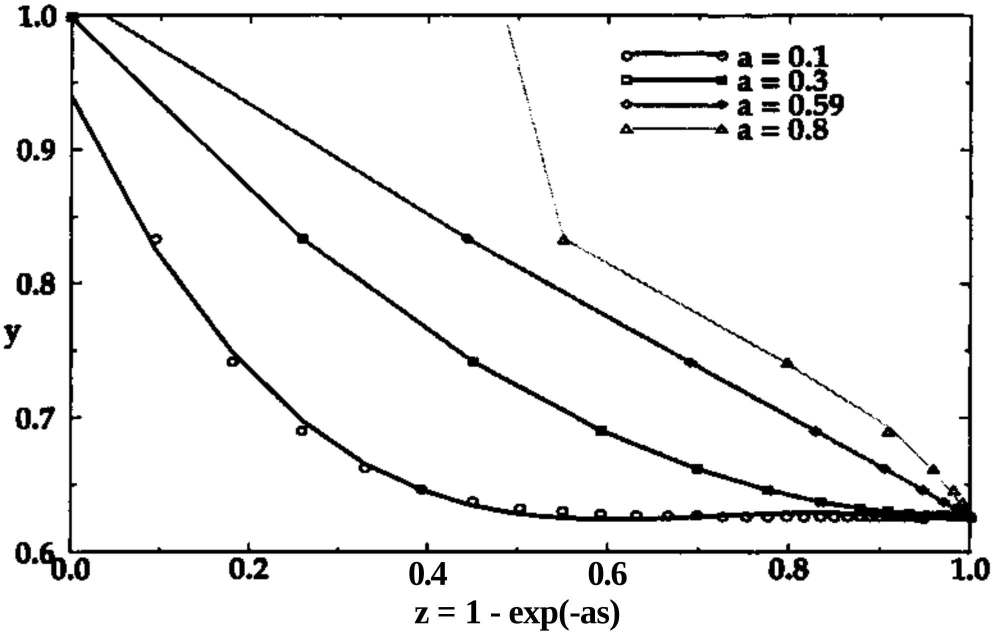

Figure 8. Effect of choice of *a*

Figure 9 shows column trajectories for a three component, constant relative volatility, constant molar overflow column with fifty trays above and below the feed, for three different reflux ratios, generated by a tray-by-tray model. Over the range of reflux ratios, r, we tested the collocation model, comparing the composition of the distillate product to the tray-by-tray calculation. The collocation model used had two collocation sections per column section, with two trays in each collocation section. We compared the *s* based and z based collocations over a range of point placements, using the point placements described in the last section. Figure 10 shows the average errors of both cases over the same range of point spreads for different reflux ratios. The z based collocation had lower average errors for every reflux ratio. For all but the lowest reflux ratio, the best solution was achieved with the z based collocation.

The second variable transformation is one on the mole fractions. When distilling to high purity, mole fractions go to one or zero, again flattening out the trajectory. We need to transform the asymptotic approach to zero and one into a decreasing and increasing function that can be fitted by the polynomial used in the collocation. We use the following transformation:

$$2*_{t}.-1 \quad = \quad \tanh(\hat{x}_i) \qquad (31)$$

As the mole fraction goes to one or zero, the transformation variable, $\hat{x}_i$, goes to negative infinity and plus infinity. Figure 11 shows the effect of this transformation. For exponential approach to one and zero, the transformation straightens the trajectory out, so the slope never goes to zero.

Without this transformation, modeling sharp splits is very difficult. As the mole fractions of some of the components approach zero or one, the polynomial will create a curved trajectory, "bouncing" off the boundary. It becomes impossible to model a column with a component going to a mole fraction of 10"^{6}

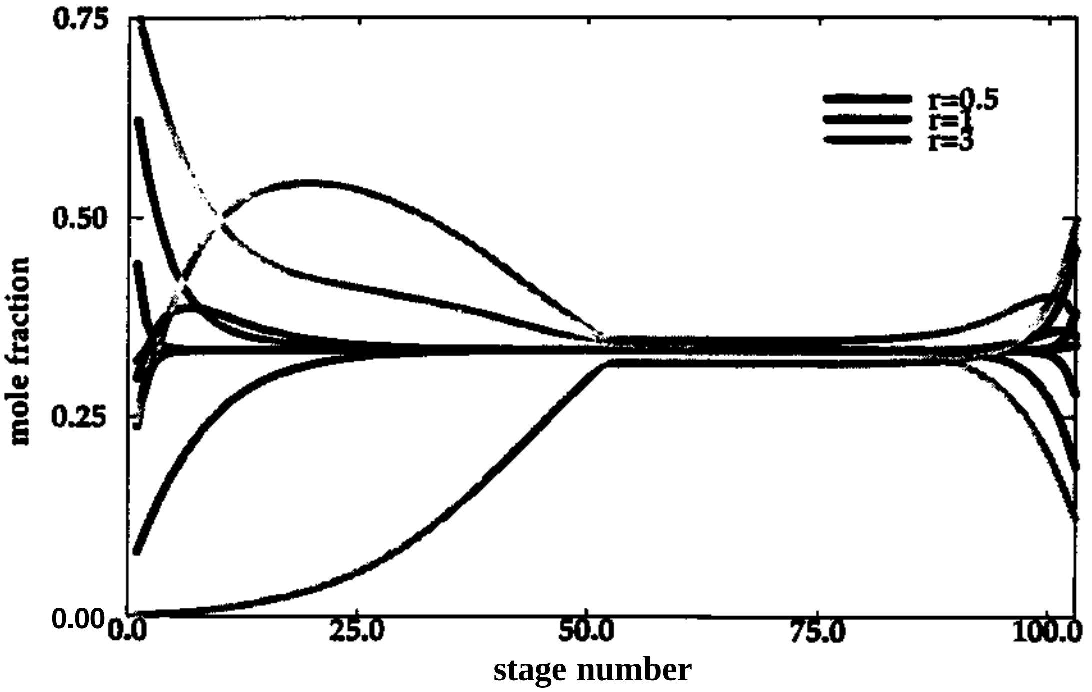

Figure 9. Column trajectories for a large column over a range of reflux ratios

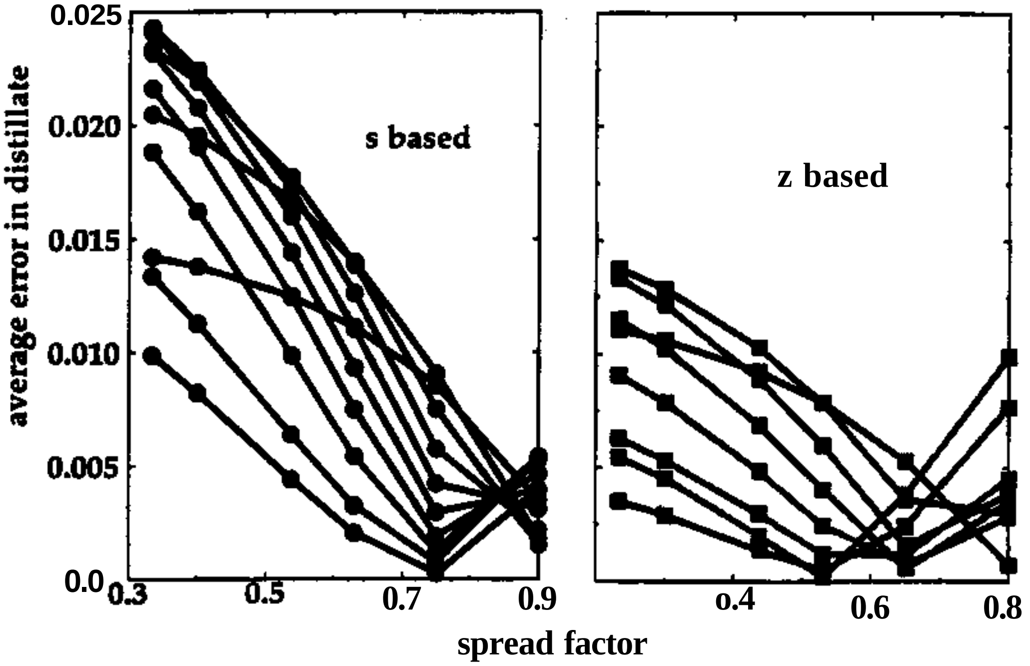

Figure 10. Error curves for s and z based collocation

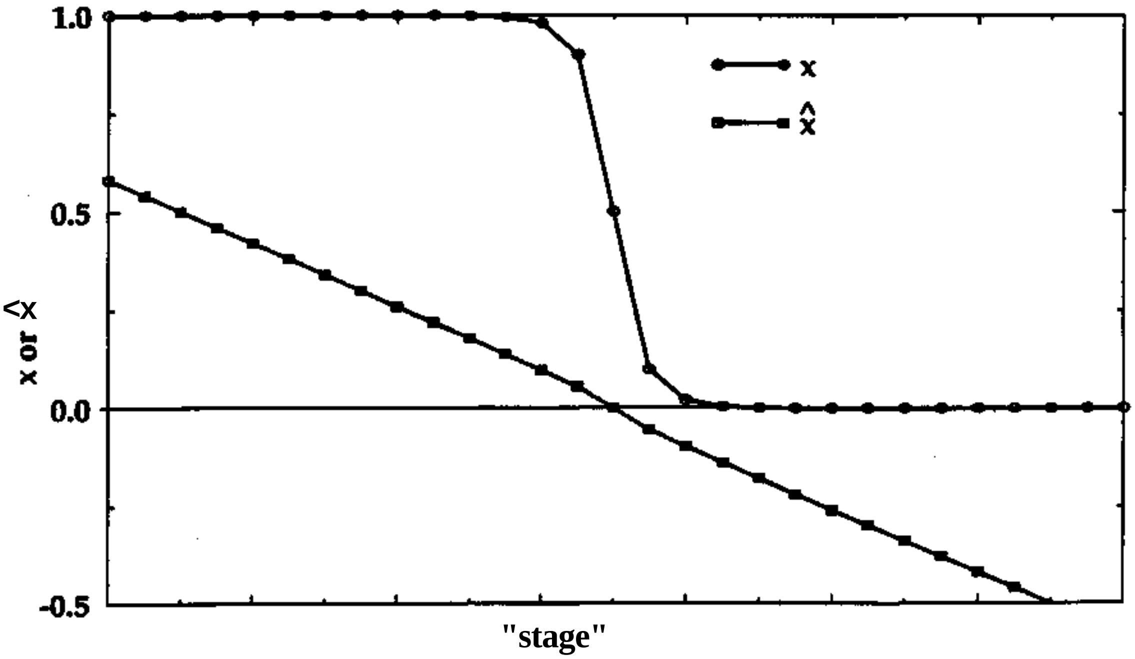

Figure 11. Effect of transformation on mole fraction, *x*

or smaller. However, the above transformation will give the polynomial room to move and will allow an asymptotic approach to the boundary. Figure 12 shows the four possible models of a 63 tray column which is removing all of the heavy component from the distillate. Figure 13 is a blowup of the trajectories for the heavy component near the top of the column. The two simulations without the transformation on mole fraction are curved and "bounce" up. The two solutions using the transformation smoothly approach the top of the column.

