Path-Following Approaches to the Solution of Multicomponent, Multistage Separation Process Problems

In solving the nonlinear algebraic equations that are normally used to model multicomponent separation processes, one is not guaranteed that Newton's method or any of its relatives will converge to the solution. This paper describes two homotopies and their use in the solution of difficult equilibrium stage separation process problems. The first, the Newton homotopy, is able to solve more problems than a standard implementation of Newton's method but is not the most reliable homotopy. Since the equations being solved no longer model a separation process unit, the Newton homotopy sometimes suffers from intermediate solutions that are physically meaningless. The second, the thermodynamic homotopy, is strongly based on the thermodynamic properties of the systems involved. This new homotopy is able to handle not only the more traditional distillation problems (hydrocarbon systems and mildly nonideal systems), but is also extremely effective at solving azeotropic and extractive distillation problems. The implementation of these methods requires only minor modifications to existing software.

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SCOPE

A common problem arising throughout various disciplines within the field of chemical engineering is the determination of an equilibrium, fixed point, or solution to a set of nonlinear algebraic equations modeling some process or system. The nonlinearities in these equations necessitate the use of some iterative scheme to obtain the desired solution.

One set of examples of equations of this type are the equations normally used to model stagewise, multicomponent separation processes, the familiar MESH equations of the equilibrium stage model. The thermodynamic quantities (*K*-values and enthalpies) within these equations tend to make them highly nonlinear. Numerous methods of solving the MESH equations have been published; the most versatile approach is to solve all of the equations simultaneously using Newton's method or one of its relatives. For ideal and mildly nonideal systems in columns with feasible specifications, it is a relatively easy task to provide estimates of the variables involved from which the methods of solution converge. The set of initial guesses from which the various equation-solving methods achieve a solution is known as the domain of convergence. Being the most rigorous method in the family of simultaneous correction procedures, Newton's method enjoys the largest domain of convergence.

However, not even Newton's method converges for all problems from all initial guesses. In fact for some problems involving very nonideal systems, it can be quite difficult to provide the equation-solving algorithm with an initial guess from which it can converge. If one

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is to deal regularly with these types of problems, it is obvious that a more reliable method for solving them will be needed.

Paths to the solution of difficult problems are provided by what are known as homotopy or continuation methods (Ortega and Rheinboldt, 1970; Garcia and Zangwill, 1981). In these methods, we start with a different problem, of the same dimension as the original problem, for which the solution is either known or easily obtainable. For example, if the system of equations to be solved is

$$F(x) = 0 \tag{A}$$

then a convenient function to start with would be

$$G(x) = F(x) - F(x_0) = 0 \tag{B}$$

where x_0 is an arbitrary vector. A solution to the set of B equations is obviously

$$x = x_0 \tag{C}$$

This new problem would then be gradually transformed or "bent," through some parameterization, into the original problem in such a way that as the parameter is varied from its initial to its final value, paths are generated by the roots of the new problem as they are bent into the roots of the original problem. To continue the above example, one such parameterization is

$$H(x, t) = tF(x) + (1 - t)G(x) = 0$$
$$t \epsilon [0, 1] \tag{D}$$

At $t = 0$, $H(x, 0) = G(x)$, and at $t = 1$, $H(x, 1) = F(x)$. As t is varied from $t = 0$ to $t = 1$, the roots of $H(x, t) =$ trace out paths that lead to the desired roots of $F(x) = 0$. This path-following approach is the key to what are termed homotopy methods.

Although homotopy or continuation methods have been used in other disciplines (mathematics and economics to name two: Garcia and Zangwill, 1981), it is only very recently that chemical engineers have started to use these methods for the solution of difficult problems (Salgovic et al., 1981; Byrne and Baird, 1983; Wayburn and Seader, 1984a, b; Bhargava and Hlavacek, 1984). This paper describes some of our experiences using the Newton homotopy, which so far as we know has been the only homotopy used to solve the equations that model separation processes; it also describes a new homotopy, one based on the thermodynamics of the problems, for the solution of the MESH equations. Evidence is given to show that both the simple Newton homotopy-continuation method and the thermodynamic homotopy, each very easily implemented if a computer code using Newton's method to solve the model equations is already available, give an existing nonlinear equation solver the ability to routinely solve separation process problems that would otherwise be considered extremely difficult if not practically impossible.

CONCLUSIONS AND SIGNIFICANCE

The most accurate mathematical description of any process is of little or no use if its solution is not readily obtainable. For the equilibrium stage model for multicomponent separation processes, it can be extremely difficult to obtain the solution of the set of nonlinear, algebraic equations modeling the stages of a separation process unit through the use of Newton's method alone.

Homotopy-continuation procedures make the solution of problems otherwise thought to be nearly impossible quite straightforward, if not routine. The Newton homotopy, $H(x) = F(x) - (1 - t)F(x_0)$, is so far the easiest continuation method to implement. The only modifications to an existing code using Newton's method are:

1. The addition of the homotopy parameter, t, to specify where on the solution path one is:
2. A redefining of the process model equations by subtracting a linear function of the homotopy parameter times the original model equations evaluated at the initial estimate of the solution.
3. Possibly, the solution of an extra set of linear equations to yield an improved estimate of the solution of subsequent problems.

This method, which is able to solve more problems than a standard Newton's method, is a very simple procedure to implement but is not the most reliable homotopy. Since the equations being solved no longer model a physical process, the Newton homotopy may suffer from intermediate solutions that are physically meaningless.

A new homotopy, the thermodynamic homotopy, takes advantage of an understanding of what causes the failures of Newton's method, the nonlinearities in the thermodynamic quantities (K-values and enthalpies), and removes them to simplify the initial problem. Nonidealities are returned to the problem in a way that makes the ultimate solution quite easy to achieve. This method is extremely reliable, giving a path to the solution of the final problem in which the variables remain realistic throughout the solution space of the homotopy function.

