Nonlinear Analysis in Process Design

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As steady-state and dynamic simulators with optimal controllers have evolved, tools for nonlinear analysis have been developed by reactor and thermophysical property specialists. Designers lag behind in developing and utilizing these tools, as many design strategies assume idealized behavior even though processes contain an increasing number of nonlinear elements. This article examines the sources of the nonlinear elements, often associated with physical and chemical interactions, in designs and their control systems. Promising methods for nonlinear analysis are reviewed.

In each design activity, involving simulation, economic optimization, projections of controllability and operability, emphasis is on the sources of nonlinearities and solution methods. These are examined for the equality constraints and nonlinear programs in phase and chemical equilibria, in reactors and separators, and in the simulation and optimization of flowsheets. Also examined are the impact of nonlinear predictive control in screening designs and methods to insure operability, in the face of uncertainties.

Introduction

Over the past 30 years, many computer-aided methods for process design and control have evolved. In the 1960s, programs for the steady-state simulation of the process flowsheet were introduced (e.g., PACER, FLOWTRAN, and CHESS). These programs incorporated subsystems for the estimation of thermophysical properties and the calculation of phase equilibria. Their emphasis was on the convergence of recycle loops and control strategies for satisfying the design specifications. In the 1970s and early 1980s, they were augmented with new optimization techniques and emphasis shifted from procedures (subroutines for each unit process) to more equation-oriented strategies for the unit processes and the collection of equations that represent the process flowsheet. More recently, mixed-integer nonlinear programming techniques have been prepared to select the unit processes and optimize the flowsheet simultaneously. These are gaining favor as compared with more conventional heuristic (rule-based) methods for process synthesis.

At the same time, many strategies were developed for modeling the dynamics of unit processes. In the 1960s, simple nonlinear integrators (mostly for nonstiff problems) were utilized (e.g., MIMIC and CSMP) and the unit processes were simulated in the open loop and under conventional PID control. The 1970s saw the birth of stiff integrators without step-size limitations to maintain numerical stability, which permitted the efficient integration of more accurate models for the unit processes. Simple optimal control problems were solved, but only for processes for which the stationarity conditions (Euler-Lagrange conditions) had bang-bang and simple intermediate solutions. With the advent of fast, small, inexpensive minicomputers and microcomputers, in the late 1970s and early 1980s, feedback control strategies evolved that incorporate the process model in the control loop. The early algorithms, which were limited to linear models, are being extended or modified to handle nonlinear models and the controllers are exhibiting much improved disturbance rejections and setpoint responses. (See the section on Nonlinear Predictive Control.) Now, research is emphasizing the coordination of design and control optimizations in the face of uncertainties.

Concurrently, new tools for nonlinear analysis were developed. While process designers throughout the 1960s and 1970s were concerned principally with local convergence methods (e.g., Wegstein's method, the Newton-Raphson method and the dominant eigenvalue method), their counterparts in reactor

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design, and thermodynamics examined the sources of the nonlinearities more closely and characterized the solution spaces for a host of unit processes, including exothermic and autocatalytic reactors. They utilized and developed global convergence methods, algorithms for parameterization and stability analysis, methods for locating singularities and bifurcation points, and algorithms for tracking periodic solutions and locating secondary bifurcations. Their methods also utilized singularity and bifurcation theories, with expansions in the vicinity of singular points, such as vapor-liquid critical points.

Today, processes are being designed with an increasing number of nonlinear elements and yet many of the new methodologies for the synthesis and analysis of process designs, and their control systems, tend to ignore the sources of the nonlinearities. For example, the new equation-oriented simulators are tested for process flowsheets with few complex nonlinearities (or where the specifications eliminate the nonlinear elements) and are reported to have difficulties when simulating processes with complex nonlinearities. (See the section on Process Flowsheet Analysis.) Moreover, nonlinearities are often introduced through process integration, such as heat and power integration. Yet, many industrial processes are designed with inadequate consideration of potential operability and control problems (McAvoy, 1987), which are often related to their nonlinearities.

Consequently, it is the principal objective of this article to examine the impact of nonlinearities on all aspects of the analysis and synthesis of process designs and their control systems. Through a comprehensive review, it should be possible to expose new applications of nonlinear analysis, as well as areas in which more work is needed. The first two sections on Equality Constraints and Nonlinear Programming emphasize how the nonlinearities arise in design models, with many examples in chemical processing. Then, the sections on Phase and Chemical Equilibrium and Process Flowsheet Analysis show how nonlinearities arise with phase uncertainty and recycle and how a broad array of solution strategies are affected by these nonlinearities.

In the first section, equality constraints (which are common to all process models) are examined with emphasis on the sources of nonlinearities and the methods for characterizing the solution spaces and finding all of the solutions. After nonlinear equations are covered, first derivatives are added, and the section concludes with a discussion of differential-algebraic equations.

Next, the objective function is added and the nonlinear program is formulated. Again, emphasis is placed on the nonlinearities that often lead to nonconvex programs with local and global optima. Here, improved strategies are needed to solve the Kuhn-Tucker conditions (stationarity conditions), which include the complementary slackness conditions associated with the inequality constraints. Several recent techniques to achieve local convergence and to improve the reliability of obtaining global optima are reviewed. The section concludes with a brief discussion of the optimization of dynamic systems, that is, optimal control.

Having concentrated on equality constraints and nonlinear programs, i.e., the mathematical structures of process design problems, the next sections focus on specific applications, beginning with the calculation of phase and chemical equilibrium. The phase and chemical equilibrium subproblem of staged separator and reactor analysis is usually solved repeatedly as the states of the process streams vary during design. This subproblem, in which the Gibbs free energy is minimized, is formulated as a nonlinear program (NLP), and is solved using the methodologies described in the nonlinear programming section. Here, singularities often arise as phases appear and disappear for nonideal solutions and at elevated pressures in the critical region. This section shows examples of these singularities for processes involving a vapor and two liquid phases, azeotropic mixtures, reactive azeotropes, and high pressure phase equilibria. The latest methods are reviewed for seeking the global minimum and checking the stability of the phase distribution at the minimum Gibbs free energy. In addition, the impact of phase shifts on the higher levels of analysis (e.g., design optimization) are examined. The section concludes with applications of geometric theory to determine residue curve maps and the minimum reflux ratio for the distillation of nonideal solutions.

The optimization of the process flowsheet can be viewed as a multilevel analysis problem. At an intermediate level are the models of the unit processes, and at a lower level are the NLPs for phase equilibria of many process streams. Before considering the evolution of solution strategies, the section on flowsheet analysis examines the impact of recycle on the nonlinear behavior of the unit processes. Then, strategies that utilize procedures to solve the equality constraints for the unit processes are reviewed, that is, the so-called sequential modular approach. The latest optimization methods are discussed before the most recent equation-oriented approaches are reviewed, with and without optimization. Here, emphasis is placed upon decomposition methods to reduce the effort in solving large problems. Finally, the section concludes with a review of the recent methods for dynamic simulation of process flowsheets. Throughout, an attempt is made to examine the effectiveness of the methods for processes involving the complex nonlinearities due to recycle, as well as those that arise in chemical reactors, phase equilibria, etc.

With more accurate steady-state and dynamic models, model predictive controllers (MPCs) can be developed in the design stage that have improved setpoint response and disturbance rejection characteristics. For nonlinear processes, the MPCs have the potential to permit operation near or within regimes that exhibit hysteresis and periodic behavior (Seider et al., 1990). Consequently, the section on model predictive control presents the NLP for MPC and refers to several recent strategies for incorporating the nonlinear process model. Finally, to achieve controllable designs in regimes having complex nonlinearities, it is recommended that economic and control optimizations be coordinated. The section concludes with a call for new solution strategies.

Finally, methods for uncertainty analysis are considered. For steady-state processes, design specifications (e.g., product purity and recovery) must be satisfied in spite of long-term fluctuations (e.g., changing feedstock) and short-term disturbances (e.g., temporary increase in heat loss). Methods for obtaining flexible designs in the long term are reviewed, with emphasis on how the nonlinearities affect the inequality constraints, leading to nonconvex feasible regions. Methods for selecting designs that permit robust MPC, in the face of short-term disturbances, are not covered, primarily because they

involve linearizations about the desired steady state and strategies for processes having complex nonlinearities have not yet been developed.

Parallel computing is gaining importance in process design as vectorization algorithms are developed that permit the solution of increasingly large problems in real time. To our knowledge, however, no papers have been published that show how vectorization algorithms are affected by nonlinearities. Since the sources and impact of nonlinearities are emphasized here, parallel computing is beyond the scope of this review.

The impact of nonlinearities on process synthesis (creation of the process flowsheet) can be difficult to assess. It seems clear that heuristics, on which decisions are based, need be applied cautiously for processes with complex physical and chemical interactions. These designs often justify the preparation of rigorous models in concert with laboratory measurements. Such models are both dynamic and steady state, permitting an examination of the controllability and operability as the design evolves. In the future, with improved mixed-integer nonlinear programming (MINLP) strategies, designers will screen the structural alternatives as the flowsheet is optimized. Several sources of the nonlinearities in such mathematical programs and their potential impact are considered in this article.

Equality Constraints

Much of the design literature is concerned with solving the material and energy balances, phase equilibria, transport equations, and chemical kinetic expressions that model a process flowsheet. Often these equations include both temporal and spatial derivatives. The spatial derivatives, when they exist, are normally approximated with finite differences or trial functions in the form of the polynomials. When the temporal derivatives are zero, for steady-state analysis, the resulting nonlinear equations (NLEs):

$$\underline{f}\{\underline{x}, \underline{p}\} = 0 \tag{1}$$

are solved for the most part using Newton-based methods. Here, $\underline{f}$ is the vector of m residuals in m unknowns, $\underline{x}$, and $\underline{p}$ is a vector of k parameters.