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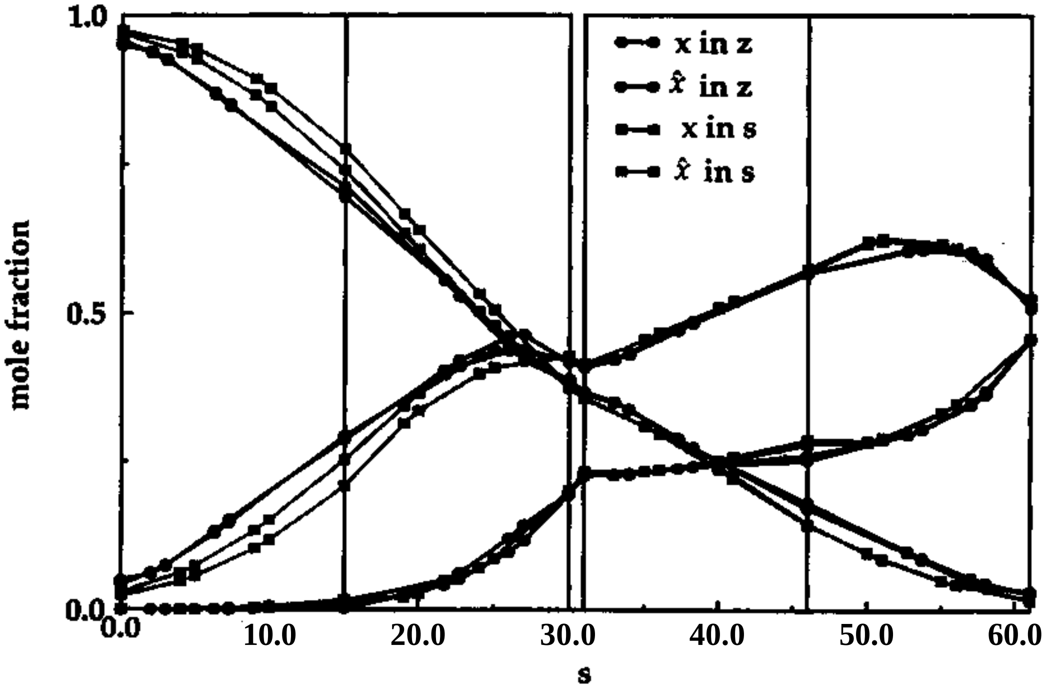
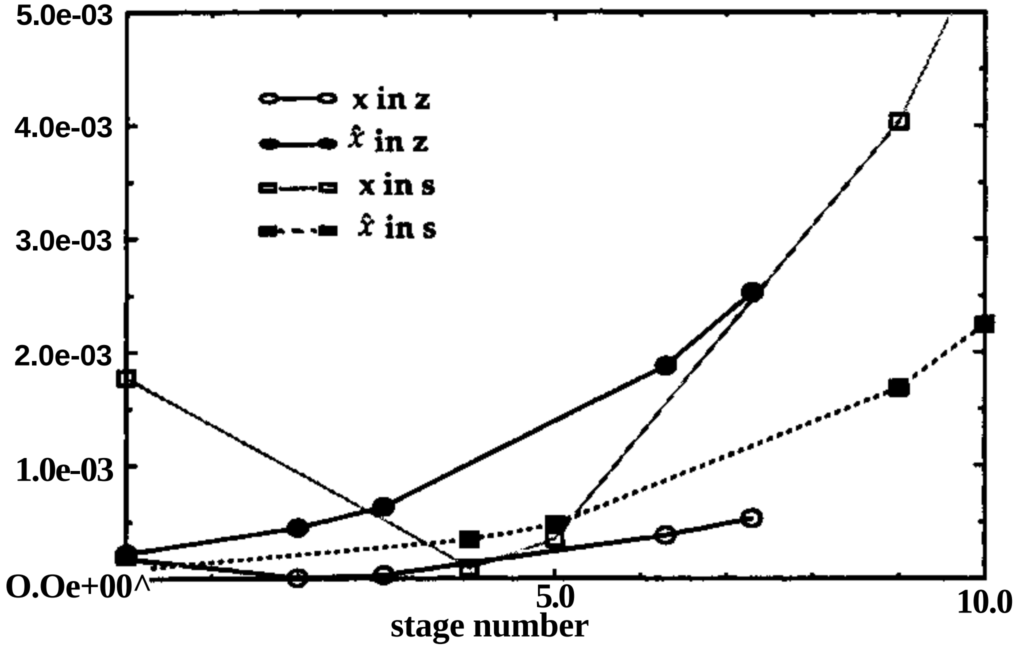


Figure 12. Effect of *x* transformation in a **column simulation**



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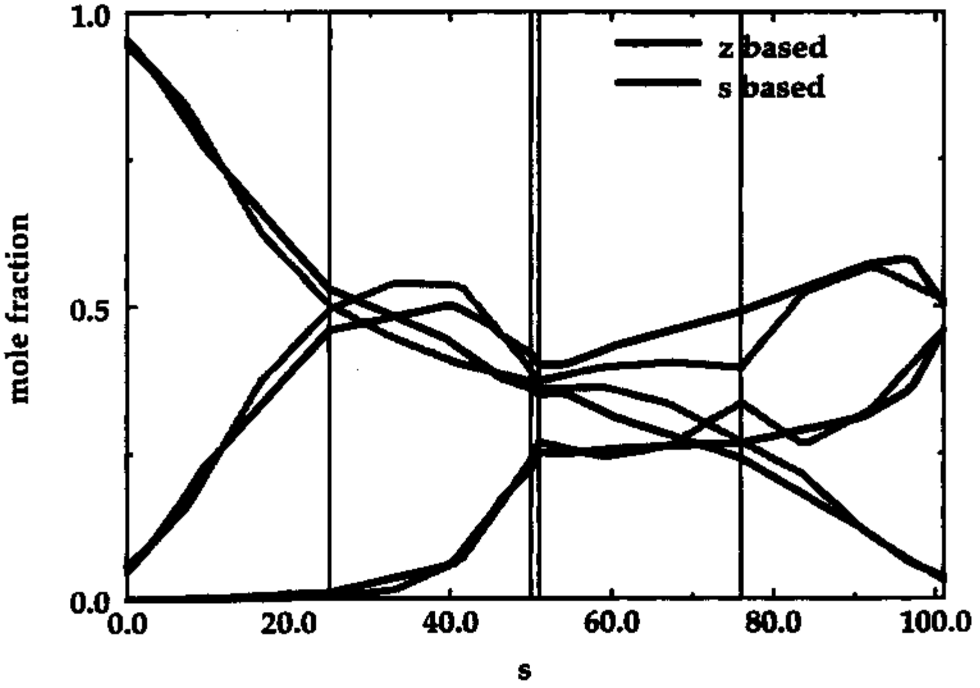

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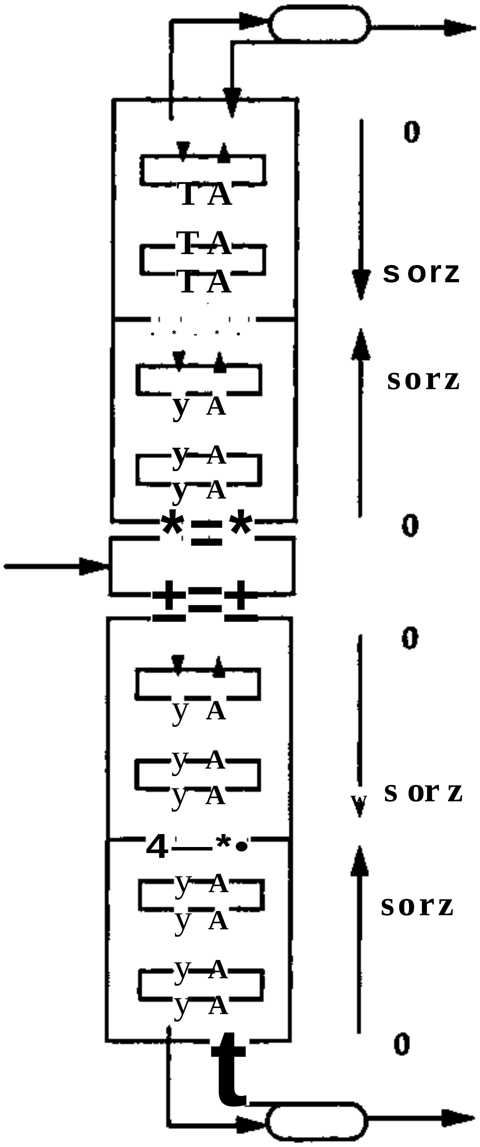

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Using the acetone, chloroform, benzene system, we performed many tests of the collocation model. The feed was a 36/24/40 mixture of acetone, chloroform, and benzene. A 33 tray column with a reflux ratio of 4.0 was used. We performed a search over the range of distillate to feed ratios to find the maximum binary separations, as done by Wahnschafft [1992]. Figure 17 shows the comparison of the binary separation range plots with those for a tray-by-tray calculation. The chloroform benzene binary separation factor is not meaningful before a D:F of 0.3, since practically nothing of either component is coming out of the distillate at low D:F. For the acetone-benzene binary separation factor curve the average error was 1%, and for the acetone-chloroform separation factor curve the average error was 3%. The collocation shows very good agreement with tray-by-tray calculations. The error in the acetone concentration in the distillate was less than 2% over the range of D:F ratios, with an average error of 1%. Figure 18 shows comparisons of three different column simulations on a ternary diagram. Including all the thermodynamic calculations, the tray-by-tray and collocation models had 3144 and 1811 equations respectively.