Nonlinear Equation Solving

General Considerations

In considering a multicomponent separation process, one often models the process using a set of nonlinear, algebraic equations. For the equilibrium stage model, the set of equations is referred to as the MESH equations; an acronym for *M*aterial balance equations, *E*quilibrium equations, *S*ummation equations, and enthalpy or *H*eat balance equations (Wang and Henke, 1966; Wang and Wang, 1981).

$$M_{i,j} \equiv L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_j z_{i,j} - (L_j + S_{Lj})x_{i,j} - (V_j + S_{Vj})y_{i,j} = 0 \quad (1)$$

$$E_{i,j} \equiv K_{i,j}x_{i,j} - y_{i,j} = 0 \quad (2)$$

$$S_{yj} \equiv \sum_{i=1}^{c} y_{i,j} - 1 = 0$$

$$S_{xj} \equiv \sum_{i=1}^{c} x_{i,j} - 1 = 0 \quad (3)$$

$$H_j \equiv L_{j-1}h^L_{j-1} + V_{j+1}H^V_{j+1} + F_j H^F_j - (L_j + S_{Lj})h^L_j - (V_j + S_{Vj})H^V_j - Q_j = 0 \quad (4)$$

This set of *2c + 3* functions corresponds in a one-to-one manner to a vector of variables, x, used in the function evaluations. For the equilibrium stage model, these variables include the component mole fractions in each phase of each stage, the total liquid and vapor flow rates on each stage, the stage temperatures, and possibly some operation variables (e.g., the reflux ratio).

We chose the *2c + 3* formulation of the MESH equations over the *2c + 1* formulation of Naphtali and Sandholm (1971) and many others because the new homotopy to be described later was more easily applied to this form.

Specific algorithms for equilibrium stage problems are too numerous to list here, the review of Wang and Wang (1981) is a convenient source of literature citations. Briefly, most methods for solving systems of nonlinear, algebraic equations that make up separation process models fall into two general classes, simultaneous correction or convergence (SC) techniques and tearing strategies. In tearing strategies, a subset of the variables and a corresponding subset of equations are removed or "torn" from the total sets of variables and equations, and the remaining equations are solved for the remaining variables with the assumption that the values chosen for the tear variables are correct. The tear variables are then reestimated and the procedure repeated until all the equations are satisfied. This procedure reduces the size of the problem being dealt with at any given moment, but it also calls for the exact solution of the remaining set of equations even for incorrect values of the tear variables.

Simultaneous correction procedures—e.g., Newton's method, quasi-Newton methods, and their relatives—attempt to solve all the equations for all the variables on each iteration. Although this increases the amount of storage necessary to solve a given problem, today's large computers and sparse matrix techniques allow the use of these methods for even very large problems. (For further information on nonlinear, algebraic equation solving techniques see Ortega and Rheinboldt, 1970.)

Past experience with many different methods has convinced us that SC methods are more reliable for the solution of the fully nonlinear equation sets being considered here than are the tearing algorithms. For this reason, in this paper only SC methods are considered as the main equation-solving algorithm.

Newton's method and related fixed-point algorithms

The best known of the simultaneous correction procedures is Newton's method, which makes use of derivative information to create a linear approximation at some estimate of the variable vector x_k to the function surface being considered. (Again, see Ortega and Rheinboldt, 1970, for more information.) The resulting linear equations are then solved using an appropriate technique and the solution is used to obtain a new estimate of the solution vector.

$$[J]s_k = -F(x_k) \quad (5)$$

s_k being the change in the variable vector $x_{k+1} - x_k$. This derivative information is calculated and stored in a matrix called the Jacobian, $[J]$. Newton's method provides a very good approximation to the functions being considered if one starts with an estimate of the vector x which is close to the actual solution x^*. It is the fact that this linear approximation is often very good that makes the method very robust.

There are, however, drawbacks to Newton's method. The first is that to evaluate the Jacobian, one must obtain the partial derivative of each function with respect to every variable. This can be a very time consuming step even if many of these derivatives are known to be zero. The second probem is not as clearly defined. Newton's method works well if the initial estimate of the solution vector is near the actual solution. Outside this near region, the method may converge slowly, oscillate, or diverge. The question is, what exactly is "near"?

In order to reduce the time required to calculate the necessary derivative information for the Jacobian, a class of methods termed quasi-Newton methods has been developed. In these methods, approximations to the Jacobian are made and updated through the use of formulae derived to satisfy certain constraints that have been chosen to force the approximate Jacobian to mimic the behavior of the actual Jacobian. One such update formula is given by Broyden (1965).

$$B_{k+1} = B_k + \frac{(y_k - B_k s_k)s_k^T}{s_k^T s_k} \quad (6)$$

where B_k is the kth approximation to the Jacobian, s_k is last change in the variable vector, $x_{k+1} - x_k$, and y_k is the corresponding change in the function vector $F(x_{k+1}) - F(x_k)$. These methods, which make use of the step changes in the function and variable vectors, may also be designed to preserve known sparsity patterns within the matrix (Schubert, 1970).

Although these methods can considerably reduce the amount of computer time necessary to evaluate the Jacobian, they also generally increase the number of iterations necessary to obtain convergence to an extent where the quasi-Newton solution procedure may very well end up taking more time than the unaltered Newton's method. Furthermore, the methods tend to reduce the domain of convergence from that of Newton's method. That is, even though Newton's method worked from a given initial estimate of the solution vector, a quasi-Newton method may very well fail.

In an effort both to decrease the number of iterations required by a pure quasi-Newton method and to try to maintain the region of convergence of Newton's method, Lucia and coworkers (Lucia and Macchietto, 1983; Lucia and Westman, 1984; Westman et al., 1984) have developed a hybrid approach to the solution of sets of model equations. In this approach, any derivative information that is easy (inexpensive) to calculate is included in a computed part of the Jacobian, $[C]$, while derivative information that is difficult or expensive to obtain is included in an approximated part of the Jacobian, $[A]$. On each iteration in the solution procedure, $[C]$ is calculated exactly and $[A]$ is updated using some appropriate quasi-Newton formula. The result is a method that, while taking more iterations than Newton's method to solve a given problem, generally takes about 50% less computer time to converge and has nearly the same region of convergence as Newton's method.