When complex nonlinearities, such as those occurring in exothermic reactors and heterogeneous azeotropic distillation towers, are present, two important problems arise, involving the location of single solutions and families of solutions, when they exist. The former is often solved using local convergence methods, and usually arises when a good initialization, within the radius of convergence of one or more numerical algorithms, is provided. The latter is often solved using global convergence methods, and usually involves the systematic variation of a parameter to track branches of solutions that exhibit multiple solutions. Global convergence methods are also utilized to locate solutions given poor initializations, outside of the radius of convergence of the common numerical algorithms.

To expand upon these distinctions, local convergence algorithms usually require a good initialization, often utilizing a succession of approximate models to provide guess values in the vicinity of the solution. Whereas global convergence algorithms emphasize the automatic adjustment of poor guesses to achieve convergence by transforming the original problem into a simpler problem that is gradually made more complicated. To obtain better initializations, physical insights often suggest the proper sequence of initializations. Furthermore, Seider (1984) showed how the utilization of physical insights can lead to more efficient convergence algorithms, although in recent years, with the availability of high-speed work stations, generalized Newton-based algorithms have been found to be sufficiently efficient and are often easier to implement. In fact, Newton-based algorithms are increasingly incorporated in *equation-oriented* simulators. Here, physical insights can help to identify the regions in which multiple steady states and singularities are associated with nonlinear processes. In many cases, these nonlinearities are sufficiently severe to justify the use of the global convergence algorithms.

Several sources provide excellent coverage of the convergence algorithms for use in process design. These include chapter 3 of *Process Flowsheeting* (Westerberg et al., 1979) and three review articles (Hlavacek, 1977, part II; Sargent, 1981; Shacham et al., 1982). Comparative analyses of many numerical methods are presented, with emphasis on the rate of convergence, methods of extending the radius of convergence, techniques for avoiding singularities and other related concerns. The principal deficiency of these sources, which extends into much of the process design literature, is that the numerical methods are presented, for the most part, independently of the process model. They do not consider the advantages and disadvantages of these methods in dealing with the complex nonlinearities encountered in phase equilibria, adiabatic reactors, and elsewhere.

Unfortunately, the design literature is heavily biased toward the synthesis and analysis of highly idealized processes, with some generalizations concerning pathological problems, such as singularities. Perhaps there is less interest in the specific nonlinearities and their impact because they are often isolated in individual applications, and are considered to belong to the domain of specialists in these areas. But, these are gaining importance in the design of processes that, to be competitive, involve complex nonlinear effects (e.g., in reactive and azeotropic distillation, natural gas separation in the critical region with heat and power integration, catalytic and fermentation reactors).

In this section and throughout the article, an attempt is made to come to grips with the nonlinearities that often arise in process design, considering only those solution methods that have successfully dealt with or have had difficulties in dealing with them. For each method, one or more references are described, in which the methodology has been applied for solution of specific process design problems.

With faster work stations, having more memory, more accurate process models are evolving. Many new effects are being recognized and the design methodologies are being tested more severely. Herein, a sampling of the growing literature is presented, with emphasis on many of the unresolved issues and areas for future research.

Local convergence algorithms

In process design, several first-order methods (e.g., direct substitutions), with accelerators (e.g., the generalized dominant eigenvalue method; Orbach and Crowe, 1971, and Crowe and Nishio, 1975), are utilized, but the advantages and disadvantages of the Newton-Raphson (N-R) method:

$$\underline{\Delta x}^{(k)} = -\underline{\underline{J}}^{-1}\{\underline{x}^{(k)}\}\underline{f}\{\underline{x}^{(k)}\} \quad k = 1, 2, \ldots \qquad (2)$$

are well understood. Close to the solution, quadratic convergence is achieved, although the Jacobian and its inverse must be calculated. To reduce this effort, at the cost of additional iterations, variations on the N-R method, so-called Newton-like methods, have been introduced. In this subsection, emphasis is placed on the so-called hybrid quasi-Newton methods designed to cope with the nonlinearities in the phase equilibrium problem for highly nonideal solutions. The quasi-Newton (and Newton-like) methods have been reviewed extensively in previous articles (Sargent, 1981; Bogle and Perkins, 1988). Here, just three of the principal variations are reviewed, as these are the basis for the hybrid methods that follow. The subsection concludes with a discussion of Powell's dogleg method, which has been tested for the solution of many process design problems.

Hybrid Quasi-Newton Methods. To obtain second-order convergence, an accurate Jacobian is required. When analytical derivatives are difficult to express, finite differences may be computed, but these require at least $m+1$ evaluations of $\underline{f}$ and may not be sufficiently accurate to provide second-order convergence. The Quasi-Newton methods are a popular alternative. These begin with an approximation to the Jacobian or its inverse and utilize rank-1 updates. In one implementation of the Broyden update,

$$\underline{\underline{A}}^{(k+1)} = \underline{\underline{A}}^{(k)} + \frac{[\underline{\Delta e}^{(k)} - \underline{\underline{A}}^{(k)}\,\underline{\Delta x}^{(k)}]\,(\underline{\Delta x}^{(k)})^T}{(\underline{\Delta x}^{(k)})^T\underline{\Delta x}^{(k)}} \qquad (3)$$

the approximation to the Jacobian, $\underline{\underline{A}}$, which is typically a sparse matrix, becomes a dense matrix after a single update. Here, $\underline{\underline{A}}^{(k+1)}$ is the approximation to the Jacobian after iteration k; $\underline{\Delta e}^{(k)}$ is the error vector, $\underline{f}^{(k)} - \underline{f}^{(k-1)}$; and $\underline{\Delta x}^{(k)}$ is the last increment vector, $\underline{x}^{(k)} - \underline{x}^{(k-1)}$. Three alternatives have been used to retain a sparse approximation. One, introduced by Schubert (1970), sets the new nonzero elements to zero, and scales the remaining elements to satisfy the secant approximation,

$$\underline{\Delta e}^{(k)} = \underline{\underline{A}}^{(k+1)}\,\underline{\Delta x}^{(k)} \qquad (4)$$

Another, attributed to Bennett (1965), updates the sparse L-U factors so as to maintain a sparse representation of the Jacobian matrix. In the third, Bogle and Perkins (1987) derive a modified Broyden update that minimizes the norm of the relative changes in $\underline{\underline{A}}$ while updating only the nonzero elements.

The hybrid method by Dennis et al. (1977), more recently introduced in process simulation by Lucia and Macchietto (1983), involves updates for just part of the Jacobian matrix; the portion that is difficult to evaluate analytically. These authors split the Jacobian matrix into two parts:

$$\underline{\underline{J}}^{(k)} \cong \underline{\underline{C}}^{(k)} + \underline{\underline{A}}^{(k)} \qquad (5)$$

where $\underline{\underline{C}}^{(k)}$ contains the portion of the derivatives that can easily be evaluated analytically and $\underline{\underline{A}}^{(k)}$ contains an approximation to the remainder of the derivative elements. For models involving the chemical potential of species in nonideal liquid phases, $\underline{\underline{A}}^{(k)}$ contains the approximation to terms that are difficult to evaluate analytically, such as $x_j\,(\partial K_j/\partial x_k)$. Here, x_j is the mole fraction and K_j is the vapor–liquid equilibrium constant for species j. When using the Schubert scaling, to maintain a sparse matrix $\underline{\underline{A}}$, the update to the approximation portion of the Jacobian becomes:

$$\underline{\underline{A}}^{(k+1)} = \underline{\underline{A}}^{(k)} + \sum_{i=1}^{m} \underline{e}_i^T\,[\underline{\Delta e}^{(k)} - \underline{\underline{C}}^{(k+1)}\,\underline{\Delta x}^{(k)} - \underline{\underline{A}}^{(k)}\,\underline{\Delta x}^{(k)}]\,\underline{e}_i\,\underline{\Delta x}_i^T/[\underline{\Delta x}_i^{(k)T}\,\underline{\Delta x}_i^{(k)}] \qquad (6)$$

where $\underline{e}_i$ is the ith unit vector. For solution of the MESH (material balance, equilibria, summation of mole fractions, and heat balance) equations associated with "flash" vessels and distillation columns (Westman et al., 1984), this algorithm has been found to require only a few more iterations than the Newton-Raphson method, but 60–70% fewer rigorous estimates of the physical properties (fugacity and activity coefficients).

Using Eq. 6, the approximation to the Jacobian, $\underline{\underline{J}}^{(k)}$, is not normally thermodynamically consistent; that is, the Gibbs-Duhem and Gibbs-Helmholtz equations are not satisfied. In a novel approach, Lucia et al. (1985) and Venkataraman and Lucia (1986) extended the hybrid method to yield thermodynamically-consistent approximations to the Jacobian. Numerical results for highly nonideal mixtures show improvements in the reliability and computational efficiency as compared with the aforementioned Newton-like methods.

The question of the efficiency of this approach, as compared with Newton's method using analytical derivatives, remains unresolved. Michelsen and Mollerup (1986) argue that the partial derivatives of the thermodynamic properties are not difficult to evaluate analytically. Rather, they can be evaluated with just a few operations in excess of those necessary to evaluate the functions, $\underline{f}$, and, because they are evaluated exactly, they satisfy the Gibbs-Duhem and Gibbs-Helmholtz equations. On the other hand, Venkataraman and Lucia (1988) contend that their thermodynamically consistent hybrid method is as reliable and more efficient.

Powell's Dogleg Method. This method, attributed to Powell (1970), adds a threshold radius to the Marquardt method (1963) and often extends the radius of convergence of the Newton-Raphson method, but does not have the global convergence properties of the homotopy-continuation algorithms presented in the next section. It has been tested extensively for solving the equality constraints in process simulation and is being developed to solve the larger problems associated with process flowsheets. However, it has had only limited success when complex nonlinearities exist in the process model. It is reviewed here because of the considerable interest in its development and to provide a comparison with the homotopy-continuation algorithms.