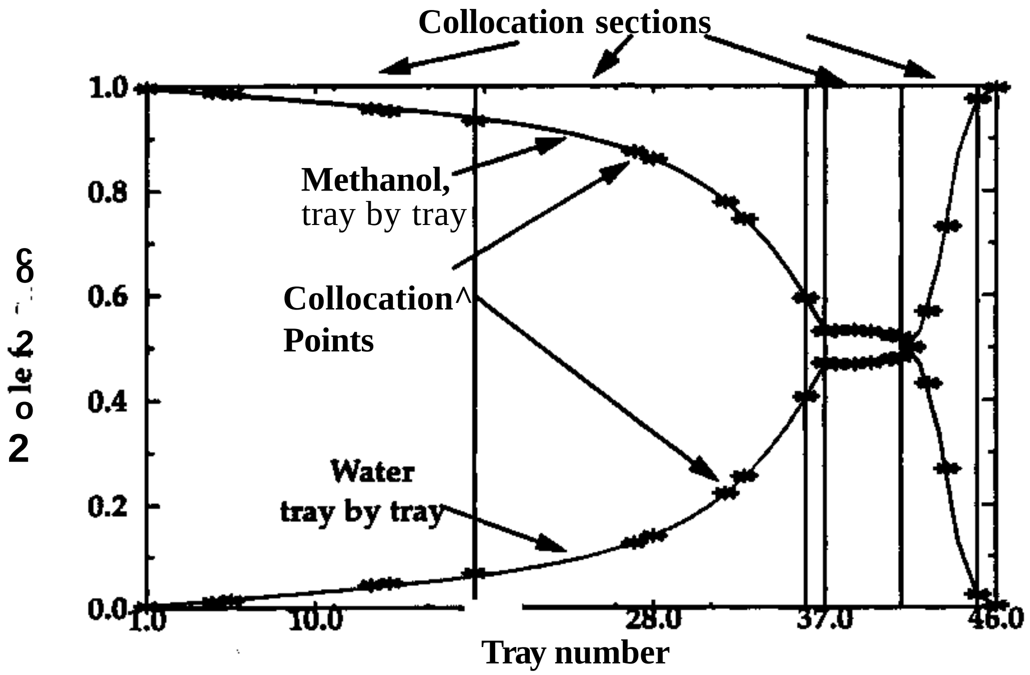


Figure 16. Comparison of collocation to rigorous model for methanol-water column

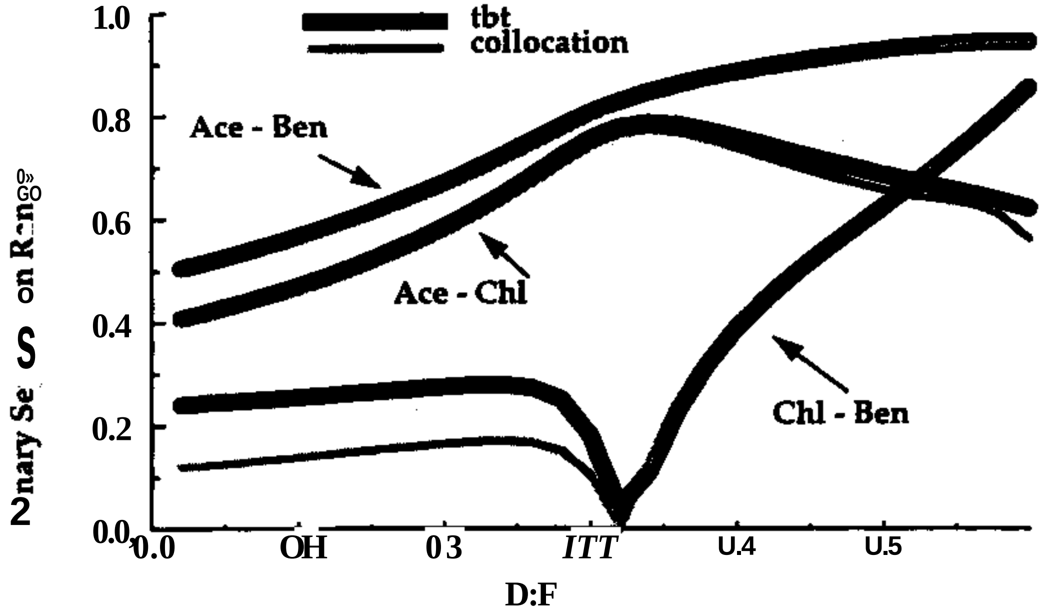


Figure 17. Comparison of collocation to rigorous model of separation range over D:F ratio for acetone-benzene-chloroform system

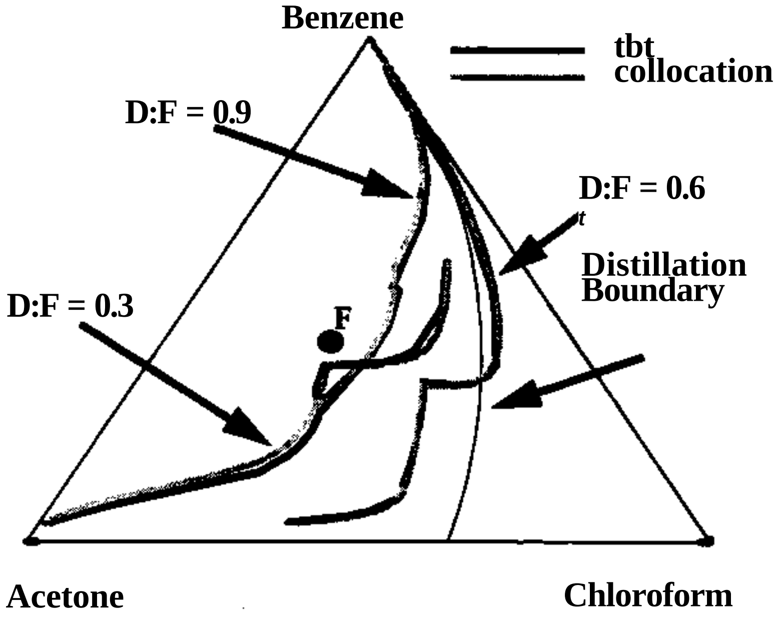


Figure 18. Comparison of collocation to rigorous model for acetone-benzene-chloroform column, for three different D:F ratios

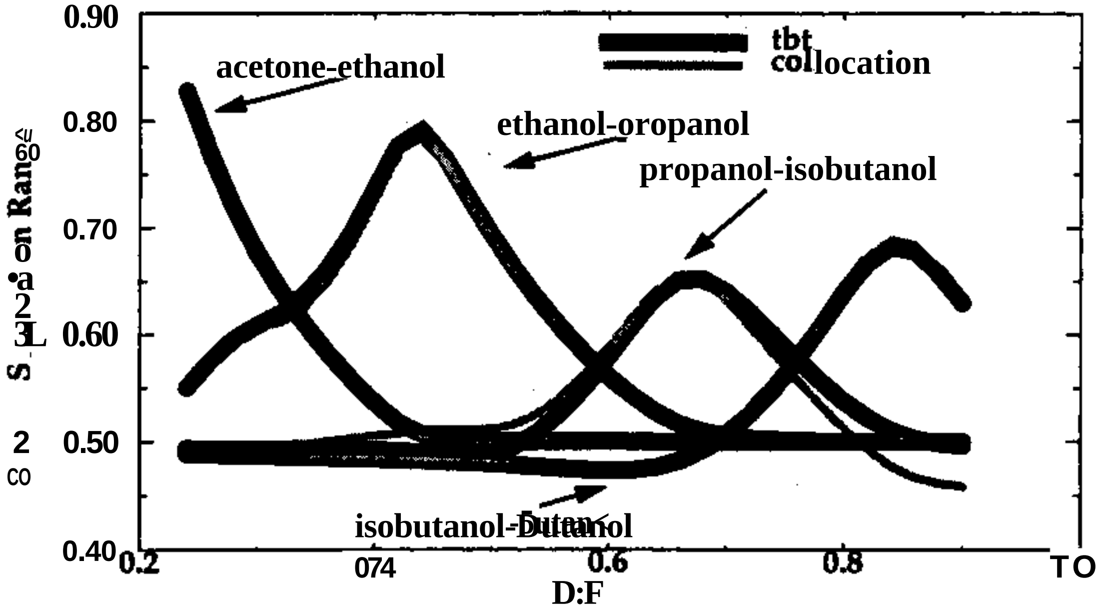


Figure 19. Comparison of collocation to rigorous model of separation range over D:F ratio for acetone-ethanol-propanol-isobutanol-butanol system

Finally, we performed a set of tests on an equimolar mixture of acetone, ethanol, propanol, isobutanol, and normal butanol, using a 23 tray column with a reflux ratio of 0.8. Figure 19 shows the comparison of the binary separation range plots for the components which are adjacent in the order of relative volatility. The other binary separation ranges compare equally well but would clutter the figure.

Conclusions

In this paper, we have demonstrated that this new collocation method can accurately reduce the order of column models. The two variable transformations greatly expand the capabilities of standard collocation methods. We have found that the degrees of freedom selection is important, and demonstrated what equations can be ignored. The choice of point placement is non-trivial, and no particular polynomial will give optimal point placement. Variable transformations more significantly reduce errors than proper point placement.

In two companion papers, we will discuss how collocation provides the missing link for simulation of minimum reflux conditions. We will also discuss a design algorithm for designing arbitrary columns using the collocation model.

Acknowledgment

Support from Eastman Chemicals and DOE contract number DE FG02-85ER13396 provide support for this research. Facilities support is from NSF grant number EEC-8942146 which supports the EDRC, an NSF funded Engineering Research Center.

Nomenclature

A	Simplification variable for Kremser approximation (L/KV)
a	Mole fraction average relative volatility
a	Parameter for exponential transformation of stage location
a	Parameter of Jacobi polynomial
α_i	Relative volatility of species i
p	Parameter of Jacobi polynomial
$fint$	Factor for selection of spread of collocation points
f_{mid}	Factor for selection of the midpoint of collocation points
h	Liquid molar enthalpy
H	Vapor molar enthalpy
K	Equilibrium constant used in Kremser approximation
L	Liquid molar flowrate
n	Order of polynomial
$*_c$	Number of components
n_p	Number of phases
$"_s$	Number of collocation points
P	Pressure
Pn	Jacobi polynomial of order n
s	Stage location
T	Temperature
V	Vapor molar flowrate
W_k	kth term of Lagrange polynomial
w_k	Position of bottom of tray k
$U>mid$	Midpoint for placement of collocation points
$wtop_k$	Position of top of tray k
x_i	Liquid mole fraction of component i
x_i	Transformed mole fraction
y_i	Vapor mole fraction of component i
z	Transformed stage location

References

Carnahan B., Luther H. A., Wilkes J. O., 1969, Applied Numerical Methods, Wiley, New York.