Several attempts have been made to increase the size of the region from which Newton's method (or one of its relatives) will converge to the desired solution (something that none of the quasi-Newton methods nor the hybrid method do.) Among them are the use of a damped Newton's method, where a line search is used to minimize the 2-norm of the function vector in the direction predicted by the Newton correction (Naphtali and Sandholm, 1971). Powell (1970) suggested a modification to the Levenberg-Marquardt method—a combination of the method of steepest descent (a minimization procedure) and Newton's method called the dogleg method—to keep the subsequent iterate in a "trust" region. This idea has been adapted (without complete success) for solving problems with a chemical engineering origin by Westerberg and Director (1978) and by Chen and Stadtherr (1981). Yet another suggestion was to use a relaxation technique to bring the variable estimates from some initial guess to a point from which Newton's method converges (Ketchum, 1979).

The techniques most recently applied to difficult separation problems are the homotopy or continuation methods.

Homotopy Methods

Homotopy methods, also referred to as continuation methods or embedding techniques, form a class of methods for continuously deforming one function, $G(x):R^n \rightarrow R^m$, into another function, $F(x):R^n \rightarrow R^m$. This deformation is accomplished by forming a third function, $H(x, t):R^{n+1} \rightarrow R^m$, which has an extra parameter, $t \in [t_0, t_f]$, such that

$$H(x, t_0) = G(x) \text{ and } H(x, t_f) = F(x) \tag{7}$$

Without loss of generality, t_0 can be taken as 0 and t_f as 1, i.e., $t \in [0, 1]$.

Among the most common homotopies are the linear homotopies

$$\begin{aligned} H(x, t) &= tF(x) + (1 - t)G(x) \\ &= G(x) + t[F(x) - G(x)] \end{aligned} \tag{8}$$

so named because $H(x, t)$ is linear in the parameter t. Two specific examples in this class are:

1. The fixed-point homotopy

$$H(x, t) = tF(x) + (1 - t)(x - x_0) \tag{9}$$

and 2. The Newton homotopy

$$\begin{aligned} H(x, t) &= tF(x) + (1 - t)[F(x) - F(x_0)] \\ &= F(x) - (1 - t)F(x_0) \end{aligned} \tag{10}$$

The first gets its name from the fact that $G(x)$ can be rewritten as the fixed point problem

$$x = x_0 \tag{11}$$

while the second gets its name from its relation to Newton's method (Garcia and Zangwill, 1981). It is also possible to derive many nonlinear homotopies.

Solution of the homotopy equations

In general, one would like to find the solution to $H(x, t) = 0$, $x^*(t)$, as an explicit function of t. Starting with

$$H(x, t) = 0 \tag{12}$$

differentiation with respect to t yields

$$H'_x \frac{dx}{dt} + H'_t = 0 \tag{13}$$

where

$$H = (h_1\, h_2 \cdots h_n)^T \tag{14}$$

$$x = (x_1\, x_2 \cdots x_n)^T \tag{15}$$

$$H'_x = \begin{bmatrix} \frac{\partial h_1}{\partial x_1} & \frac{\partial h_1}{\partial x_2} & \cdots & \frac{\partial h_1}{\partial x_n} \\ \frac{\partial h_2}{\partial x_1} & \frac{\partial h_2}{\partial x_2} & \cdots & \frac{\partial h_2}{\partial x_n} \\ \vdots & \vdots & & \vdots \\ \frac{\partial h_n}{\partial x_1} & \frac{\partial h_n}{\partial x_2} & \cdots & \frac{\partial h_n}{\partial x_n} \end{bmatrix} \tag{16}$$

and

$$H'_t = \left(\frac{\partial h_1}{\partial t}\, \frac{\partial h_2}{\partial t} \cdots \frac{\partial h_n}{\partial t}\right)^T \tag{17}$$

Upon rearrangement

$$\frac{dx}{dt} = -H'^{-1}_x H'_t \tag{18}$$

Equations 18 are known as the homotopy differential equations (HDE's). If H'^{-1}_x exists for $x(t)$ along the path, then the system Eq. 18, along with the initial conditions

$$x(0) = x_0 \tag{19}$$

can be integrated to obtain $x^*(t)$ directly. This integration can be carried out using any numerical integration scheme. If Euler's method is used to solve this problem for a change in the parameter value of Δt, then $x_{t+\Delta t} = x_t + \Delta t dx/dt$, where dx/dt is obtained from the solution of the linear system Eq. 18. In fact, using Euler's method with a step size $\Delta t = 1$ to solve the homotopy differential equations and a restart using this result as the new initial guess is completely equivalent to Newton's method. After the numerical integration step is taken, the variable vector can be corrected to be closer to the actual solution through the use of Newton's method or one of its relatives. This is a form of a predictor-corrector method, but in this case the corrector part of the pair that is normally an implicit integration step is replaced by some iterative nonlinear algebraic equation-solving technique.

If $H_x'^{-1}$ does not exist at some point, one can either perturb x slightly so that $H_x'^{-1}$ does exist or try recasting the differential equations in another form. This recasting can be accomplished by assuming that both x and t can be written as functions of the arclength, p, of the path. Define

$$z(p) = [x^*(p), t(p)]^T \tag{20}$$

then

$$z_j' = \frac{dz_j}{dp} \quad j = 1, 2, \dots, n + 1 \tag{21}$$

Since x^* is a solution to the homotopy Eq. 12 at t,

$$H[z(p)] = 0 \tag{22}$$

Differentiation of Eq. 22 with respect to p yields

$$\sum_{j=1}^{n+1} \frac{\partial H}{\partial z_j} z_j' = 0 \tag{23}$$

A solution to this system, the basic differential equations (BDE's), can be shown to be (Garcia and Zangwill, 1981)

$$z_j' = (-1)^j \det H'_{-j}(z) \quad j = 1, 2, \dots, n + 1 \tag{24}$$

where H'_{-j} is the Jacobian of $H(x, t)$ with its jth column deleted. For example,

$$H'_{-n+1} = H'_{-t} = H_x' \tag{25}$$

An equivalent and possibly more obvious method for solving this system of equations is given by Wayburn and Seader (1984a). The initial conditions for both solution methods are

$$z(0) = (x_0, 0)^T \tag{26}$$

Homotopies for solution of the equilibrium stage model

In choosing a homotopy function for use in the solution of the equations of the equilibrium stage model, several points were taken into consideration. The method should be easy to implement; that is, it should involve a minimal number of changes to software that had already been written to solve the equilibrium model equations using Newton's method or one of its relatives described above. It should be reliable; if the new equations are no easier to solve than the original ones, then it is useless. The solution of the equations should be as efficient as possible. Although it should be realized that in general no method that uses Newton's method to solve a subset of problems of complexity equal to that of the original problem can be more efficient than Newton's method, the solution of the new set of problems should not take an unreasonable amount of computer time. (Exceptions can occur if, for example, the initial estimate used for Newton's method is very near the boundary of the Newton's method region of convergence.)