The dogleg method implements a compromise between the first-order steepest descent (SD) and Newton-like methods in a so-called hybrid approach. First, the minimum of Σf_i^2 is located in the direction of steepest descent. Then, the Newton-like step is computed. Given a specification for the threshold radius, a compromise parameter, t, is computed for the iteration rule:

$$\underline{\Delta x}^{(k)} = -(2\underline{\underline{A}}\{\underline{x}^{(k)}\}^T\underline{\underline{A}}\{\underline{x}^{(k)}\} + t\underline{\underline{I}})^{-1}\nabla\underline{F}\{\underline{x}^{(k)}\} \qquad (7)$$

where $\underline{\underline{A}}$ is an approximation to the Jacobian of Eq. 1 and $F = \Sigma f_i^2$. When $t = 0$, a Newton-like step is computed, and when t is large (far from the solution), a steepest descent step is obtained. In this way, the matrix in parentheses can be inverted when singularities in the Jacobian occur (using large t) as the solution is approached from poor starting points.

In principle, the Newton-Raphson method is scale-independent. This, however, is not so for Newton-like methods in which the Jacobian and Hessian matrices are approximated, especially when the off-diagonal elements of these matrices are strong functions of the independent variables (e.g., when modeling phase equilibria in nonideal solutions). For this reason, Chen and Stadtherr (1981) developed methods for automatically scaling both the functions and the variables. Then, to avoid the need for scaling, Perkins and Sargent (1982) introduced a scale-invariant Jacobian update. This was extended by Bogle and Perkins (1988) to apply to sparse Jacobian matrices.

Powell's method was modified by Chen and Stadtherr (1981), who introduced automatic scaling and a limit on the step-size adjustment, and tested successfully on 14 standard problems. Subsequently, Shacham (1985) compared its performance with other methods for the solution of several small process engineering problems (having a maximum of 39 unknowns). Two implementations of the dogleg method provided significantly different performance and were found to be unpredictable and unreliable. More recently, Sun and Stadtherr (1988) extended the comparison, utilizing various scaling techniques and the Jacobian update of Bogle and Perkins (1987). These authors added larger test problems (having up to 240 unknowns) and found these modifications of the dogleg method to perform very well for all of the test problems. Furthermore, when they incorporated the Schubert update, similar good performance was obtained.

The test problems of Shacham (1984, 1985), extended by Sun and Stadtherr (1988), involve flash vessels, reactors in chemical equilibrium, flow in a network of pipelines, cascades of chlor-alkali cells for caustic concentration, and cascades of electrodialyzers for the desalination of water. While their degree of nonlinearity varies and is difficult to quantify, in many cases they require good initializations and it seems clear that the emphasis is on locating single solutions, rather than convergence to all of the solutions from poor starting points. In several cases, the use of global convergence methods would be preferable.

Global convergence algorithms

When process nonlinearities result in multiple solutions (e.g., in exothermic and autocatalytic reactors), problems arise as the local convergence algorithms encounter singularities (e.g., at limit, or turning, points, where the iterates can oscillate between two steady-state attractors). Here, the homotopy-continuation methods are very effective, though less efficient, in achieving global convergence, i.e., in finding the desired solution and when necessary locating *all* of the solutions. In this area, an extensive literature has also been generated (Garcia and Zangwill, 1981; Wayburn and Seader, 1984; Seader, 1990), and hence, only the more important methods are reviewed briefly, with emphasis on the methods applied to solve problems in process engineering and on recent developments. First, the most common homotopy methods are briefly reviewed.

The homotopy methods provide a smooth transition between an approximation to the solution (often linear or nearly linear) and the true solution(s) of Eq. 1. In this way, they gradually introduce the complex nonlinearities.

In many formulations, a convex, linear homotopy function is utilized:

$$\underline{H}\{\underline{x}, t\} = t\underline{f}\{\underline{x}\} + (1-t)\,\underline{g}\{\underline{x}\} = 0 \tag{8}$$

where t is a real, scalar parameter and $\underline{g}\{\underline{x}\}$ is a vector of residuals that can easily be solved for $\underline{x}$. Continuation algorithms solve Eq. 8 beginning with $t = 0$ and track the *homotopy path* as t is increased to unity. Two choices for $\underline{g}\{\underline{x}\}$ are widely used:

Homotopy	$\underline{g}\{\underline{x}\}$	$\underline{H}\{\underline{x}, t\}$
Newton	$\underline{f}\{\underline{x}\} - \underline{f}\{\underline{x}^0\}$	$\underline{f}\{\underline{x}\} - (1-t)\underline{f}\{\underline{x}^0\}$
Fixed-Point	$\underline{x} - \underline{x}^0$	$t\underline{f}\{\underline{x}\} - (1-t)(\underline{x} - \underline{x}^0)$

Here, $\underline{x}^0$ is the vector of guessed values. Since homotopy-continuation paths often include singular points, such as limit points, where $|\underline{\underline{J}}| = 0$, it is important to trace the paths with sufficient accuracy, while bypassing the singular points. One effective algorithm, introduced by Klopfenstein (1961) utilizes a differentiated form of Eq. 8 suggested by Davidenko (1953), expressed here for the Newton homotopy:

$$\underline{\underline{J}}\{\underline{x}\}\frac{d\underline{x}}{dp} - \frac{d\lambda}{dp}\underline{f}\{\underline{x}^0\} = 0 \tag{9a}$$

where $\lambda = 1 - t$ and p is an arc-length parameter defined by:

$$\left(\frac{d\underline{x}}{dp}\right)^T\left(\frac{d\underline{x}}{dp}\right) + \left(\frac{d\lambda}{dp}\right)^2 = 1 \tag{9b}$$

Allgower and Georg (1980) presented a differential arclength homotopy-continuation algorithm that integrates the ODEs along the arclength using an Euler predictor step followed by Newton correction steps. This strategy was implemented by Wayburn and Seader (1984) with special attention to the methods for step-size adjustment and parameter-variable exchange to avoid singularities near limit points. The turning point algorithm was further extended by Kovach and Seider (1987b) to bypass the limit points when multiple solutions are encountered as a second liquid phase is introduced on the trays of a heterogeneous azeotropic distillation tower. Although these programs have not been widely distributed, HOMPACK (Watson et al., 1987) is widely used for the implementation of Newton and fixed-point homotopies.

These and other continuation methods have been applied successfully for the solution of the phase equilibrium equations involving nonideal phases. In one approach, Vickery and Taylor (1986) first solve the MESH equations for a distillation tower assuming ideal liquid phases and use the homotopy parameter to introduce gradually the nonideal terms in the model. In another approach, Kovach and Seider (1987b) solve the liquid-liquid equilibrium equations using the Newton homotopy. Initially, none of the distributing solute is present in the

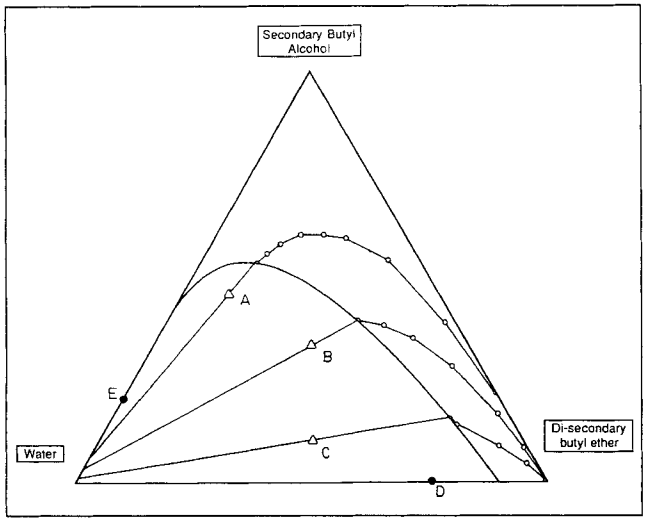

Figure 1. Mole fractions along the homotopy path for feed compositions at *A*, *B*, and *C*.
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feed and the two liquid phases are assumed to be pure. As the homotopy parameter is varied, the solute is added to the feed. For the system secbutanol, disecbutylether, and water, the continuation paths for three feeds (points A, B and C) are illustrated in Figure 1.

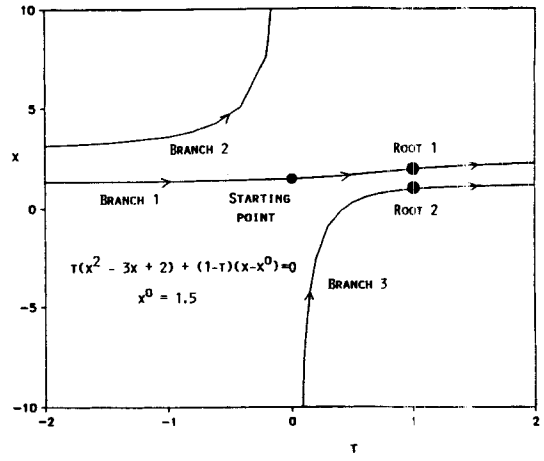
Recently, Seader et al. (1990) introduced a *boomerang* transformation that has not failed to locate *all* of the solutions for the sets of NLEs they tested. To solve the nonlinear equations (Eq. 1), they utilize a fixed-point homotopy, which has the advantage that only one solution to $\underline{H} = 0$ can exist at $t = 0$, but the disadvantage that $\underline{x}$ and t can extend to $+\infty$ and return from $-\infty$ along the paths, as illustrated for the solution of a simple quadratic equation in Figure 2a. The boomerang mapping:

$$y_i' = \frac{2y_i}{(1+y_i^2)}, \qquad \forall i \tag{10}$$

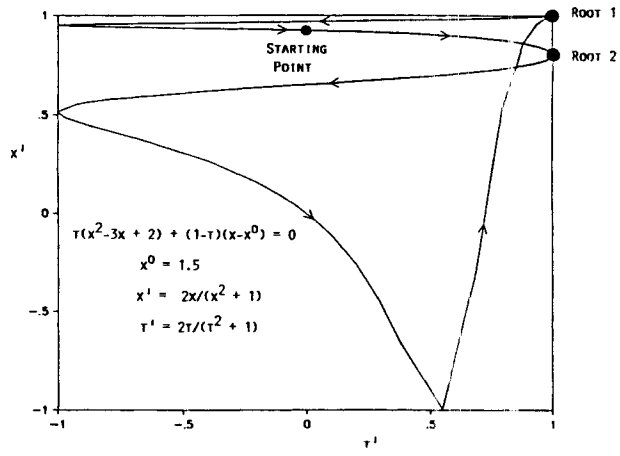
where $\underline{y}$ applies for $\underline{x}$ and t, keeps the new variables bounded such that $-1 \le \underline{y}' \le 1$, as illustrated for the quadratic equation in Figure 2b. With the variable space mapped to lie within finite bounds, all of the solutions can usually be found by tracing out a single path of finite length.