Cho Y.S. and B. Joseph., 1983. "Reduced-Order Steady-State and Dynamic Models for Separation Processes." *AIChE J.* 29,261-269,270-276

Julka V., and M. F. Doherty, 1990. Geometric Behavior and Minimum Hows for Nonideal Multicomponent Distillation. *Chemical Engineering Science,* 45, p. 1801-1822.

Koehler J., P Aguirre, and E. Blass., 1991. "Minimum Reflux Calculations for Nonideal Mixtures Using the Reversible Distillation Model." *Chem. Eng. Sci.,* 46.3007-3021.

Levy S. G., D.B. Van Dongen, and M. G. Doherty., 1985"Design and Synthesis of Homogeneous Azeotropic Distillations II: Minimum Reflux Calculations for Nonideal an d Azeotropic Columns." *Ind. and Eng. Chem. Fun.,* 24 463-474

Seferlis P and A. N. Hrymak, 1994, 'Optimization of Distillation units using collocation models', *AlChe J.* 40,813-825

Seferlis P and A. N. Hrymak, 1994, "Adaptive Collocation of Finite Elements Models for the Optimization of Multi-Stage Distillation Unit," *Chem. Eng. Sci..* 49,1369-1382

Stewart W. E., K. L. Levien, and M. Morari. 1984. "Collocation Methods in Distillation." in Westerberg, A.W., and H.H. Chien (eds), Proc. 2nd Intn'l Conf. Foundations Computer-aided Process Design (FOCAPD'83), CACHE Corp, Ann Arbor, MI, 535-569.

Swartz C. L. E. and Stewart W. E. 1986, "A Collocation Approach to Distillation Column Design," *AIChE J.* 32,1832-1838

Swartz C. L.E. and Stewart W. E. 1987, "Finite-Element Steady State Simulation of Multiphase Distillation," *AIChE J.* 33,1977-1985

Underwood, A. J. V. /. *Inst. Pet.* 1945,31, 111

Underwood, A. J. V., /. *Inst. Pet.* 1946,32,598

Underwood, A. J. V., *Chem. Eng. Prog.* 1948,44,603

Wahnschafft O. M 1992, "Synthesis of Separation Systems for Azeotropic Mixtures with and Emphasis on Distillation-Based Methods," Ph.D. Thesis, Dept of Chem. Eng., Technical University of Munich.

Appendix

Rewriting the Kremser approximation to gather terms with *s* produces the following equation.

$$Vs = \frac{\hat{}\;\hat{}}{I\text{-}A} \qquad \frac{\hat{}}{I\text{-}A}A^{s} \qquad (32)$$

Rewriting the variable transformation

$$\mathbf{z} = l\text{-}e^{(\text{-}''s)} \qquad (33)$$

for *s* in terms of z,

$$s = ln[\ (l\text{-}z)\sim^{a} J \qquad (34)$$

and placing it into the Kremser approximation produces the following equation.

$$y(z))=^{\wedge}J^{\wedge}\text{»}W\text{»}) \qquad {}^{-}\quad {}^{-a} \qquad (35)$$

If we define *A* = *exp(B),* then we can take the following steps

$$A^{ln\left(\ (\right.} \qquad n\left(\ (1-z)^{-u}\right)$$

$$^{J} = (exp\ (B))$$

$$= exp\left(\ In\left(\ (exp(B))\right.\right. \quad ^{ln\left(\ (1-z)^{-u}\right)}\Big)\Big)$$

$$*exp[B[ln[(l\text{-}z) \quad ^{-}*\Big)\Big)\Big)$$

$$= expy\ ln[\ (1\text{-}z)^{-aB}\Big)\Big)$$

$$= \ (1\text{-}z)^{-aB} \qquad (36)$$

Now equation 35 becomes the following.

$$y(z) = \frac{y_1 - A\hat{y}_0}{1-A} - \frac{y_1 - \hat{y}_0}{1-A}(1-z)^{-aB} \quad (37)$$

Therefore, when -*aB* = 1, the equation is linear in z.

w_{mid} = *U>0 +fmid(Wns+l ' ™0>* **(24)**

where/$_{m}$# is 0.5 to have w_{mid} at the actual center of the collocation section. For the two tray model, the placement of the two collocation trays is defined by,

^{w}*l* = ^{w}*mid* + *fint<*^{w}*mid ' *^{w}*0>* (25)

™*2* = ™*mid -fint^ns+l ' *^{w}*mid>* (26)

where *fj*$_{nt}$ is 03333 for evenly spaced points.

For the three tray model, zv_2 is at w_{mid}, and we define *Wi* and w_3 as we defined w_1 and w_2 for a two tray model. For the three tray model, an^$_{n}$j of 0.5 gives evenly spaced points.

For the four tray model, we define *Wj* and zv_4 as we defined *Wi* and *Wi* for a two tray model. We place the interior points, *Wi* and *w$*, one third of the distance

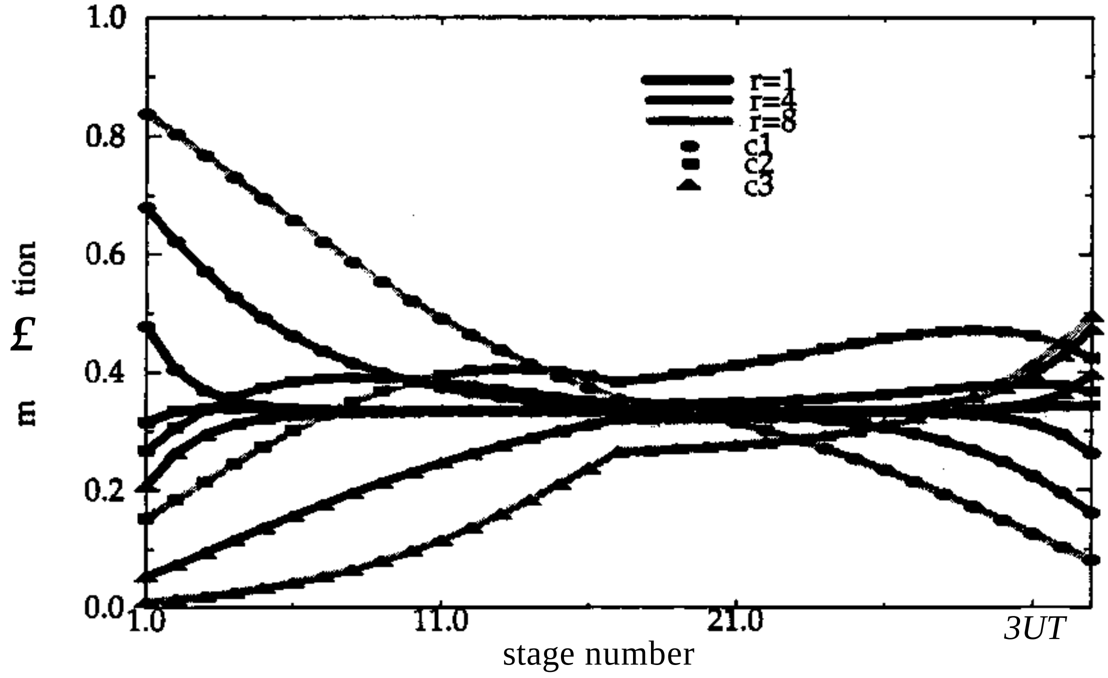


Figure 5. Column trajectories for components cl, c2, and c3 for a range of reflux ratios, r.

from w_{mid} to w_1 and w_4 respectively. For the four tray model, $anfi_{nt}$ of 0.6 gives evenly spaced points. For the two and three tray models, the Hahn placement is at a spread factor of 0.53748 and 0.71864.

For the four tray model, the Hahn placement of the outer points corresponds to a spread factor of 0.79244, but our placement of the inner points does not correspond to the Hahn placement. Figure 6 shows the average error in the mole fractions of the distillate over varying spread factors for each model at the three reflux ratios. Each plot is on a different scale, shown by the labels on the x axis, and the maximum error on the y axis. The Hahn placement points are shown with a larger data point. The standard Jacobi placement is evenly spaced points, which is atf_{int} of 0.333,0.5, and 0.6 for the two, three, and four tray collocations respectively. So, for each case, the Hahn placement has a smaller error than the default Jacobi placement, but not the minimum error possible. This figure also shows that the optimal spread of the collocation points is different for different reflux ratios.

For a low reflux ratio, the trajectories are very flat, and the minimum error occurs with a very wide spread of the collocation points, to get the nonlinear polynomial as flat as possible over the collocation section. As the reflux increases, the trajectories become less flat and then even linear with a fairly large slope. For these cases, there is an optimal spread of the collocation points. In the next section, we will show how variable transformations are more significant than point placement for increasing accuracy.