The Newton Homotopy for Separation Process Problems

Having looked at these considerations, it was decided to first try a Newton homotopy to solve the system of algebraic equations of the equilibrium stage model. This homotopy had been previously applied by Salgovic et al. (1981), who solved some problems of a chemical process origin by using Euler's method, with and without corrector iterations, to step through the range of the parameter values in order to obtain a value of the variable vector at the final parameter value. The problem was then restarted, if necessary, with this solution as an initial guess and the process repeated until the initial guess matched the final solution, that is until the variable vector did not change with changing t [or until $F(x_0)$ was equal to 0].

Wayburn and Seader (1984a) also used the Newton homotopy in their solution of the MESH equations for interlinked distillation columns. They parameterized the problem in terms of the arclength of the curves being traced out in the solution space. They used an Euler step corrected by Newton's method in the plane orthogonal to the unit normal vector at the point being considered. The problems they solved involve the ideal system benzene-toluene-xylene. With the help of the Newton homotopy Wayburn and Seader (1984a) and Seader et al. (1984) discovered multiple solutions of the MESH equations for two two-column configurations that they investigated.

Most recently, Bhargava and Hlavacek (1984) have applied a Newton homotopy that they found to be both effective and efficient. In it, they do only one Newton correction on the problems leading to the final problem to be solved. The estimate of solution of the next problem is taken to be the result of that iteration; there is no application of the homotopy differential equations. In their paper they suggested using an even step length in the range 0.2–0.5. This suggestion was based upon the results of some problems that were solvable through the use of Newton's method alone.

Byrne and Baird (1983) have also worked with homotopies to solve multistage distillation problems, but the details of methods used by them are proprietary.

In the discussion that follows, $F(x)$ refers to the function vector for the equilibrium stage model.

The first problem

For the Newton Homotopy, the initial problem to be solved is

$$F(x) - F(x_0) = 0 \tag{27}$$

x_0 is the initial estimate to the solution vector and has been obtained by assuming a linear profile for the stage temperatures. The vapor and liquid flow rates were initialized assuming constant molal overflow with the feeds saturated. In order to obtain initial estimates of the vapor and liquid compositions, it was assumed that the vapor and liquid phases were in equilibrium and that the K-values for the system were given by the ideal solution part P_i^s/P. The compositions were then obtained from a single iteration of the Wang and Henke method (1966), the approach recommended by Wayburn and Seader (1984a). Only the initial temperature profile need be guessed. All other variables can then be computed directly, i.e., without iteration.

This initial problem has the solution $x = x_0$. Furthermore, the quantity H'_x used in the homotopy differential equations (HDE's) is exactly the Jacobian involved in a Newton iteration from the present value of the variable vector without regard to the value of the parameter. This means that it is not necessary to evaluate another matrix and linear system; rather, when the linear system that defines the Newton iterate is solved, one need only solve the same problem with a new righthand side vector, H'_t, which turns out to be nothing more than $F(x_0)$.

Step size algorithms

In the studies we undertook, the step change in the parameter value was chosen as in the classical homotopy method. That is, the number of steps to be taken in attempting to solve a given problem is chosen (presently this choice is rather arbitrary) and the interval [0, 1] is split into the appropriate number of equal subintervals. For example, if one chooses to take four steps in solving the problem in addition to the solution of the initial problem ($t_0 = 0$, $t_1 = 0.25$, $t_2 = 0.5$, $t_3 = 0.75$, and $t_4 = 1$) then $t_{i+1} - t_i = (t_f - t_0)/4 = 1/4 = 0.25$.

There are a number of more sophisticated step size algorithms; some of which are reviewed by Wayburn and Seader (1983) who, in fact, used one of them. In view of their complexity, and since we have had complete success with the unsophisticated method described above, we have not yet seen the need to adopt one of these algorithms.

Implementations

Two basic implementations of the Newton homotopy were looked at. The first uses Newton's method to solve each intermediate problem to a tolerance 10^4 times greater than that of the final problem. The HDE's are used along with Euler's method as an integration scheme to predict an initial estimate of the solution for the succeeding problem; the homotopy parameter is incremented; Newton's method is used to correct the prediction; and the process is repeated throughout the range of the parameter values. The second implementation was the method of Bhargava and Hlavacek (1984) discussed above.

A New Homotopy

Although the Newton homotopy does go a long way toward achieving its goal, an enlarged domain of convergence, it does have its drawbacks. First of all, it is a purely mathematical contrivance. This of itself is not serious, but it turns out that since the sets of equations being solved (Eq. 10) no longer represent a physical process, the variables no longer need to be physically realistic at the solution to intermediate problems. In some instances we have found that the solutions to intermediate problems (the homotopy parameter not equal to zero or one) involve negative mole fractions! Again, this would be of no serious consequence were it not that the subroutines used to calculate physical and thermodynamic properties do not take kindly to such entities.

In some cases, it is possible to skip over values of the homotopy parameter for which the variables become unrealistic, but this is not always the case. However, even if one were able to do so, this would not eliminate the problem, it would merely avoid it. Furthermore, in those cases where it is not possible to step over the problem, the various implementations of the Newton homotopy would often fail.