It is noteworthy that methods are available to find all of the roots for systems of polynomial equations. As an example, the use of HOMPACK to solve the equations of chemical equilibrium is demonstrated nicely for an ionic equilibrium problem (Seader, 1990).

As global convergence strategies are improved, process engineers must weigh their advantages and disadvantages more carefully. A decade ago, with much slower computers and expensive computation time, continuation methods were for the most part too expensive to execute. Solutions of complex problems were often obtained in stages, beginning with more approximate models and utilizing their solutions as the initial guesses for more complex models. In this approach, the emphasis is upon improving the initializations for local convergence methods. Today, global convergence methods are usually



a. Untransformed homotopy path



b. Transformed path

Figure 2. Boomerang transformation for solution of $f\{x\} = x^2 - 3x + 2 = 0$.
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simpler to implement and can be adapted with relative ease to seek all of the solutions of the process equations. However, they are costly to implement and their reliability and efficiency remains to be assessed for large process models.

It is important to recognize that when complex nonlinearities exist, in some cases global convergence methods obtain solutions not obtainable with other methods (e.g., solution of the MESH equations for heterogeneous azeotropic distillation towers; Kovach and Seider, 1987a,b). In this regard, with faster computers that have more memory, more complex models, such as these, are evolving. For these models, global convergence methods are often the only reliable alternative. Given a choice, however, the engineer will often opt to utilize global convergence methods to achieve a solution reliably, even when they consume considerably more computation time. Unfortunately, few guidelines exist, and the selection of local or global convergence algorithms remains an unresolved issue, especially for processes involving complex nonlinearities.

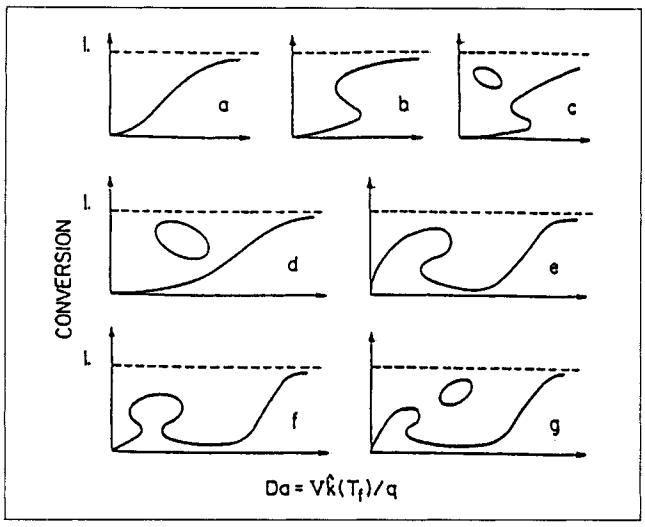

Figure 3. Seven kinds of solution diagrams for $A \rightarrow B$.
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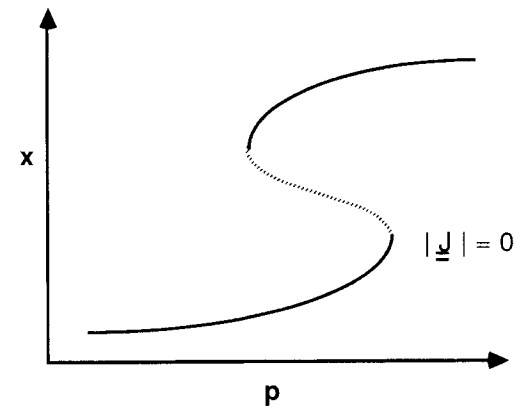

Figure 4. Stability change at limit points.
— stable solutions ----- unstable solutions

Parameterization

Probably the greatest advantage of the global convergence strategies is that they are easily adapted to explore the complex solution spaces for nonlinear processes as a parameter of the process model varies. For a single parameter value, the homotopy-continuation methods may be inefficient, especially when just one solution is desired. However, for parametric studies, they can be very effective, even when multiple solutions do not exist. Their extension for parameterization is rather straightforward. First, the NLEs are solved for a fixed value of the parameter. Then, a specification equation is added for the parameter:

$$p - p^{\text{spec}} = 0 \tag{11}$$

As discussed by Kovach and Seider (1987b), p varies linearly with the homotopy parameter as the solution branches are traced out.

This methodology has been applied for many process models, including the generation of the liquid-liquid binodal curve (Kovach and Seider, 1987b) as the feed varies from point D to E in Figure 1, variation of the reflux ratio in distillation (Lin et al., 1987; Kovach and Seider, 1987a), and the performance of an exothermic CSTR as the Damköhler number is varied (Kubicek and Marek, 1983). For such parameterization studies, several packages are available, including HOMPACK (Watson et al., 1987), PITCON (Rheinboldt and Burkardt, 1983), DERPAR (Kubicek and Marek, 1983), and AUTO (Doedel, 1986).

To illustrate the variety of solution diagrams for nonlinear reactors, consider the studies of Balakotaiah and Luss (1982) for the "diabatic" (nonadiabatic) CSTR involving the classic reaction,

$$A \rightarrow B$$

Figure 3 shows the seven kinds of solution diagrams, with a maximum of three steady-state solutions, generated by a continuation algorithm as Da varies. For the exothermic reactions, Balakotaiah and Luss (1983) identify a maximum of five steady-state solutions and 48 kinds of solution diagrams.

These two examples show that richer solution spaces are often obtained as nonlinear elements are added. The generation of complete solution diagrams can require substantial effort, and hence the alternative of qualitative analysis in the vicinity of the singular points becomes attractive (e.g., when knowledge of the number of solutions is adequate). This analysis usually applies imperfect bifurcation theory and is reviewed in the later section on Bifurcation Theory.

Bifurcation points—stability analysis

As homotopy-continuation algorithms follow the steady-state solution branches, they bracket limit points, Figure 4, where $|\underline{\underline{J}}| = 0$. However, they normally pass over higher-order singular points, such as real bifurcation points where two or more solution branches cross, Figure 5, and Hopf bifurcation points (HBP), where a periodic branch of solutions is born, Figure 6. To locate real and Hopf bifurcation points, local stability analyses can be performed along the solution

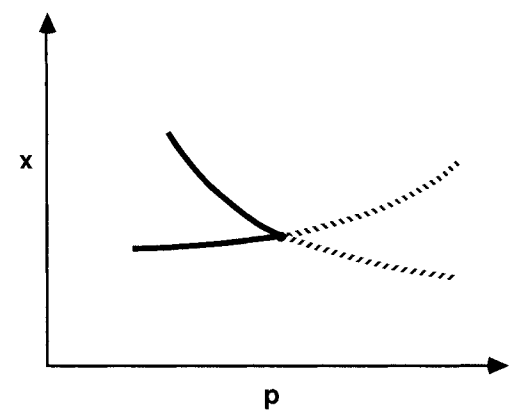

Figure 5. Real bifurcation point.

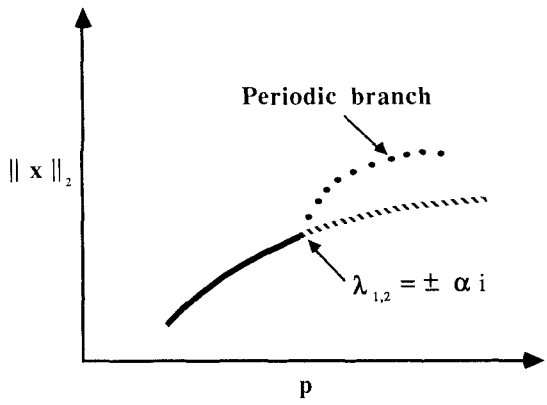

Figure 6. Hopf bifurcation point

branches (evaluation of the eigenvalues of the Jacobian) or the necessary and sufficient conditions for these points can be solved (Kubicek and Marek, 1983). At a limit point, an eigenvalue becomes zero and a change in stability often occurs. Real bifurcation points have similar properties at the intersection of two or more branches. At a HBP, two complex eigenvalues become pure imaginary, the steady-state branch destabilizes or remains unstable, and a branch of periodic solutions is born. To determine the eigenvalues of the Jacobian, packages such as EISPACK (Dongarra and Moler, 1976) are used in conjunction with the continuation packages. EISPACK is a collection of FORTRAN subroutines that compute the eigenvalues and eigenvectors of nine classes of matrices. The methods used include those described by Wilkinson (1965) in his comprehensive text.