Variable Transformations

We use two variable transformations in this model to alleviate the problem of flattened trajectories. When the mole fraction of a component is not changing over part of a tray section, we call that a flattened trajectory. Flattened trajectories

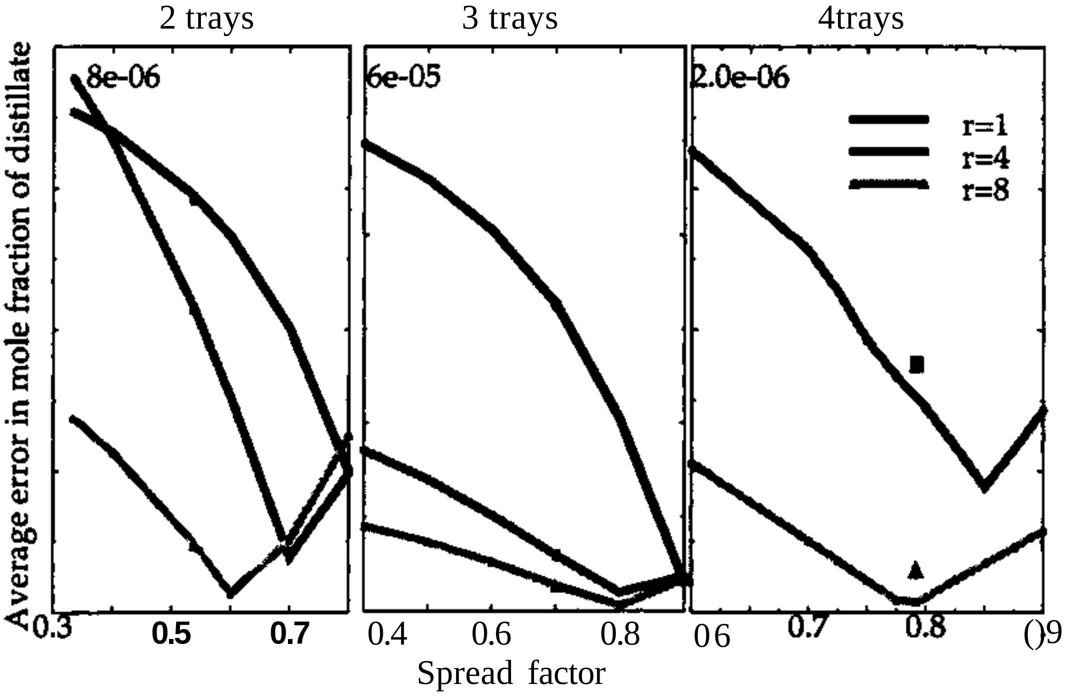


Figure 6. Effect of point placement on error

cannot be fit well with polynomials, so we perform variable transformations to alter the shape.

The first is a transformation of the tray number. To simulate a large number of trays, or an infinite number of trays, we want an index that goes to a finite value as the tray number goes to infinity. Even for finite columns with a large number of trays, the trajectories flatten out as the number of trays increases. Some possible transformations are:

$$z = 1 - e^{(-as)} \tag{27}$$

$$z = \frac{s}{s+a} \tag{28}$$

In both these equations, *s* is stage number, z is the transform variable, and a is a parameter. In both cases, z=0 when s=0, and z tends to 1 as *s* tends to infinity. To discover the better form of the transformation, we first investigated fitting results from the Kremser approximation:

$$y_s = \frac{1\text{-}A^S}{1-A} y_1 - \frac{A\text{-}A^S}{1-A} \hat{y}_0 \qquad (29)$$

A [illegible]

Figure 7 shows that the variable transformation given by equation 27 did the best at straightening out the trajectory. In the Appendix, we show that, with the exponential variable transformation, the Kremser approximation can be exactly straightened out for the correct choice of *a*. Figure 8 shows how the choice of *a* affects the shape of the trajectories. At the proper selection of *a*, the data can be fitwith a linear function. Therefore, we use the variable transformation in equation 27.

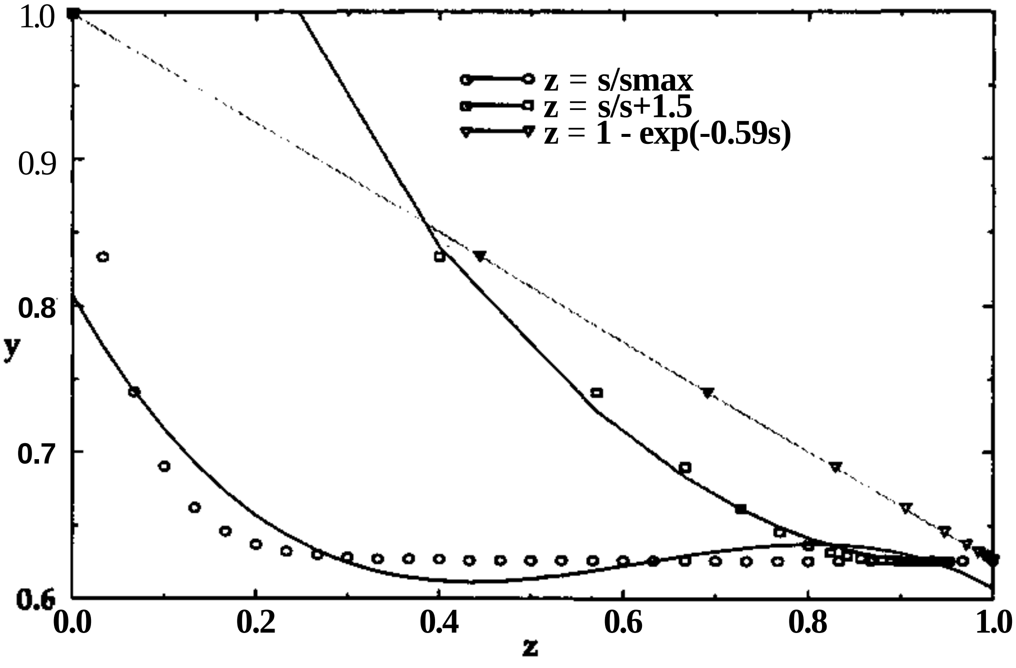


Figure 7. Comparison of variable transformations on *s*

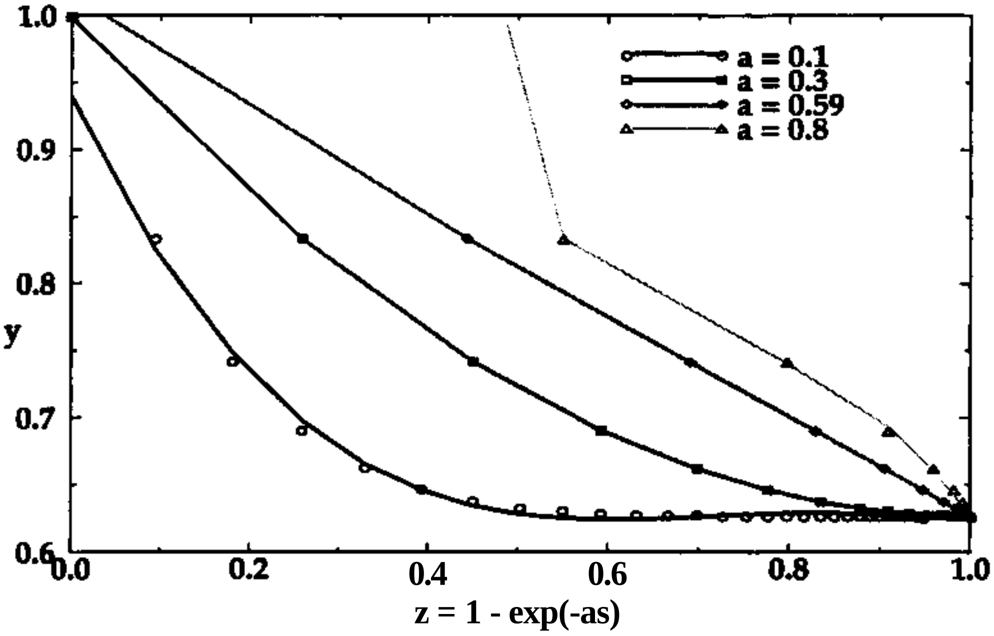


Figure 8. Effect of choice of *a*

Figure 9 shows column trajectories for a three component, constant relative volatility, constant molar overflow column with fifty trays above and below the feed, for three different reflux ratios, generated by a tray-by-tray model. Over the range of reflux ratios, r, we tested the collocation model, comparing the composition of the distillate product to the tray-by-tray calculation. The collocation model used had two collocation sections per column section, with two trays in each collocation section. We compared the *s* based and z based collocations over a range of point placements, using the point placements described in the last section. Figure 10 shows the average errors of both cases over the same range of point spreads for different reflux ratios. The z based collocation had lower average errors for every reflux ratio. For all but the lowest reflux ratio, the best solution was achieved with the z based collocation.

The second variable transformation is one on the mole fractions. When distilling to high purity, mole fractions go to one or zero, again flattening out the trajectory. We need to transform the asymptotic approach to zero and one into a decreasing and increasing function that can be fitted by the polynomial used in the collocation. We use the following transformation:

$$2x_i - 1 = \tanh(\hat{x}_i) \qquad (31)$$

As the mole fraction goes to one or zero, the transformation variable, $\hat{x}_i$, goes to negative infinity and plus infinity. Figure 11 shows the effect of this transformation. For exponential approach to one and zero, the transformation straightens the trajectory out, so the slope never goes to zero.

Without this transformation, modeling sharp splits is very difficult. As the mole fractions of some of the components approach zero or one, the polynomial will create a curved trajectory, "bouncing" off the boundary. It becomes impossible to model a column with a component going to a mole fraction of 10^{-6}