These observations strengthened our belief that some new homotopy, one that took more advantage of the physics of the problem, would be of greater value in dealing with these problems. Since it is the nonidealities in the thermodynamic quantities used—specifically the K-values and enthalpies—that cause the majority of the difficulties when solving the process model equations, we decided to create a new homotopy, one that removed most of these nonidealities from the initial problem and then added them in gradually as the homotopy parameter moved from zero to one.

As a first approach to removing the nonidealities, the K-values were reduced to their ideal form, $K_i = P_i^s/P$, where $P_i^s = P_i^s(T)$. Similarly, the enthalpies were taken to be those of an ideal mixture, $H = \Sigma_{i-1}^{c} x_i H_i$, where the H_i are the pure component enthalpies [again $H = H(T)$]. To add the nonidealities, we chose the following functions;

$$K_i(T, x, y, t) = (P_i^s/P)(\gamma_{il}/\phi_{iv})^{g(t)} \tag{28}$$

and

$$H(T, x, y, t) = w(t)H_{\text{act}} + (1 - w(t))H_{\text{ideal}} \tag{29}$$

where $g(t)$ and $w(t)$ are functions of the homotopy parameter, t. In all our calculations, we took $g(t) = w(t) = t$.

This new homotopy did solve problems that Newton's method and the Newton homotopy had failed to solve. Furthermore, although the intermediate problems were not real systems, the thermodynamics behaved as if they were, thus eliminating the problem with unrealistic quantities found in the Newton homotopy. However, there were still some systems for which the initial problem provided some difficulties that were due primarily to the enthalpy balance equations. For this reason a new replacement for the enthalpy functions was sought.

The final result was that the initial problem was reduced to the an equimolal overflow problem with the same K-value function, Eq. 28. More specifically,

$$H = [1 - w(t)]H_{EM} + w(t)H_{\text{act}} \tag{30}$$

The quantities H_{EM} are equimolal overflow values of the enthalpy of the given phase. To obtain values for these quantities, the enthalpies of the feed streams are evaluated with the homotopy parameter set to unity. If there is no vapor feed to the column, then for the sake of calculating an equimolal overflow vapor enthalpy, pseudofeeds of the same composition, temperature, and pressure as the liquid feeds to the column are assumed to exist and their enthalpies $(H^{FV})^L$ are evaluated. Correspondingly, if there is no liquid feed, pseudoliquid feeds based on the actual vapor feeds are assumed $(H^{FL})^V$. Weighted averages of these (pseudo) feeds are then taken and the equimolal overflow enthalpies are defined by

$$H^{EM} = \sum_{j-1}^{NFV} F^{Vj} H^{FVj} \quad \text{or} \quad \sum_{j-1}^{NFL} F^{Lj} (H^{FVj})^{L}$$
$$h^{EM} = \sum_{j-1}^{NFL} F^{Lj} h^{FLj} \quad \text{or} \quad \sum_{j-1}^{NFV} F^{Vj} (h^{FLj})^{V} \qquad (31)$$

These equimolal enthalpies are then independent of temperature, pressure, and composition.

With this definition of the enthalpies, the amount of vapor and liquid exiting a stage can be calculated directly once the heat input to each stage is known. (The knowledge of the heat input to the reboiler or condenser can be replaced with other independent specifications, e.g., boil-up rate or bottoms flow rate for the reboiler and condensate flow rate or reflux ratio for the condenser.) It is then possible to remove the vapor and liquid flow rates from the vector of variables, and consequently the enthalpy balance and the total mass balance from the function vector of each stage. (It is for this reason that we chose the *2c + 3* formulation of the MESH equations.)

All variables remain physically realistic at all values of the homotopy parameter, *t*. This is not surprising since the model equations do describe a physically realistic process; a characteristic not shared by the Newton homotopy.

The first problem

This means that the only equations involved in the initial problem are the component mass balance equations, a summation equation (both linear in the compositions x and y and with no temperature dependence), and the ideal equilibrium relations (now linear in the compositions x and y and nonlinear only in the temperature). The variable vector is initialized in the same manner as described for the Newton homotopy.

It is possible to use all the equations and variables in the solution of the initial problem, thus minimizing the number of modifications that have to be made to existing software. However, we have found that for this initial problem a tearing strategy such as the Wang and Henke method (1966) or the Theta method (Holland, 1981) can be faster and, for problems where one or more species is effectively nonexistent on one or more stages, more stable in their convergence than Newton's method solving the full set of MESH equations. Furthermore, in these tearing algorithms the only quantities that must be guessed are the top and bottom temperatures (with the remaining stage temperatures initialized using linear interpolation).

Implementation

When implementing this homotopy, we made use of the HDE's with Euler's method as the integration scheme to estimate the solution of a given intermediate problem from the solution (again to a tolerance of 10^4 times greater than that for the final problem) of the previous problem. The constant step size algorithm described above was also utilized for this homotopy.

By modifying the subroutines that evaluate the *K*-values and enthalpies (we used those in the book of Prausnitz et al., 1980) rather than the model equations, we were able to avoid modifying the routines that evaluated the Jacobian. That is, the derivatives of the modified thermodynamic quantities were returned directly, rather than returning the derivatives of the original thermodynamic quantities and then backing out the values for the modified quantities.

The righthand side vector for the HDE's can be broken up as follows: Those elements that correspond to the material balances or the summation equations are zero; those corresponding to the equilibrium relations are $x_{i,j} K_{i,j} \ln (\gamma_{il}/\phi_{iv})$, and those corresponding to the enthalpy balances are $L_{j-1} d_{j-1} + V_{j+1} D_{j+1} - (L_j + S_{Lj}) d_j - (V_j + S_{Vj}) D_j + F_j D_j^F$, where $D = H_{\text{act}} - H_{EM}$, and similarly for d.

A flow chart summarizing our implementation of the thermodynamic homotopy is provided in Figure 1.

The Problems

To test our homotopies we sought problems for which Newton's method alone did not converge. Data for five of the problems tested are given in Table 1. These are some of the more difficult problems attempted; they are not, however, the only problems that were solved.