Dynamic simulations, with the temporal derivatives included, are necessary to trace out the limit cycles. As a parameter of the system varies, a branch of periodic solutions can be traced, often leading to secondary bifurcations and, in some cases, chaos. At parameter values just beyond the Hopf bifurcation point, the limit cycles are traced by solving the split boundary-value problem:

$$\begin{aligned} \dot{\underline{x}}\{\tau\} &= T\underline{f}\{\underline{x}\{\tau\}, p\} \\ \underline{x}\{0\} &= \underline{x}\{1\} \end{aligned} \tag{12}$$

where T is the unknown period of oscillation, also referred to as an eigenvalue, and τ is the dimensionless time, t/T. Keller (1968) presents a comprehensive discussion of this class of boundary-value problems and Aluko and Chang (1984) present a Newton-Fox algorithm for solving Eq. 12. The Newton-Fox algorithm solves iteratively for the unknown period, T, and a point on the solution. Related variational matrix equations (Keller, 1968) are derived by introducing a perturbation and linearizing the ODEs about the limit cycle. These are integrated simultaneously with Eq. 12 and used in the iterative corrections. To determine the stability of the limit cycle, the eigenvalues of one of these matrices, the Monodromy matrix, are evaluated at $\tau = 1$. These eigenvalues are the Floquet multipliers, which can be shown to be less than unity for stable limit cycles. As a parameter varies, secondary bifurcation occurs when a Floquet multiplier passes through the unit circle and a new branch of periodic solutions is born. The value of the Floquet multiplier, as it crosses the unit circle, determines the nature of the new branch. In some cases, the period of oscillation is doubled, a new frequency is added to the previous frequency, or a limit point occurs in the periodic branch. When many secondary bifurcations occur over a small parameter range, a strange attractor or even chaos can arise.

These parameterization studies are very important in characterizing the nature of the attractors; steady-state nodes or foci, periodic, strange or chaotic attractors. To trace the periodic branches, a few packages are available, including DERPER (Holodniok and Kubicek, 1984), PEFLOQ (Aluko and Chang, 1984), and AUTO (Doedel, 1986). AUTO is the most complete package for bifurcation analysis, to our knowledge, in that it has programs to locate limit points and real and Hopf bifurcation points accurately, and to trace out the steady and periodic branches.

The diabatic CSTR involving the exothermic reactions:

$$A \rightarrow B \rightarrow C$$

has a maximum of seven steady-state solutions and 23 kinds of solution diagrams, as observed by Farr and Aris (1986). When extended to include periodic oscillations, Doedel and Heinemann (1983) obtained solution diagrams with two periodic branches. Figure 7 shows the birth of unstable limit cycles at the first HBP. Along this periodic branch, the limit cycles stabilize, destabilize, and restabilize at three turning points (secondary bifurcation points) before approaching a stable steady state at the fourth HBP. The steady-state branch restabilizes at the second HBP, where a stable branch of periodic attractors is born that destabilizes at the turning point. Clearly, small changes in *Da* can significantly shift the regime of operation and when $0.2187 < Da < 0.2395$ disturbances can cause a shift from steady to periodic operation, and vice versa.

The packages above have been quite successful in solving small problems, such as this one, although difficulties are often experienced when several secondary bifurcations occur over a small range of parameter values, especially as chaos sets in. Much work is needed to track these periodic and quasiperiodic branches more reliably and to solve larger problems in rea-

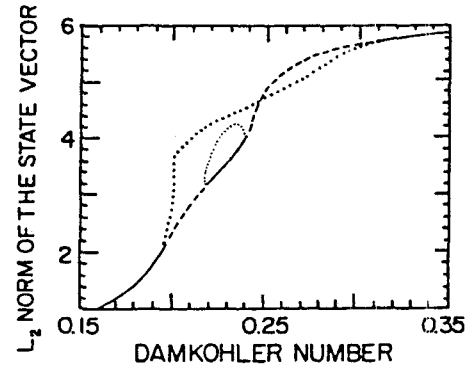

Figure 7. Typical solution diagram for $A \rightarrow B \rightarrow C$.
— Stable steady-state solutions, --- unstable steady-state solutions, · · · branches of limit cycles between four Hopf bifurcation points.
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sonable computation times. The tracking of periodic branches is very expensive computationally.

It is noteworthy that sequences of secondary bifurcations, such as in period doubling to chaos, are important to recognize when designing processes and their control systems. These sequences occur in another less obvious area of design work, as discussed by Lucia et al. (1990). These authors show, using Poincaré maps, that the iteration sequence when using the method of direct substitutions, Newton's method, as well as others, experiences period doubling as a parameter of the process varies. This bifurcation to chaos is illustrated for several examples, including a simple flowsheet with two vapor-liquid separators and recycle. With further research, bifurcation analysis may help in selecting the solution strategies for specific design problems.

Bifurcation theory

In the early design stages, when analyzing nonlinear processes, it may be sufficient to obtain a qualitative sketch of the solution space, rather than perform time-consuming continuation calculations. Such analyses, using bifurcation theory, have been applied for nonlinear chemical reactors (Balakotaiah, 1982) and can potentially be applied for a broad class of process designs. In this section, the basic principles of the theory are introduced, prior to a discussion of its potential for the solution of process design problems.

Bifurcation theory is an analytical methodology that deals with branching solutions of sets of nonlinear equations:

$$\begin{aligned} &\underline{f}\{\underline{x}, \underline{p}\} = 0 \\ &f: R^m \times R^k \rightarrow R^m;\ \underline{x} \in R^m \text{ and } \underline{p} \in R^k \end{aligned} \tag{13}$$

when the Jacobian matrix is singular. The analysis begins with the determination of the branching equations of Eq. 13, followed by the identification of the highest-order singular point, before the imperfect bifurcation theory is applied to characterize all possible solutions about the highest-order singular point. The first two steps are facilitated by the Liapunov-Schmidt reduction (LSR) method, which reduces the dimension of the problem by decomposing it into regular and singular parts.

Let $(\underline{x}_0, \underline{p}_0)$ be a solution of Eq. 13 and the Jacobian matrix, $\underline{\underline{L}}$, of the linearization of $\underline{f}$ be of rank r, where $1 \le r \le m-1$. The implicit function theorem (Golubitsky and Schaeffer, 1985) guarantees that r equations of Eqs. 13 have a unique solution of the form:

$$x_i = \Psi_i\{\underline{z}, \underline{p}\} \qquad i = 1, \ldots r \tag{14}$$

where $\underline{z}$ is a vector, of length $\ell = m - r$, of any subset of $\underline{x}$. Substituting Eq. 14 into the remaining $(m - r)$ equations gives:

$$\begin{aligned} &\underline{g}\{\underline{\Psi}\{\underline{z}, \underline{p}\}, \underline{z}, \underline{p}\} = 0 \\ &g: R^\ell \times R^k \rightarrow R^\ell \end{aligned} \tag{15}$$

Equations 15, which are commonly called the branching or bifurcation equations about $(\underline{x}_0, \underline{p}_0)$, contain sufficient information to characterize the solutions of Eq. 13 in the vicinity of the singular point. Note that Eqs. 15 need not be expressed explicitly because only the derivatives of the branching equations are needed explicitly.

To simplify this discussion, without loss of generality, it is assumed that $r = m-1$ ($\ell = 1$), and hence, Eqs. 15 reduce to a single equation:

$$g\{z, \underline{p}\} = 0 \tag{16}$$

The maximum number of solutions is obtained by determining the highest codimension, α, of Eq. 16 such that:

$$g = \frac{dg}{dz} = \frac{d^2g}{dz^2} = \ldots = \frac{d^\alpha g}{dz^\alpha} = 0;\ \frac{\mathrm{d}^{\alpha+1}\mathrm{g}}{\mathrm{dz}^{\alpha+1}} \neq 0\ \ \alpha \le m \tag{17}$$

Then, the maximum number of solutions in the vicinity of the singular point is $\alpha+1$. The LSR method facilitates the computation of these derivatives, which can be expressed as a function of the null vectors of $\underline{\underline{L}}$ and $\underline{\underline{L}}^T$ and the derivatives of Eq. 13. For example, the third derivative of g is given by the inner product:

$$\frac{d^3g}{dz^3} = \langle \underline{v}, d^3\underline{f}[\underline{u}, \underline{u}, \underline{u}] + 3d^2\underline{f}[\underline{u}, \underline{\zeta}^1] \rangle \tag{18a}$$

where

$$\underline{\underline{L}}\,\underline{u} = 0 \tag{18b}$$

$$\underline{\underline{L}}^T\underline{v} = 0 \tag{18c}$$

$$\underline{\underline{L}}\underline{\zeta}^1 + \underline{\underline{E}}d^2\underline{f}[\underline{u}, \underline{u}] = 0 \tag{18d}$$

$$\underline{\underline{E}} = \underline{\underline{I}} - \frac{\underline{v}\,\underline{v}^T}{\langle \underline{v}, \underline{v} \rangle} \tag{18e}$$

and the qth differential of the vector function $\underline{f}$ at $(\underline{x}_0, \underline{p}_0)$ is defined by:

$$d^q\underline{f}|_{\underline{x}_0,\underline{p}_0}[\underline{w}^1, \underline{w}^2, \ldots, \underline{w}^q] = \sum_{\beta_1=1}^{m} \sum_{\beta_2=1}^{m} \cdots \sum_{\beta_q=1}^{m} \frac{\partial^q \underline{f}|_{\underline{x}_0,\underline{p}_0}}{\partial x_{\beta_1} \cdots \partial x_{\beta_q}} w^1_{\beta_1} w^2_{\beta_2} \cdots w^q_{\beta_q} \tag{18f}$$

The principal difficulties in evaluating the derivatives in Eq. 17 lie in the computation of $d^q\underline{f}$ and $\underline{\zeta}^s$, especially, since it requires the solution of a system of linear equations (Eq. 18d for $s=1$). These difficulties become more pronounced with larger process models. The use of symbolic manipulation software, such as REDUCE, MACSYMA, or MATHEMATICA, can significantly reduce the effort in obtaining analytical expressions for the derivatives, but may not be practical for large systems. The LSR procedure is described by Golubitsky and Schaeffer (1985) and is applied to chemical reactors by Balakotaiah et al. (1985).