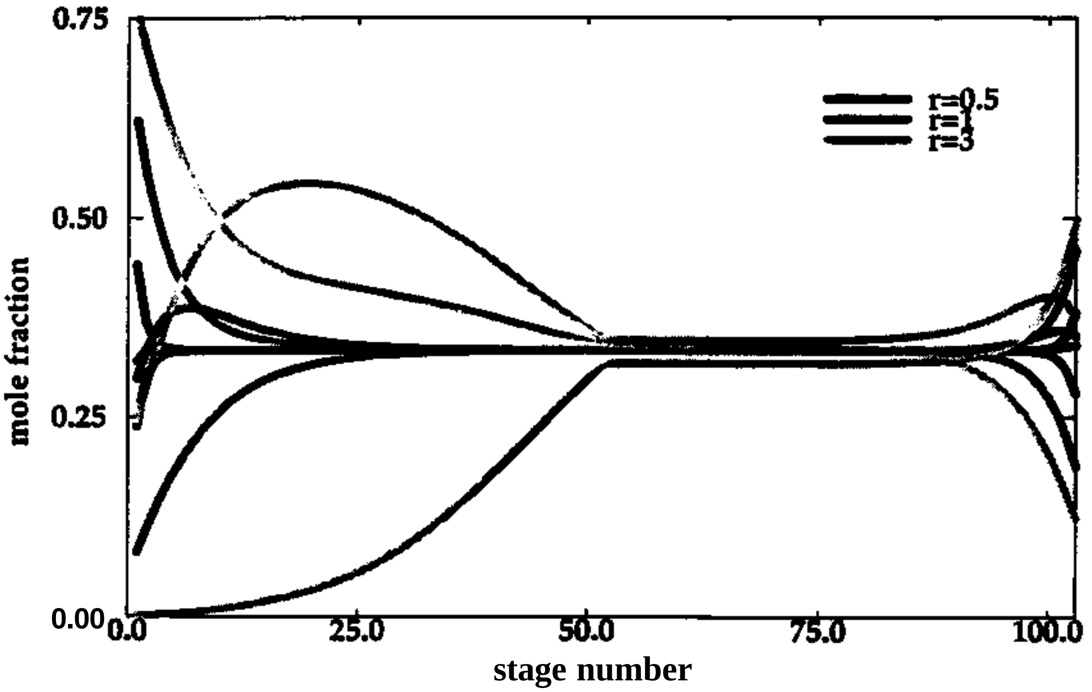


Figure 9. Column trajectories for a large column over a range of reflux ratios

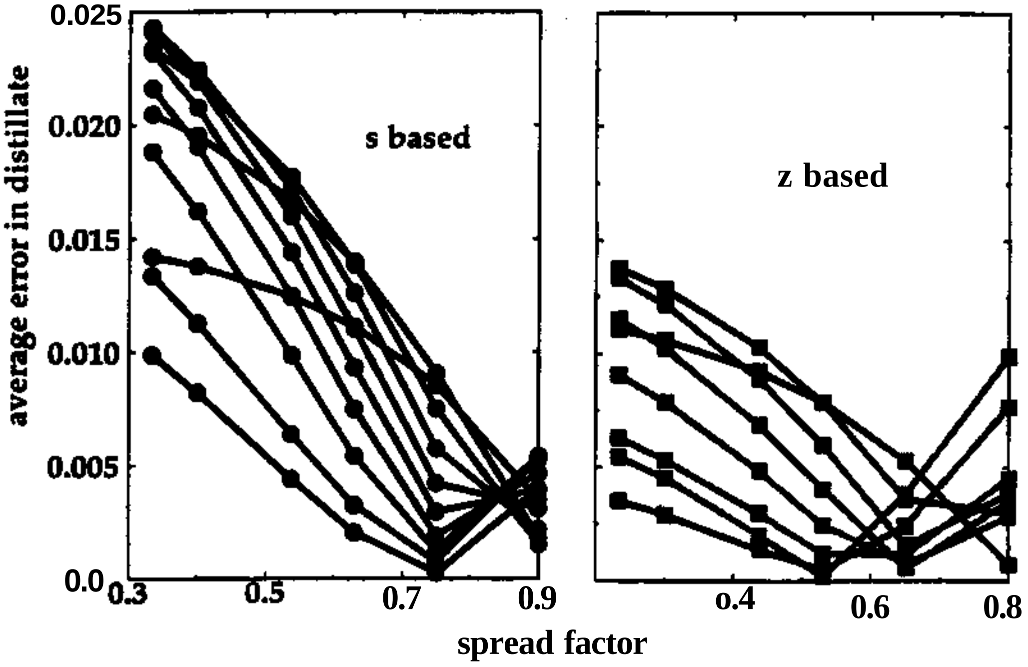
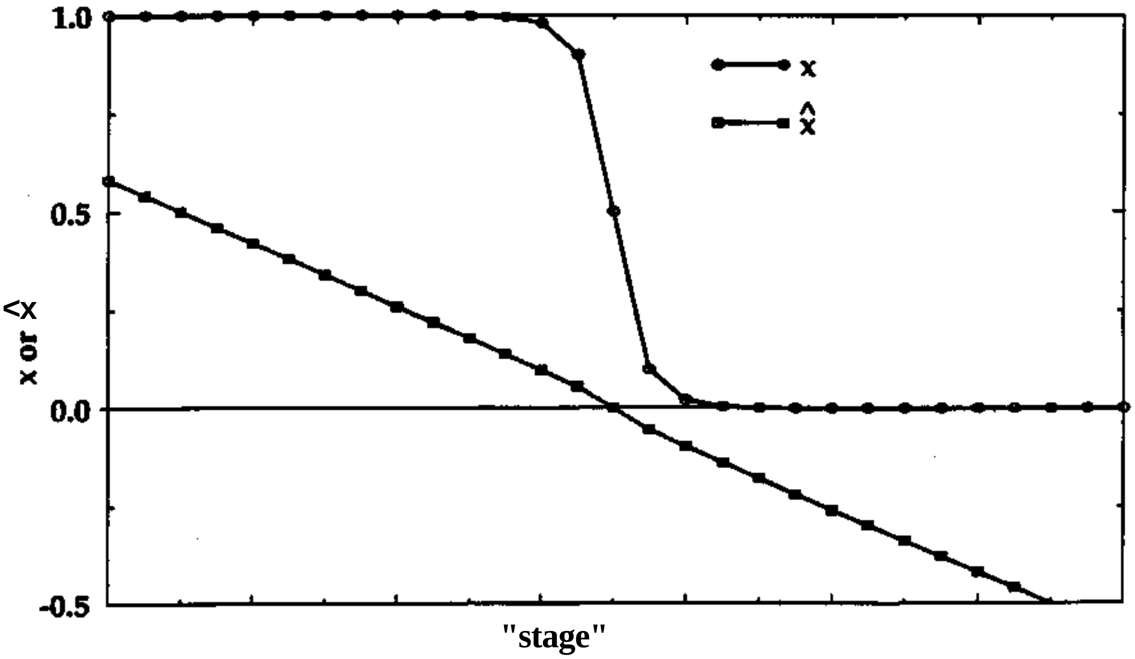


Figure 10. Error curves for s and z based collocation



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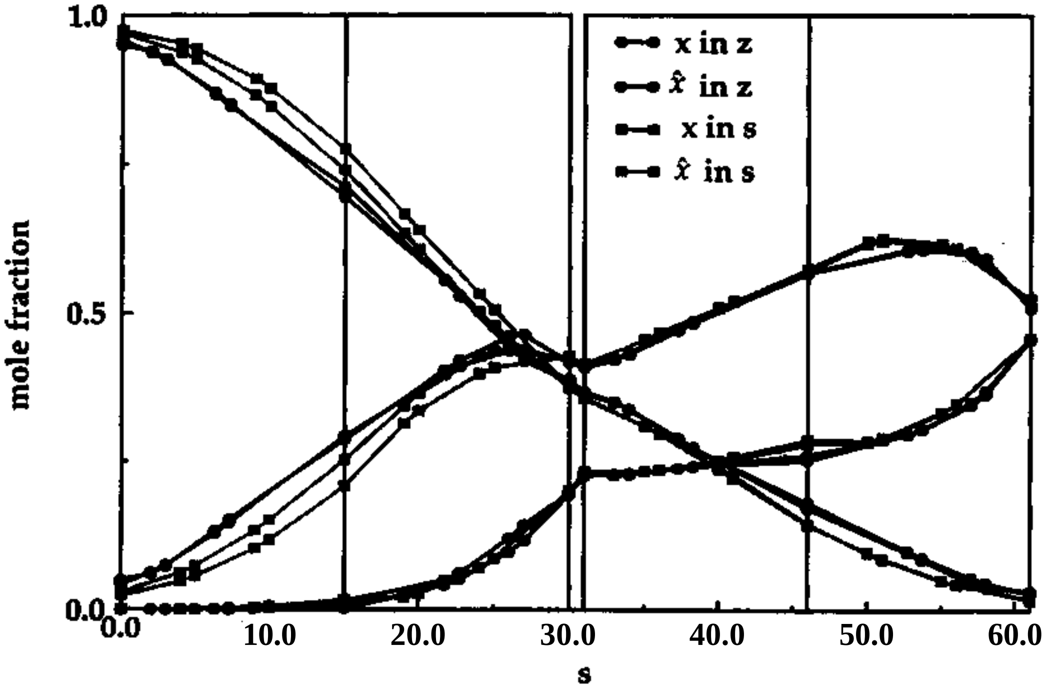

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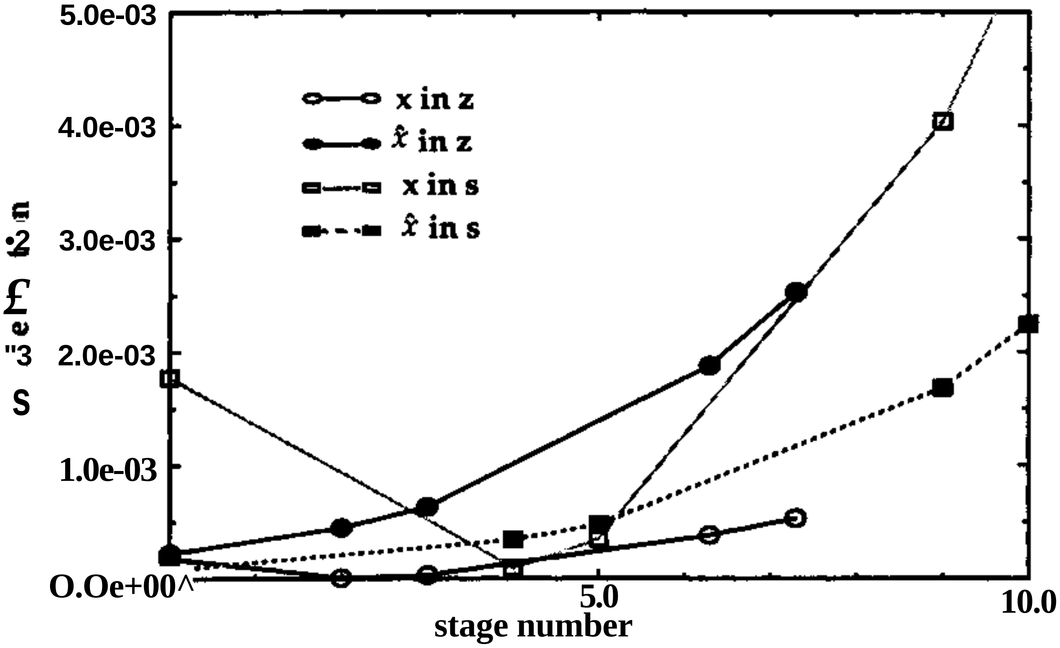