The first problem tested is a four-component extractive distillation problem taken from Holland (1981, p. 190). This problem has also been solved by Westman et al. (1984) using both Newton's method and the hybrid method. Both methods were extremely sensitive to the initial estimate of the temperature profiles; even a change of as little as 4 K in the estimates of the end points of the temperature profile would cause a failure. Attempts were made by Westman et al. to extend the domain of convergence using line searching and the dogleg strategy, but these attempts were unsuccessful.

Our own experience mirrors that of Westman et al. We were able to get Newton's method to work from the same starting point used by them and by Holland, by making the same approximations in the evaluation of the Jacobian that they and Holland made. However, we have had no success with any other reasonable starting point and can confirm the sensitivity of the initial temperature profile reported by Westman et al.

The second problem is based on an example considered by Krishnamurthy and Taylor (1985). Their work compared design results for equilibrium and nonequilibrium stage models of a distillation column. This was one system for which they had a great deal of difficulty finding an effective initial estimate of the solution.

The third and fourth problems are taken from Kinoshita et al. (1983). In the third problem, the furfural stays almost exclusively within the bottom of the column. Thus, furfural is essentially nonexistent in the top of the column (something that has been seen to cause some convergence difficulties) and there should be a sharp temperature rise on the bottom trays.

The fifth problem, similar to a problem mentioned in Kinoshita et al., was chosen because the system exhibits a homogeneous, ternary azeotrope (using UNIQUAC, the azeotrope is located at 330.28 K, $x_{\text{meth}} = 0.446$, $x_{\text{acet}} = 0.324$, and $x_{\text{chloro}} = 0.230$).

We have also solved a number of problems involving other systems that exhibit homogeneous azeotropes (ethanol-*n*-hexane and water-ethanol-ethyl acetate, to name two); no details are given because results for the problems discussed here hold for these examples also.

Thermodynamic property values were calculated using the UNIQUAC routines of Anderson (Prausnitz et al., 1980).

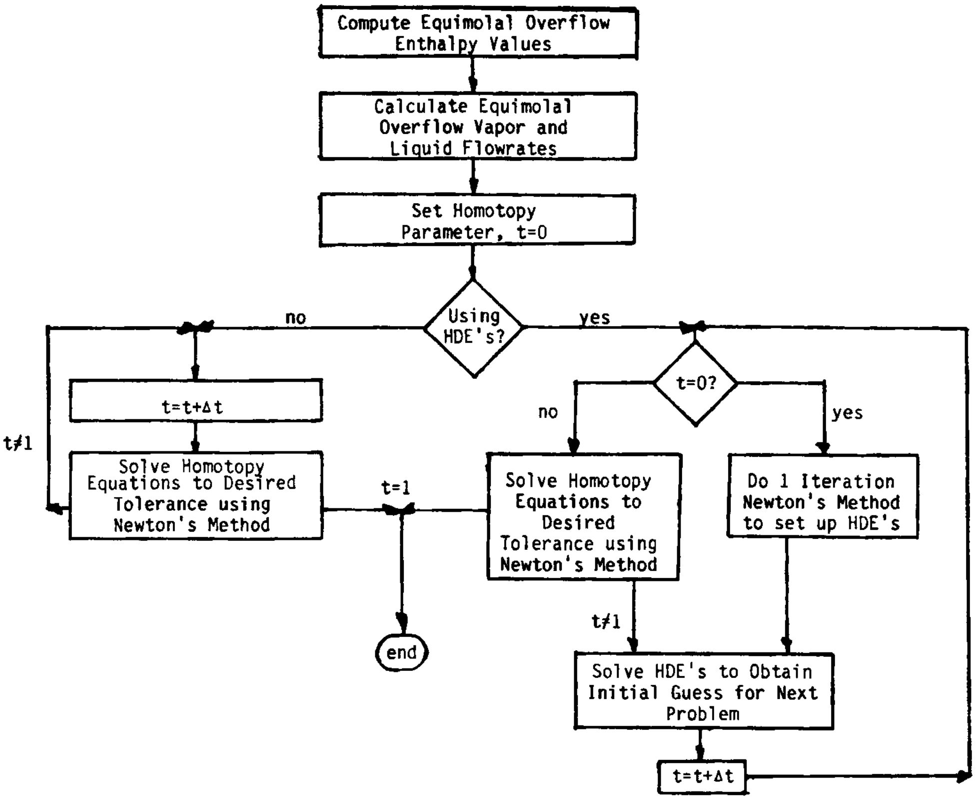

Figure 1. Flow chart of implementation of thermodynamic homotopy.

Interaction parameters not given by Prausnitz et al. were taken from the compilation of Gmehling and Onken (1977).

Results

The main purpose of continuation methods is to increase the reliability of the solution procedures used on the model equations, not to reduce the computational time requirements (number of iterations, physical property calculations, etc.) to an absolute minimum. Since we made no attempts to find the number of steps that gives the fastest convergence of each method, any tabular or graphical presentation of our results would be incomplete and misleading. For this reason, only a summary of our observations is given below.

The problems tested fell generally into four categories.

1. Newton's method works.
2. Newton's method fails, but both the Newton homotopy and the thermodynamic homotopy work and provide realistic variable values throughout the solution procedure (given a small enough parameter step size).
3. Both homotopies work, but the Newton homotopy gives physically unrealistic solutions at some parameter values.
4. Only the thermodynamic homotopy works.

The problems in the first category are inappropriate for comparison in this paper: if Newton's method works, then any reasonable implementation of any reasonable homotopy that uses Newton's method to solve the intermediate problems should also work. Hence, little real knowledge of the effectiveness of the method is gained.

In the second category of problems is the methanol-acetone-chloroform problem, problem 5 in Table 1. While the thermodynamic homotopy and both implementations of the Newton homotopy work on this problem, one pattern (which becomes even more marked as the difficulty of the problems increases) emerges here. That is, the thermodynamic homotopy requires the fewest parameter steps to solve a problem, only two steps and a total of 11 iterations; next comes the version of the Newton homotopy in which each intermediate problem is fully solved (hereafter referred to as the complete solution Newton homotopy), three steps and 13 iterations; and then the method that consistently took the most steps, if it worked at all, the method of Bhargava and Hlavacek (1984): six steps and 11 iterations for this problem.