Imperfect or perturbed bifurcation theory is an extension of the classical bifurcation theory developed by Golubitsky and Schaeffer (1985). It accounts for imperfections in Eq. 13,

e.g., those due to uncertainties, by including a vector of perturbation variables, $\underline{\epsilon} \in R^e$, and hence, Eq. 13 is restated:

$$\underline{F}\{\underline{x}, \underline{p}, \underline{\epsilon}\} = 0 \tag{19}$$

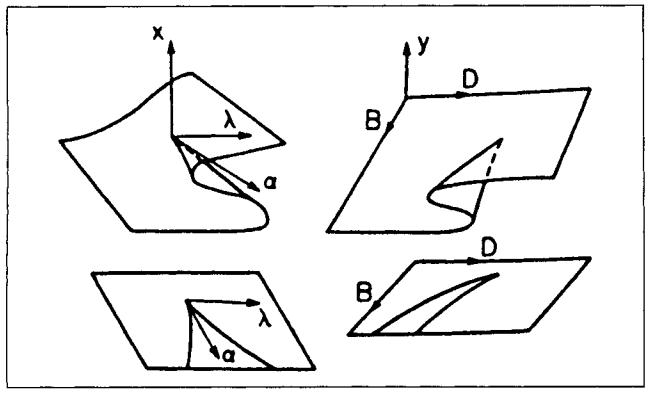
In the analysis, after the highest-order singularity is identified, a transformation creates a new set of equations having the same qualitative structure in the vicinity of the singular points; that is, regions with the same numbers of solutions. The transformed equations are polynomials that are said to be contact equivalent to Eqs. 15: that is, the polynomials preserve the structure of the zeroes of Eqs. 15 in the vicinity of the singular points. When normalized, these normal-form polynomials comprise the lowest-order, nonzero monomials in the Taylor series of Eqs. 15 about the highest-order singular point. The order of the normal form polynomial is $\alpha + 1$ (the maximum number of solutions of Eqs. 15 in the vicinity of the singular point). To examine the structure of the solutions near the singular point, perturbation variables, $\underline{\epsilon}$, are introduced. The fewest perturbation variables to give a normal form that has the same qualitative structure of Eqs. 15 near the singular point are identified. When added to the normal form, these define a universal unfolding that gives all possible structures of the solutions to Eqs. 15 about the highest-order singular point.

This analysis is easily applied to small systems that are reducible to a single equation. Such systems often arise in the analysis of chemical reactors and have been studied extensively by Balakotaiah (1982) through the use of the imperfect bifurcation theory.

As an illustration, consider a CSTR with an exothermic, first-order reaction, $A \rightarrow B$, and heat transfer to the surroundings. As mentioned in the section on Parameterization, this system can have three steady-state solutions. The mass and energy balances at steady state are:

$$0 = q(C_{A0} - C_A) - Vk\{T\}C_A \tag{20a}$$

$$0 = q\rho c_p(T_0 - T) - V(\Delta H_r)k\{T\}C_A - UA(T - T_c) \tag{20b}$$



a. Solution of Eq. 26; universal unfolding

b. Solution of Eq. 21; CSTR model

Figure 8. Contact equivalent surfaces about a second-order singular point.
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where

$$k\{T\} = k_0 e^{\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

When C_A is eliminated, Eqs. 20 reduce to:

$$F\{Y, D, B\} = Y - D(B - Y)e^Y = 0 \tag{21}$$

where

$$Y = \frac{E}{RT_0}\left(1 - \frac{T_0}{T}\right)$$

$$D = \frac{Vk_0}{q}(1 + \beta)$$

$$B = \frac{E}{RT_0}\left(\frac{\beta}{1+\beta}\right)$$

$$\beta = \frac{(-\Delta H_r)C_{A0}}{\rho c_p T_0(1+H)}$$

$$H = \frac{UA}{q\rho c_p}$$

The system has a second-order singular point (codimension 2),

$$F = \frac{\partial F}{\partial Y} = \frac{\partial^2 F}{\partial Y^2} = 0$$
$$Y^0 = 2,\ D^0 = e^{-2},\ B^0 = 4 \tag{22}$$

At this singular point,

$$\frac{\partial^3 F}{\partial Y^3} \neq 0;\ \frac{\partial F}{\partial D} < 0;\ \frac{\partial F}{\partial B} < 0 \tag{23}$$

Thus, the Taylor series approximation to Eq. 21 about the singular point gives:

$$F\{Y, D, B\} \cong a_1 Y^3 - a_2 B - a_3 D \tag{24}$$

Using either B or D as a bifurcation parameter, Eq. 24 can be transformed and normalized to give

$$G\{x, \lambda\} \equiv x^3 - \lambda = 0 \tag{25}$$

which is the normal form of Eq. 21. Balakotaiah and Luss (1982) show that the minimum number of perturbation variables for this system is one. Thus, the universal unfolding of Eq. 21 is:

$$G\{x, \lambda, \alpha\} \equiv x^3 - \lambda - \alpha x = 0 \tag{26}$$

Equation 26 has a maximum of three steady-state solutions, and furthermore preserves the qualitative structure of the solutions of Eq. 21 as illustrated in Figure 8.

The previous analysis applies when the reduced dimension r is greater than unity, but the algebraic manipulations are more cumbersome than for systems with $r = 1$. Bifurcation theory is also capable of determining the stability of the branching equations. When r is unity, the first derivative of Eq. 16, dg/dz, has the same sign as the eigenvalue of $\underline{\underline{L}}$ that crosses the imaginary axis in the vicinity of the singular point. Fur-

thermore, this theory can analyze Hopf bifurcation phenomena by providing a transformation whose zeroes, after the application of the LSR method, are the zeroes of the periodic orbits. Golubitsky and Schaeffer (1985) show that when Eqs. 15 have only one pair of pure imaginary eigenvalues, the linearization matrix, $\underline{\underline{L}}$, is of rank $n-2$ ($r = 2$).

In summary, bifurcation theory is potentially useful for small systems that arise in the models for many process units, but is currently unwieldy for the large systems that model most flowsheets.

Differential-algebraic systems

When complex nonlinearities occur (e.g., in exothermic and autocatalytic reactors and supercritical extractors), the dynamic response to disturbances is often difficult to calculate. In many cases, these systems experience intermittent rapid transients and slow, stabilizing motion, especially when their steady-state attractors are unstable and they undergo quasi-periodic or even chaotic motion.

For dynamic systems, the temporal derivatives are not set to zero, and initial-value problems often result:

$$\underline{F}\{\dot{\underline{x}}, \underline{x}, \underline{y}, t\} = 0 \qquad \underline{x}\{0\} = \underline{x}_0, \dot{\underline{x}}\{0\} = \dot{\underline{x}}_0 \quad (27a)$$

$$\underline{G}\{\underline{x}, \underline{y}, t\} = 0 \qquad \underline{y}\{0\} = \underline{y}_0, \dot{\underline{y}}\{0\} = \dot{\underline{y}}_0 \quad (27b)$$

The n ODEs (Eq. 27a) are expressed as a function of n state variables, $\underline{x}$, and the m NLEs (Eq. 27b) involve m additional unknowns, $\underline{y}$, often referred to as algebraic variables. The $\underline{F}$ equations are typically material and energy balances and the $\underline{G}$ equations often express phase equilibria, design constraints, and other related factors. Together, they comprise a system of so-called differential-algebraic equations (DAEs).

In this section, the impact of nonlinearities on the index of the DAEs and on their stiffness is considered. First, however, the concept of the index is introduced.

For the simplest case, in the absence of algebraic constraints, the ODEs can be integrated with an initial-value integrator, such as LSODE (Hindmarsh, 1980). Similarly, a system of DAEs can be integrated with an initial-value integrator. Beginning at ($\underline{x}_0$, $\underline{y}_0$, t_0), the integrator computes $\underline{x}\{t\}$ across a time step and Eq. 27b is solved for $\underline{y}\{t\}$. This procedure requires that $\underline{\underline{G}}_y$, the Jacobian of Eq. 27b with respect to $\underline{y}$, be regular. Such a system has an index equal to unity, where the index is the minimum number of differentiations of Eqs. 27a and 27b, with respect to time, required to entirely convert the system to ODEs. When $\underline{\underline{G}}_y$ is not invertible, the system has a higher index, and Eq. 27b cannot be solved. Note that the index of a system of DAEs is a measure of its deviation from a system of ODEs. It can also be viewed as the degree of coupling between the subsystems of ODEs and NLEs.

Often nonlinear systems experience abrupt changes over short time intervals, for example, autocatalytic reaction systems that operate in limit cycles or as chaotic attractors, such as the Belousov reaction system. For this system, the three intermediates, $HBrO_2$, Br^-, and Ce^{4+}, exhibit changes of up to five orders of magnitude during a rapid transient, as illustrated in Figure 9. Seider et al. (1982) integrate the mass balances (three ODEs) using LSODE and compute the eigenvalues of the Jacobian as the integration proceeds. They show the effectiveness of LSODE in error estimation and step-size adjustment, especially as the rapid transient is negotiated. Furthermore, they demonstrate that the largest negative eigenvalue decreases sharply as the rapid transient is approached and increases rapidly upon leaving the rapid transient, as the system stabilizes. This confirms the earlier observation of Shampine and Gear (1979) that systems stiffen as they stabilize. Most systems, like this one, are not stiff in the rapid transient.