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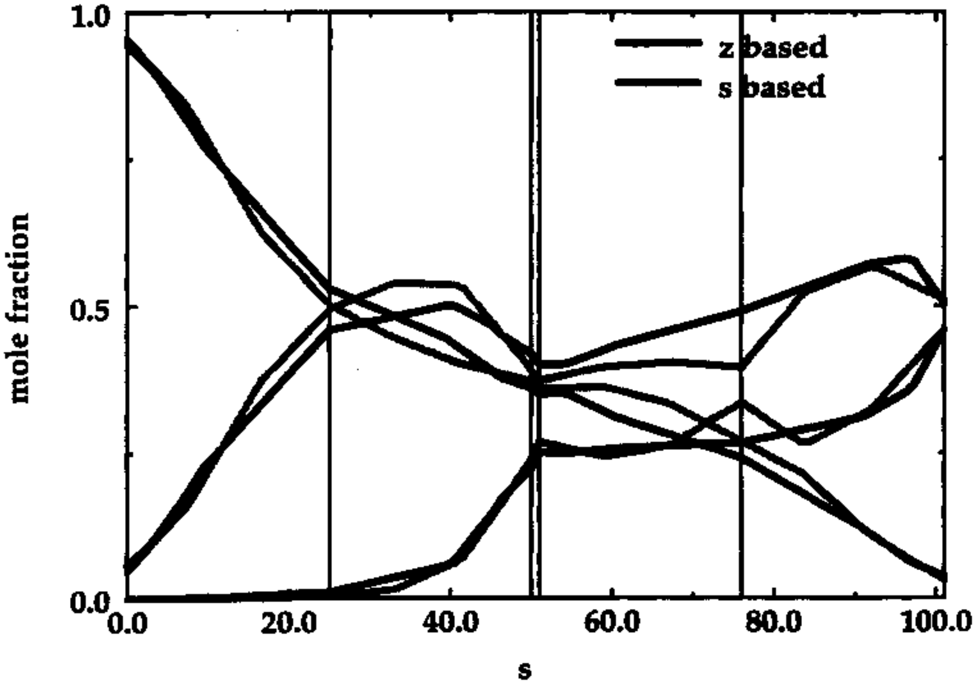

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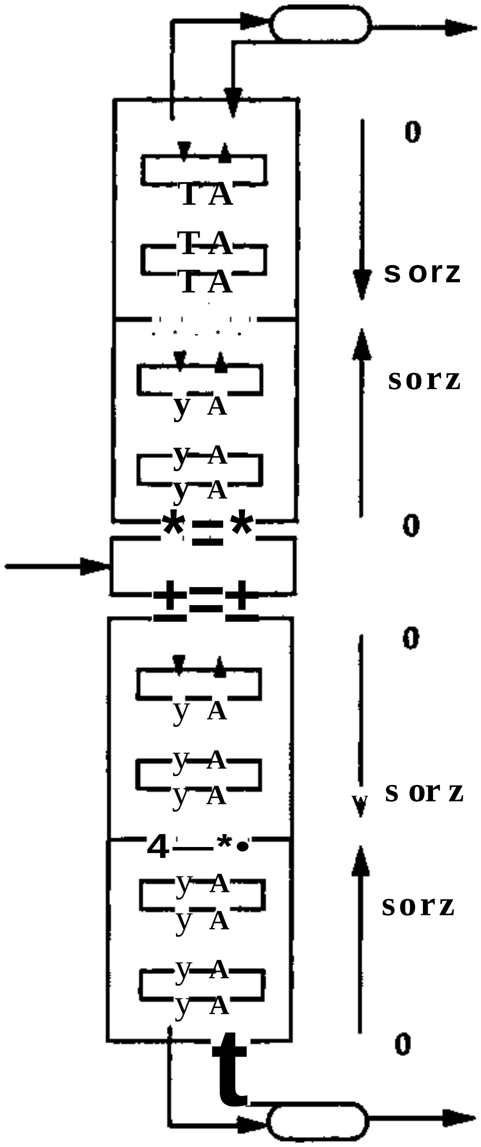

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We have performed several tests of the collocation model using nonideal thermodynamics. In each of the following examples, the standard collocation model was used, with four collocation sections of two trays each. We used UNIFAC liquid mixture and Pitzer vapor mixture models for the thermodynamics and equilibrium, and assumed constant molar overflow. We would like to note that performing tests like these is a nontrivial task. The process of obtaining a full thermodynamic model is complex, but once a tray-by-tray collocation model has been successfully refined and converged, it is relatively easy to perform many sequential incremental changes to obtain a wealth of data. The two examples below where we performed a series of calculations to determine the binary separations over a range of operations required 50 solutions of the tray-by-tray and collocation models. Most of the work was done in getting that first useful solution. Then the models could be resolved repeatedly as the distillate to feed ratio was increased incrementally. The collocation has many parameters that can be adjusted, but it is much more robust than a tray-by-tray model. The process of solving these models will be discussed further in a two follow-up papers.

The first example is the separation of a 50/50 mixture of methanol and water. The column has 46 trays, and a reflux of 1.0. The purity of each product is 99.6%. Figure 16 shows a comparision between the tray-by-tray solution and the collocation model. The curves are the tray-by-tray, and the points are the collocation. The figure shows an excellent fit. Including all the thermodynamic calculations, the tray-by-tray and collocation models had 3255 and 1407 equations respectively. The error in the distillate composition is 0.02 percent.

Using the acetone, chloroform, benzene system, we performed many tests of the collocation model. The feed was a 36/24/40 mixture of acetone, chloroform, and benzene. A 33 tray column with a reflux ratio of 4.0 was used. We performed a search over the range of distillate to feed ratios to find the maximum binary separations, as done by Wahnschafft [1992]. Figure 17 shows the comparison of the binary separation range plots with those for a tray-by-tray calculation. The chloroform benzene binary separation factor is not meaningful before a D:F of 0.3, since practically nothing of either component is coming out of the distillate at low D:F. For the acetone-benzene binary separation factor curve the average error was 1%, and for the acetone-chloroform separation factor curve the average error was 3%. The collocation shows very good agreement with tray-by-tray calculations. The error in the acetone concentration in the distillate was less than 2% over the range of D:F ratios, with an average error of 1%. Figure 18 shows comparisons of three different column simulations on a ternary diagram. Including all the thermodynamic calculations, the tray-by-tray and collocation models had 3144 and 1811 equations respectively.

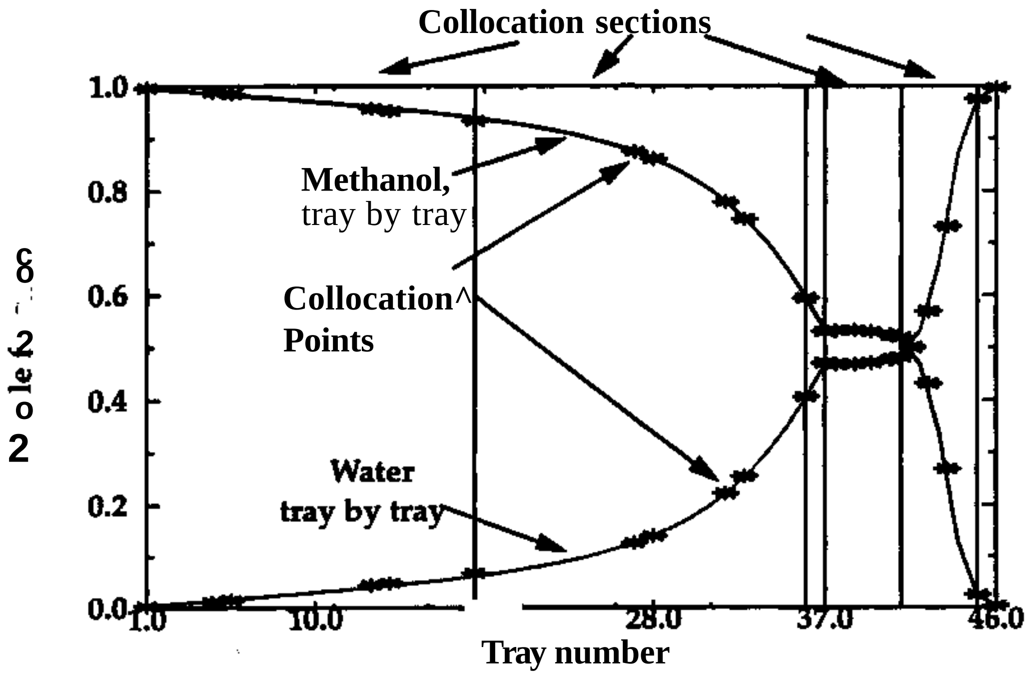

Figure 16. Comparison of collocation to rigorous model for methanol-water column

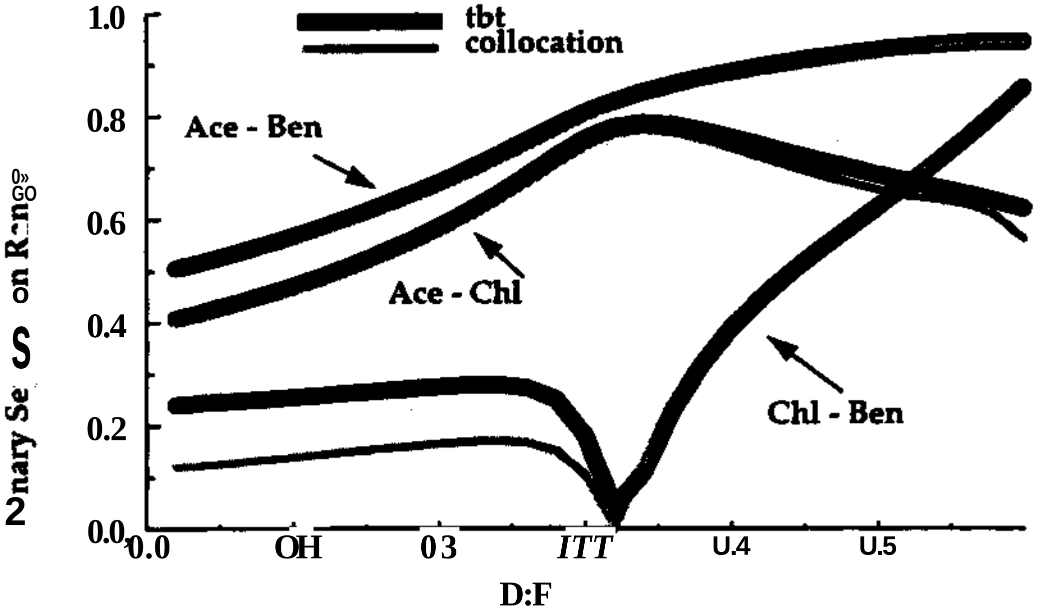

Figure 17. Comparison of collocation to rigorous model of separation range over D:F ratio for acetone-benzene-chloroform system