The extractive distillation problem (number 1, Table 1) also fell into this category, with the same observations as to the relative number of steps required by each method to achieve a converged solution. However, the homotopy methods were insensitive to the initial estimate of the temperature profiles.

The methanol-ethanol-water problem (number 4) fell into category number three. The thermodynamic homotopy solved this problem in five steps. (It might have been possible to use even fewer steps, but since the problem was solved, and considering what happened with the Newton homotopy, we did not try fewer.) When using the complete solution Newton homotopy with 20 steps (10 had not worked), we found that a few of the liquid mole fractions went negative at the intermediate solutions. In order to avoid problems with the physical and thermodynamic property routines, these variables were reset to very small positive numbers (10^{-11}). The method of Bhargava and Hlavacek failed with even 40 steps for this problem.

The final two problems fall into the fourth category, at least for a reasonable number of steps in the homotopy parameter.

Table 1. Test Problems

Problem No.	No. Components	No. Stages	Column Press. Bar	Condenser	Reboiler	Feed(s) (Flows in kmol/hr)
1	4	42	1.0	Total $R = 3$	Partial $B = 124$	2 liquids Stg. 6, 321.9 K Stg. 21, 310.8 K 0 Methanol 65 0 Acetone 25 50 Water 5 0 Ethanol 5
2	3	45	1.013	Total $R = 12.5$	Split stream vaporizer $B = 45$	1 liquid Stg. 25, 352.2 K Ethanol 55 *t*-butanol 20 Water 25
3	3	15	1.0	Partial $R = 2.5$	Partial $B = 50$	1 liquid Stg. 8, 334.7 K Water 45 Acetone 50 Furfural 5
4	3	22	1.0	Total $R = 3$	Partial $B = 50$	1 liquid Stg. 12, 353.2 K Methanol 10 Ethanol 20 Water 70
5	3	25	1.0	Partial $R = 10$	Partial $B = 75$	1 liquid Stg. 15, 330.7 K Methanol 23 Acetone 30 Chloroform 47

SI conversion: kPa = bar × 100.

(Theoretically, as long as the variables remain realistic, the Newton homotopy should converge given enough steps. However, this number may become very large, making the method impractical.) Both of these problems, numbers 2 and 3, were readily solved by the thermodynamic homotopy in five steps. Again we did not feel it necessary to determine the absolute minimum number of steps for solution since the purpose of the homotopy is increased reliability with reasonable efficiency. The Newton homotopy, both implementations, was unable to solve the problem in 20 steps. Even if the Newton homotopy had been able to solve the problems with an increased number of steps, the computer time required to do so would have been much greater than that required by the thermodynamic homotopy.

Discussion

Although the Newton homotopy is very easy to implement and can be quite effective as a method of solving difficult separation problems, our results show that its lack of a strong physical basis and its subsequent tendency to predict unrealistic intermediate results or to fail completely make it a less than optimal choice for a more reliable equation-solving technique for the separation problems being considered.

On the other hand, we have had complete success with our thermodynamic homotopy. Although the solution to the initial problem is not known a priori, the ideal, equimolal overflow problem is quite easily solved. Once this initial problem has been solved, the homotopy differential equations give good to excellent estimates of the solution of the next problem (reducing the 2-norm of the function vector by one to three orders of magnitude). Also, even if the Newton homotopy did work for a problem, this new homotopy would take an amount of time to solve the problem on the same order or less than the time required by implementations of the Newton homotopy that were tried (not only of the two listed, but several others as well).

We have noted that the numerical solution routines do not always fail because the equations being solved are highly nonlinear (at least not directly). Failures may also be due simply to inadequacies in the linear equation-solving routines or in the precision capabilities of the machine on which the problem is solved. We found that both homotopies were able, in part, to reduce the severity of these problems. For example, the sparse matrix package used did not do partial pivoting even when this was necessary; this did cause problems in some of the example problems that we tried. By using the continuation techniques, many of these problems were avoided.

What should be emphasized at this point is that this method is not intended to replace Newton's method as a solution procedure. Rather, it is to be used to increase the number of problems for which Newton's method can be effectively used: it is intended to increase the reliability of an already versatile and powerful nonlinear equation-solving technique. However, if two possible methods are available for achieving this goal, then the more reliable one would be the best choice for use, and if they are equally reliable then the more efficient one, computationally, is probably a better choice (unless there are specific reasons to do otherwise).

When attempting to solve a problem, one should always try Newton's method before resorting to any homotopy: if Newton's method works, it will be a much more efficient way of solving the problem. If, however, Newton's method does not work, we recommend using the thermodynamic homotopy with a step size initially set equal to 0.2. Although it may be possible to solve the problem with a larger step size, at this point the most important thing is to solve the problem with a minimum of effort. If necessary, the step size can be decreased if there is still trouble solving the problem, but we have not yet found a problem for which this step size did not work.

Acknowledgment

The authors would like to thank R. Krishnamurthy for the original equilibrium stage model solving programs, which were modified for this work. Additionally, David Vickery would like to acknowledge financial support of a National Science Foundation Graduate Fellowship during the period of this work.