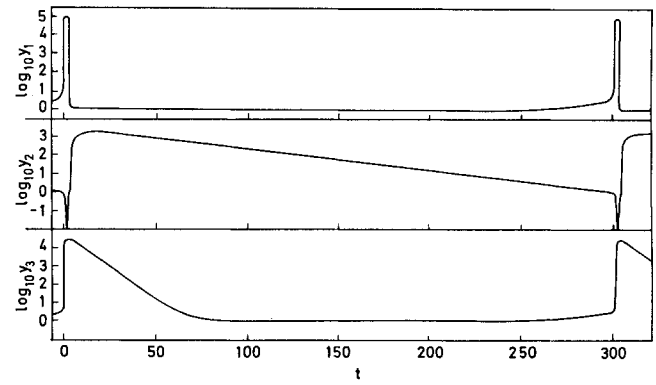


Figure 9. Dimensionless concentrations of the intermediates $HBrO_2(y_1)$, Br^- (y_2), and Ce^{4+} (y_3) in the Belousov reaction system.

DAEs that have an index ≥ 1 pose two additional problems. Consistent initialization for $\underline{x}_0$, $\underline{y}_0$ and $\dot{\underline{x}}_0$, $\dot{\underline{y}}_0$ is difficult to achieve. Also, the errors are more difficult to estimate, especially for the algebraic variables. Hence, the step-size control algorithms are less reliable. For discussion of these problems and other considerations, see Brenan et al. (1989).

Several DAE solvers are available, such as LSODI (Hindmarsh, 1983) for linearly-implicit DAEs, and DASSL (Petzold, 1982a,b) for implicit DAEs. Like LSODE, LSODI and DASSL implement the backward difference formulas (BDFs) of Gear and are available in the ODEPACK. LSODI and DASSL are intended to solve systems with index = 1. DASSL provides an option for consistent initialization which, unfortunately, is unreliable (Byrne, 1989; Petzold, 1989). Other, more experimental, codes are available to solve semiexplicit systems with index = 1, including LIMEX (Deuflhard and Nowak, 1987), DASP3 (Soderlind, 1980), and DRIBLOCK (Mach, 1986).

Pantelides et al. (1988) show examples of higher index systems, often involving phase equilibrium. They also show that design specifications can increase the index and that different specifications can result in different indexes. For example, in a distillation tower, when the distillate pressure is specified, the index is 2, and when the bottoms pressure is specified, the index is $N+1$, where N is the number of stages. These observations are expanded upon by Lefkopoulos and Stadtherr (1988), who suggest an algorithm for the selection of specification (design) variables to give lower index formulations, preferably with index = 1.

Alternatively, it is possible to transform higher index processes into systems having index = 1 (Bachmann et al., 1989; Gear, 1988). This transformation can be automated and is potentially able to circumvent the need to integrate high-index systems. However, as the NLEs are differentiated, information can be lost (e.g., $x = 4$ becomes $dx/dt = 0, x\{0\} = 4$). Clearly, the proper initialization is required to obtain the correct solution and the integration must be sufficiently accurate to

prevent the solution from drifting. To avoid these problems (for more complex systems), Bachmann et al. (1989) propose a method that lowers the index by replacing ODEs with NLEs, while preserving the correct solution. This is a promising approach, but needs testing.

In a noteworthy application of LSODI, Cesari et al. (1989) integrated the DAEs for a semibatch extractor under PI control to dehydrate ethanol using supercritical CO_2. At each integration time step, tangent-plane stability analysis (Michelsen, 1982; and see the section on Phase Stability Analysis) is performed to maintain the proper phase distribution in the critical region. Furthermore, it is noteworthy that Lefkopoulos and Stadtherr (1988) have initiated the development of an algorithm to minimize the index of DAEs that represent a large process network.

In summary, DAE solvers are currently effective for systems with index = 1. Unfortunately, this limitation places a burden on the designer, who might choose to circumvent higher-index formulations. Research is needed to develop solvers for higher-index systems and to better relate the index to the nonlinear equality and inequality constraints.

Parameterization. When the DAEs exhibit complex nonlinearities, these can vary significantly with a parameter of the system. This has been demonstrated beautifully by Jensen and Ray (1982) for the exothermic reaction, $A \rightarrow B$, in diabatic, packed-bed, tubular reactors, using a pseudo-homogeneous model for dispersion. These authors constructed maps of the solution diagrams as the dimensionless heat of reaction and dimensionless heat transfer coefficient vary, at several values of the Peclet numbers for heat and mass transfer, where $Pe = Pe_h = Pe_m$. At high Pe (as $Pe \rightarrow \infty$), plug flow occurs with no dispersion in the absence of hysteresis or periodic operation. At intermediate $Pe = 5$, 14 kinds of solution diagrams were computed, with a maximum of five steady states and a maximum of three Hopf bifurcation points. For the other extreme, as $Pe \rightarrow 0$, complete backmixing occurs (as in a CSTR). Here, only six kinds of solution-diagrams were computed, with a maximum of three steady states and a maximum of two Hopf bifurcation points. In summary, even for the simple exothermic reaction, $A \rightarrow B$, the impact of backmixing is not easily generalized. When introduced through dispersion, the solution space gains in complexity, approaching the maximum complexity for intermediate dispersion before becoming simpler in the limit of complete backmixing.

Parameterization for DAEs is often accomplished after the derivatives have been discretized using the method of weighted residuals. Unfortunately, the results can be sensitive to the accuracy of the discretization. Here, is it very important that the error estimates be sufficiently accurate and the finite elements be positioned properly. See the later section on Optimal Control for a more complete discussion of this subject.

When solving a DAE system with NLEs for phase equilibria, an unresolved issue concerns the impact of the phase distribution on the index. As the simulation proceeds, phases can be added and deleted, with an accompanying change in index. The impact of such index shifts needs to be investigated.

Stability Analysis. Unlike a system of ODEs, the Jacobian matrix for DAEs (Widagdo et al., 1989) is:

$$\underline{\underline{J}} = \left(\frac{\partial \underline{\dot{x}}}{\partial \underline{x}}\right)_{\underline{G}=0} \tag{28a}$$

Applying the implicit function theorem (Golubitsky and Schaeffer, 1985) results in:

$$\underline{\underline{J}} = -\left(\frac{\partial \underline{F}}{\partial \underline{\dot{x}}}\right)^{-1}\left[\left(\frac{\partial \underline{F}}{\partial \underline{x}}\right) - \left(\frac{\partial \underline{F}}{\partial \underline{y}}\right)\left(\frac{\partial \underline{G}}{\partial \underline{y}}\right)^{-1}\left(\frac{\partial \underline{G}}{\partial \underline{x}}\right)\right] \tag{28b}$$

Unfortunately, $(\partial \underline{G}/\partial \underline{y})$ is singular for high-index systems and, consequently, stability analysis has not been accomplished for these systems. The index can be reduced to unity by repeated differentiation of the NLEs, by selection of alternate specifications, of by using the method of Bachmann et al. (1989). However, the resulting Jacobian, with higher-order derivatives, is more sensitive to truncation errors when numerical approximations are utilized, the alternate specifications may be inconvenient for the designer to prepare, and the latter method needs more testing.

It is noteworthy that, in the example, Jensen and Ray (1982) utilized Eq. 28b to identify the three Hopf bifurcation points.

Nonlinear Programming

Practical design problems are formulated with one or more objective functions, for example:

$$\text{Optimize}_{\underline{x},\,\underline{d},\,\underline{u}} \quad f\{\underline{x}, \underline{d}, \underline{u}, \underline{p}\} \tag{29a}$$

$$\text{ST:} \quad \underline{h}\{\underline{x}, \underline{\dot{x}}, \underline{d}, \underline{u}, \underline{p}\} = 0 \tag{29b}$$

$$\underline{g}\{\underline{x}, \underline{d}, \underline{u}, \underline{p}\} \geq 0 \tag{29c}$$

where $\underline{x}$, $\underline{d}$, $\underline{u}$, and $\underline{p}$ are vectors of state and design variables, manipulated inputs, and parameters, respectively. When derivatives are present in the constraints, their discretization is a key to the solution procedure, with polynomial trial functions often utilized in a collocation method. This is particularly crucial when the equality constraints in the process model are a system of DAEs with an index greater than unity.

The constrained optimization problem (Eq. 29) can be transformed into an unconstrained problem by forming the Lagrangian, L, and applying the stationarity conditions, $\underline{\nabla} L = 0$. The result is a system of NLEs known as the Kuhn-Tucker (K-T) necessary conditions:

$$\underline{\nabla}\,(f + \underline{\pi}^T\underline{h} + \underline{\lambda}^T\underline{g}) = 0 \tag{30a}$$

$$\underline{h} = 0 \tag{30b}$$

$$g_i\lambda_i = 0 \qquad \forall i \tag{30c}$$

where $\underline{\pi}$ and $\underline{\lambda}$ are vectors of the Lagrange and Kuhn-Tucker multipliers, with the additional requirements that:

$$g \geq 0 \tag{30d}$$

$$\lambda_i \geq 0 \qquad \forall i \text{ (for a maximum)}$$

$$\lambda_i \leq 0 \qquad \forall i \text{ (for a minimum)} \tag{30e}$$

During the past decade, two approaches have been applied,

almost exclusively, to solve the K-T conditions arising from process design optimizations. One is successive quadratic programming (SQP), as implemented in the OPT program (Biegler and Cuthrell, 1985). The other is the reduced-gradient (RG) algorithm implemented in the MINOS program (Murtagh and Saunders, 1983).