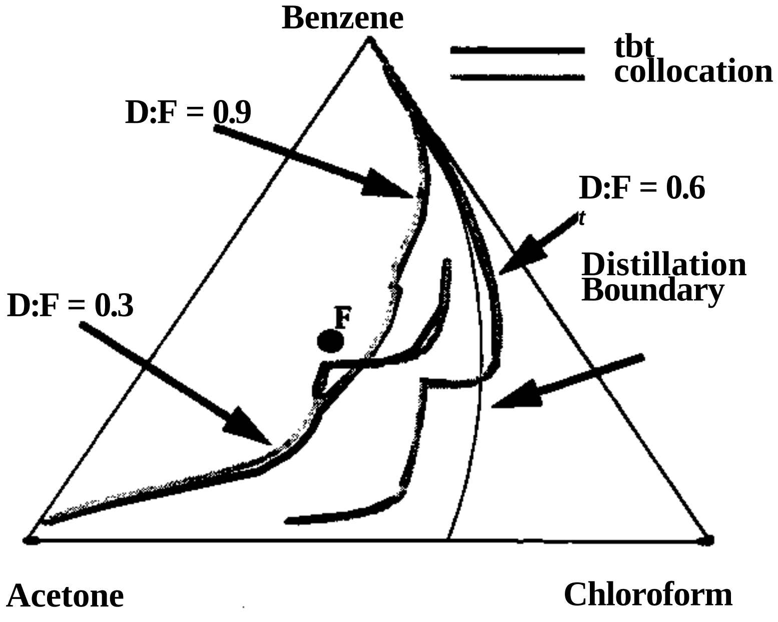

Figure 18. Comparison of collocation to rigorous model for acetone-benzene-chloroform column, for three different D:F ratios

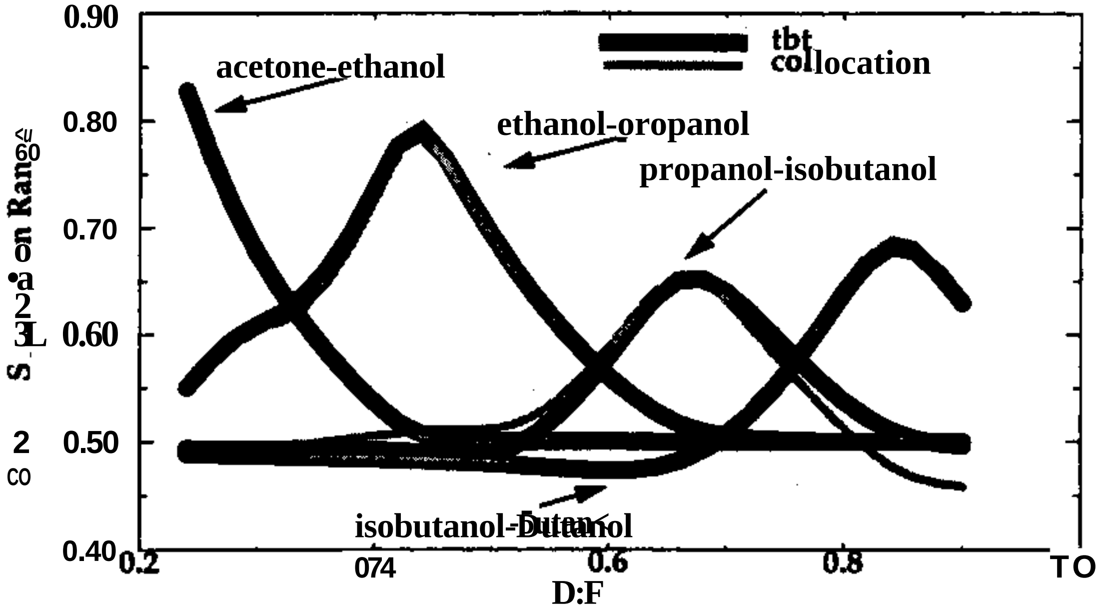

Figure 19. Comparison of collocation to rigorous model of separation range over D:F ratio for acetone-ethanol-propanol-isobutanol-butanol system

Finally, we performed a set of tests on an equimolar mixture of acetone, ethanol, propanol, isobutanol, and normal butanol, using a 23 tray column with a reflux ratio of 0.8. Figure 19 shows the comparison of the binary separation range plots for the components which are adjacent in the order of relative volatility. The other binary separation ranges compare equally well but would clutter the figure.

Conclusions

In this paper, we have demonstrated that this new collocation method can accurately reduce the order of column models. The two variable transformations greatly expand the capabilities of standard collocation methods. We have found that the degrees of freedom selection is important, and demonstrated what equations can be ignored. The choice of point placement is non-trivial, and no particular polynomial will give optimal point placement. Variable transformations more significantly reduce errors than proper point placement.

In two companion papers, we will discuss how collocation provides the

missing link for simulation of minimum reflux conditions. We will also discuss a design algorithm for designing arbitrary columns using the collocation model.

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Support from Eastman Chemicals and DOE contract number DE FG02-85ER13396 provide support for this research. Facilities support is from NSF grant number EEC-8942146 which supports the EDRC, an NSF funded Engineering Research Center.

Nomenclature

A	Simplification variable for Kremser approximation (L/KV)
a	Mole fraction average relative volatility
a	Parameter for exponential transformation of stage location
a	Parameter of Jacobi polynomial
α_i	Relative volatility of species i
p	Parameter of Jacobi polynomial
$fint$	Factor for selection of spread of collocation points
f_{Jmid}	Factor for selection of the midpoint of collocation points
h	Liquid molar enthalpy
H	Vapor molar enthalpy
K	Equilibrium constant used in Kremser approximation
L	Liquid molar flowrate
n	Order of polynomial
$*_c$	Number of components
n_p	Number of phases
$''_s$	Number of collocation points
P	Pressure
Pn	Jacobi polynomial of order n
s	Stage location
T	Temperature
V	Vapor molar flowrate
W_k	kth term of Lagrange polynomial
w_k	Position of bottom of tray k
$U{>}mid$	Midpoint for placement of collocation points
$wtop_k$	Position of top of tray k
x_i	Liquid mole fraction of component i
X_i	Transformed mole fraction
y_i	Vapor mole fraction of component i
z	Transformed stage location

References

Carnahan B., Luther H. A., Wilkes J. O., 1969, Applied Numerical Methods, Wiley, New York.

Cho Y.S. and B. Joseph., 1983. "Reduced-Order Steady-State and Dynamic Models for Separation Processes." *AIChE J.* 29,261-269,270-276

Julka V., and M. F. Doherty, 1990. Geometric Behavior and Minimum Hows for Nonideal Multicomponent Distillation. *Chemical Engineering Science,* 45, p. 1801-1822.

Koehler J., P Aguirre, and E. Blass., 1991. "Minimum Reflux Calculations for Nonideal Mixtures Using the Reversible Distillation Model." *Chem. Eng. Sci.,* 46.3007-3021.

Levy S. G., D.B. Van Dongen, and M. G. Doherty., 1985"Design and Synthesis of Homogeneous Azeotropic Distillations II: Minimum Reflux Calculations for Nonideal an d Azeotropic Columns." *Ind. and Eng. Chem. Fun.,* 24 463-474

Seferlis P and A. N. Hrymak, 1994, 'Optimization of Distillation units using collocation models', *AlChe J.* 40,813-825

Seferlis P and A. N. Hrymak, 1994, "Adaptive Collocation of Finite Elements Models for the Optimization of Multi-Stage Distillation Unit," *Chem. Eng. Sci..* 49,1369-1382

Stewart W. E., K. L. Levien, and M. Morari. 1984. "Collocation Methods in Distillation." in Westerberg, A.W., and H.H. Chien (eds), Proc. 2nd Intn'l Conf. Foundations Computer-aided Process Design (FOCAPD'83), CACHE Corp, Ann Arbor, MI, 535-569.

Swartz C. L. E. and Stewart W. E. 1986, "A Collocation Approach to Distillation Column Design," *AIChE J.* 32,1832-1838

Swartz C. L.E. and Stewart W. E. 1987, "Finite-Element Steady State Simulation of Multiphase Distillation," *AIChE J.* 33,1977-1985

Underwood, A. J. V. /. *Inst. Pet.* 1945,31, 111

Underwood, A. J. V., /. *Inst. Pet.* 1946,32,598

Underwood, A. J. V., *Chem. Eng. Prog.* 1948,44,603

Wahnschafft O. M 1992, "Synthesis of Separation Systems for Azeotropic Mixtures with and Emphasis on Distillation-Based Methods," Ph.D. Thesis, Dept of Chem. Eng., Technical University of Munich.

Appendix

Rewriting the Kremser approximation to gather terms with *s* produces the following equation.

$$Vs = \frac{\hat{}\ \hat{}}{I\text{-}A} \quad \frac{\hat{}}{I\text{-}A} A^{s} \tag{32}$$

Rewriting the variable transformation

$$z = l\text{-}e^{(\text{-}''s)} \tag{33}$$

for *s* in terms of z,

$$s = ln[\ (l\text{-}z)\sim^{a} J \tag{34}$$

and placing it into the Kremser approximation produces the following equation.

$$y(z)) = {}^{\wedge}J^{\wedge}\gg W\gg) \qquad - \quad ^{-a} \tag{35}$$

If we define *A = exp(B),* then we can take the following steps

$$A^{ln\left(\ (\right.} \qquad n\left(\ (1-z)^{-u}\right)$$

$$^{J} = (exp\ (B))$$

$$= exp\left(\ In\left(\ (exp(B))\right.\right. \quad ln\left(\ (1-z)^{-u}\right)\Big)\Big)$$

$$*exp[B[ln[(l\text{-}z) \quad ^{-}*\Big)\Big)\Big)$$

$$= exp\!\left(y\ ln\left[\ (1\text{-}z)^{-aB}\right)\right)$$

$$= (1\text{-}z)^{-aB} \tag{36}$$

Now equation 35 becomes the following.

$$y(z) = \frac{y_1 - A\hat{y}_0}{1-A} - \frac{y_1 - \hat{y}_0}{1-A}(1-z)^{-aB} \tag{37}$$

Therefore, when -*aB* = 1, the equation is linear in z.