Notation

$[A]$ = approximated part of Jacobian
B = approximated Jacobian of Broyden (1965)
$[C]$ = computed part of Jacobian
c = number of components
$D(d)$ = difference between actual enthalpy and equimolar enthalpy, $H(h)_{\text{act}} - H(h)_{EM}$
E = equilibrium relation
F = function vector of x
G = function vector of x
H, h = enthalpy balance equation or enthalpy in general
$H(x, t)$ = function vector of x and t
H' = Jacobian of H
$[J]$ = Jacobian matrix of F
M = mass balance equation
NFV/NFL = number of vapor/liquid feeds
p = arclength
R^n = n-dimensional real space
S = summation equation or, with subscript, a sidestream flow rate
s = change in the variable vector, Eq. 5
t = homotopy parameter
x = variable vector
y = change in the function vector, Eq. 6
$z(p)$ = variable vector that is a function of the arclength p
z_j' = derivative of z_j, Eq. 17

Subscripts

act = actual value (makes use of true thermodynamics)
EM = equimolal overflow value (as opposed to actual value)
i = counter for parameter values
ideal = ideal solution value
j = counter for variable position in vector
k = iteration counter
t, x = when used with H', a Jacobian, Eqs. 16, 17, 25
0 = initial value

Superscripts

F = feed quantity
L = liquid phase
T = transpose of a matrix
V = vapor phase
-1 = inverse of matrix
$*$ = solution quantity
$'$ = derivative

Symbols and special expressive

$[\ ]$ = matrix
$[a, b]$ = the closed interval from a to b, inclusive
$F(x){:}R^n \longrightarrow R^m$ = a function F that takes an n-dimensional vector into an m-dimensional vector
γ = activity coefficient
ϕ = fugacity coefficient

Literature Cited

Bharagava, R., and V. Hlavacek, "Experience with Adopting One-Parameter Imbedding Methods Toward Calculation of Countercurrent Separation Processes," *Chem. Eng. Commun.*, **28,** 165 (1984).

Broyden, C. G., "A Class of Methods for Solving Nonlinear Simultaneous Equations," *Math. Comp.*, **19,** 577 (1965).

Byrne, G. D., and L. A. Baird, "Research on the Convergence of a Distillation Code," AIChE Nat. Meet., Houston (Mar., 1983).

Chen, H. S., and M. A. Stadtherr, "A Modification of Powell's Dogleg Method for Solving Systems of Nonlinear Equations," *Comp. Chem. Eng.*, **5**(3), 143 (1981).

Garcia, C. B., and W. I. Zangwill, *Pathways to Solutions, Fixed Points, and Equilibria;* Prentice-Hall, Englewood, NJ (1981).

Gmehling, J., and U. Onken, *Vapor-Liquid Equilibria Data Collection,* Aqueous Organic Systems, Chem. Data Ser., DECHEMA, Frankfurt, **1,** Pt. 1 (1977).

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

Ketchum, R. G., "A Combined Relaxation-Newton Method as a Global Approach to the Computation of Thermal Separation Processes," *Chem. Eng. Sci.*, **34,** 387 (1979).

Kinoshita, M., I. Hashimoto, and T. Takamatsu, "A New Simulation Procedure for Multicomponent Distillation Column Processing of Nonideal Solutions or Reactive Solutions," *J. Chem. Eng. Japan.*, **16**(5), 370 (1983).

Krishnamurthy, R., and R. Taylor, "A Nonequilibrium Stage Model of Multicomponent Separation Processes. III: The Influence of Unequal Component Efficiencies in Process Design Problems," *AIChE J.*, **31,** 1,973 (1985).

Lucia, A., and S. Macchietto, "A New Approach to the Approximation of Quantites Involving Physical Properties Derivatives in Equation-Oriented Process Design," *AIChE J.*, **29,** 705 (1983).

Lucia, A., and K. R. Westman, "Low-Cost Solutions to Multistage, Multicomponent Separation Problems by a Hybrid Fixed Point Algorithm," *Proc. 2nd Int. Conf. Found. Computer-Aided Process Design,* A. W. Westerberg and H. H. Chen, eds., CACHE, 741 (1984).

Naphtali, L. M., and D. P. Sandholm, "Multicomponent Separation Calculations by Linearization," *AIChE J.*, **17**(1), 148 (1971).

Ortega, J. M., and W. C. Rheinboldt, *Iterative Solution of Nonlinear Equations in Several Variables,* Academic Press, New York (1970).

Powell, M. J. D., "A Hybrid Method for Nonlinear Equations," *Numerical Methods for Nonlinear Algebraic Equations,* P. Rabinowitz, ed., Gordon and Breach, New York (1970).

Prausnitz, J. M., et al., *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria,* Prentice-Hall, Englewood Cliffs, NJ (1980).

Salgovic, A., V. Hlavacek, and J. Ilavsky, "Global Simulation of Countercurrent Separation Processes via One-Parameter Imbedding Techniques," *Chem. Eng. Sci.*, **36**(10), 1,599 (1981).

Schubert, J. K., "Modification of a Quasi-Newton Method for Nonlinear Equations with a Sparse Jacobian," *Math. Comp.*, **24,** 27 (1970).

Seader, J. D., C. C. Rafael, and T. L. Wayburn, "Multiple Solutions to Systems of Interlinked Distillation Columns by Differential Homotopy Continuation," Paper 63f, AIChE Nat. Meet., San Francisco (Nov., 1984).

Wang, J. C., and G. E. Henke, "Tridiagonal Matrix for Distillation," *Hyd. Proc.*, **45**(8), 155 (1966).

Wang, J. C., and Y. L. Wang, "A Review of the Modeling and Simulation of Multistage Separation Processes," *Foundations of Computer-Aided Chemical Process Design,* R. S. H. Mah and W. D. Seider, eds., Engineering Foundation, **2,** 121 (1981).

Wayburn, T. L., and J. D. Seader, "Solutions of Systems of Interlinked Distillation Columns by Differential Homotopy-Continuation Methods," *Proc. 2nd Int. Conf. Found. Computer-Aided Process Design,* A. W. Westerberg and H. H. Chen, eds., CACHE, 765 (1984).

Wayburn, T. L., and J. D. Seader, "Degree Theory and Homotopy: Tools for Computer-Aided Process Design," Paper 27d, AIChE Nat. Meet., San Francisco (Nov., 1984b).

Westerberg, A. W., and S. W. Director, "A Modified Least-Squares Algorithm for Solving Sparse $n \times n$ Sets of Nonlinear Equations," *Comp. Chem. Eng.*, **2,** 77 (1978).

Westman, K. R., A. Lucia, and D. Miller, "Flash and Distillation Calculations by a Newtonlike Method," *Comp. Chem. Eng.*, **8**(3/4), 219 (1984).

Manuscript received Feb. 14, 1985, and revision received July 25, 1985.