As emphasized in the previous section, equality constraints with singularities (e.g., limit and real bifurcation points) usually exhibit complex solution spaces having qualitatively different regimes as their parameters vary. When the parameters are design variables in an NLP, local optima are often associated with each of the regimes (or solutions of Eq. 29b). Highly nonlinear inequality constraints, $\underline{g}\{\underline{x}, \underline{d}, \underline{u}, \underline{p}\} \geq 0$, can further complicate the optimization problem, especially when they define a nonconvex feasible region. When singularities are introduced as the inequalities become active ($\underline{g} = 0$), the optimization problem is even more difficult to solve. In this regard, when the equalities are DAEs and the inequalities become active, the index of the DAEs is often increased and the NLP is further complicated.

In this section, these complications are introduced before several chemical process examples are presented in the sections on Phase and Chemical Equilibria and on Process Flowsheet Analysis. To set the stage, this section concentrates on the latest solution algorithms.

Equality constraints

Both the SQP and RG algorithms implement an infeasible path strategy with respect to the equality constraints, Eq. 30b; that is, the equality constraints are not satisfied after the design variables are adjusted, but only as the algorithm converges to an optimum. Among the advantages of this method, compared with a feasible path strategy, are its increased computational speed and that its derivatives of the objective function, f, with respect to the design variables, are unconstrained. This is particularly important when optimizing process flowsheets (see Process Flowsheet Analysis).

When using these algorithms, several cautions are necessary. These NLPs are nonconvex, and consequently convergence to the global optimum cannot be guaranteed. Furthermore, when the equality constraints, $\underline{h} = 0$, exhibit multiple solutions the K-T conditions may not apply (Doedel, p. 22, 1986). Finally, our experience has shown that these optimization algorithms have difficulty converging highly nonlinear equality constraints. External algorithms can be used to solve these constraints in a modular fashion (satisfying them during each iteration of the optimization algorithm). However, these combined algorithms can have difficulty rounding limit points and can jump between solution branches, as the decision variables are adjusted, in the vicinity of multiple steady states. While this is not surprising, it supports the need to take special care when optimizing these systems and can justify the implementation of algorithms that deal explicitly with these difficulties.

Successive Continuation. There are several approaches to solving the K-T conditions using the homotopy-continuation methods. In a conservative strategy (i.e., reliable, but slow), implemented in the AUTO program (Doedel, 1986), stationary points are located using successive continuation. This strategy has been applied to locate *all* of the solutions of a liquid-liquid equilibrium problem (Lin, 1988). Although it has not been applied to satisfy the complementary slackness equations (Eq. 30c) associated with the inequality constraints, a strategy for accomplishing this is suggested in the next subsection.

Consider the optimization problem:

$$\underset{\underline{p}}{\text{Optimize}} \quad f\{\underline{x}, \underline{p}\} \tag{31a}$$

$$\text{ST:} \quad \underline{h}\{\underline{x}, \underline{p}\} = 0 \tag{31b}$$

where $\underline{x} \in R^n$, $\underline{p} \in R^m$. Define ω, the value of the objective function, as

$$\omega - f\{\underline{x}, \underline{p}\} = 0 \tag{32}$$

As mentioned previously, if for a given $\underline{p}$, $\underline{h}\{\underline{x}, \underline{p}\}$ admits multiple solutions, $\underline{x}$, the usual optimality conditions may not hold. In this case, it is important to force the path toward an optimum to lie on the solution manifold, $\underline{h}\{\underline{x}, \underline{p}\} = 0$ (Doedel, 1986). To accomplish this, homotopy continuation can be applied to determine parameter p_1 (p_2, ..., p_m fixed) as ω varies from an initial point ($\underline{x}^0$, $\underline{p}^0$, $\omega^0 = f\{\underline{x}^0, \underline{p}^0\}$). Extrema of ω are located at limit points in the $p_1 - \omega$ solution diagram, with the equality constraints satisfied for all values of p_1. At an extremum ($\underline{x}^*$, $\underline{p}^*$, ω^*) the necessary conditions for optimality with respect to $\underline{x}$ and p_1 are satisfied, in addition to Eqs. 31b and 32. Doedel formulates the Fritz-John (F-J) necessary conditions:

$$\underline{\nabla}_x (\alpha f + \underline{v}^T \underline{h}) = 0 \tag{33a}$$

$$\underline{\nabla}_{p_i} (\alpha f + \underline{v}^T \underline{h}) = 0 \qquad i = 1 \tag{33b}$$

$$\alpha^2 + \underline{v}^T \underline{v} - 1 = 0 \tag{33c}$$

$$\underline{h}\{\underline{x}, \underline{p}\} = 0 \tag{31b}$$

$$\omega - f\{\underline{x}, \underline{p}\} = 0 \tag{32}$$

When $\underline{v} = \alpha \underline{\pi}$, these reduce to the K-T conditions. With α varying, they permit $\underline{\pi}$ to extend into regions not attainable when $\alpha = 1$. By applying homotopy continuation to determine parameter p_2 (p_3, ..., p_m fixed) starting at *all* the extrema with respect to p_1, the extrema with respect to both p_1 and p_2 can be located.

To find the extrema of ω with respect to $\underline{p}$, one additional F-J equation must be added as each successive p_k is introduced (Eq. 33b; $i = 1, \ldots, k-1$). In search of the global optimum, the continuation method is applied from each extremum that is located, except for cusps which do not represent optima.

This conservative methodology appears to be reliable, but requires extensive computations. In our experience, when the differential-arclength homotopy-continuation method is applied to solve the Kuhn-Tucker equations, it is very reliable and somewhat more efficient. The class of problems for which the greater reliability of the successive-continuation method is important remains to be determined.

Inequality constraints

Both the SQP and RG algorithms attempt to enforce feasibility with respect to the inequality constraints, Eq. 29c, and

the equations of complementary slackness (Eq. 30c) are satisfied as the iterations proceed. This is important for two reasons. If feasibility were not maintained and the K-T necessary conditions solved using local or global convergence algorithms, the optimum might not be feasible. Furthermore, inequality constraints can be added to exclude values of the design variables for which the objective function or any of the constraints have singularity or are undefined. However, for nonconvex NLPs, with narrow and curved feasible regions, these algorithms can require more iterations than those that permit the inequality constraints to be violated during the iteration sequence.

When the differential-arclength homotopy-continuation method is applied to solve the Kuhn-Tucker equations (Eq. 30a-c), the solutions may be infeasible and, depending on the signs of the multipliers, may be maxima, minima, or saddle points. A more reliable method involves application of the Mangasarian theorem (1976), as recommended by Vasudevan et al. (1989).

Mangasarian Theorem. When applying this theorem, the complementary slackness conditions ($g_i\lambda_i = 0, \forall i$) are replaced with NLEs whose solution is guaranteed to be feasible and to have the proper sign for the K-T multipliers. Although this formulation does not guarantee location of the global optimum, continuation with a boomerang transformation (Seader et al., 1990) may be able to locate all of the feasible local optima (maxima or minima), and thus, the global optimum.

More specifically, application of the Mangasarian theorem is demonstrated with the following example:

$$\text{Optimize} \quad f = x_1 + x_2 \tag{34a}$$

$$\text{ST:} \quad g = -x_1^2 - x_2^2 + 1 \geq 0 \tag{34b}$$

Forming the Lagrangian, $L = x_1 + x_2 + \lambda\,(-x_1^2 - x_2^2 + 1)$, and applying the stationarity conditions, the K-T necessary conditions become:

$$1 - 2x_1\lambda = 0 \tag{35a}$$

$$1 - 2x_2\lambda = 0 \tag{35b}$$

$$\lambda(-x_1^2 - x_2^2 + 1) = 0 \tag{35c}$$

Two solutions exist; at the maximum, $x_1 = x_2 = 1/\sqrt{2}$, $\lambda = 1/\sqrt{2}$, and at the minimum, $x_1 = x_2 = -1/\sqrt{2}$, $\lambda = -1/\sqrt{2}$. Using the Newton differential-arclength homotopy-continuation method, convergence to the maximum is achieved when the initial points ($\underline{x}^0$, λ^0) lies above the separatrix, $f = x_1 + x_2 = 0$, and convergence to the minimum occurs when the initial point lies below.

To obtain the maximum, over a broader range of initializations, each complementary slackness equation (Eq. 35c) is replaced with an NLE that guarantees both feasibility and the proper sign of the K-T multipliers. For m inequality constraints, $\underline{g}\{\underline{x}, \underline{p}\} \geq 0$, the Mangasarian theorem assures that if a monotonically increasing function θ exists such that $\theta\{0\} = \theta'\{0\} = 0$, then:

$$\theta\{|g_i\{\underline{x}, \underline{p}\} - \lambda_i|\} - \theta\{g_i\{\underline{x}, \underline{p}\}\} - \theta\{\lambda_i\} = 0 \qquad i = 1, \ldots, m \tag{36}$$

is satisfied if and only if the solution: 1. satisfies the equations of complementary slackness, $g_i\lambda_i = 0$; 2. is feasible, $g_i \geq 0$; and 3. has the proper sign of the K-T multipliers, $\lambda_i \geq 0$. To obtain the minimum, Eq. 30a can be rewritten as:

$$\underline{\nabla}\,(f - \underline{\lambda}^T\underline{g} + \underline{\pi}^T\underline{h}) = 0 \tag{37}$$

For this formulation, the proper sign of the multipliers is $\lambda_i \geq 0$, and the Mangasarian Theorem can be applied.

One such θ is $\theta\{z\} = z|z|$ or $\theta\{z\} = z\sqrt{z^2}$. Substituting in Eq. 36:

$$(g_i - \lambda_i)^2 - g_i\sqrt{g_i^2} - \lambda_i\sqrt{\lambda_i^2} = 0 \tag{38}$$

For the example, Eq. 35c is replaced by Eq. 38 where $g_i = g = -x_1^2 - x_2^2 + 1$ and $\lambda_i = \lambda$. When solving the revised stationarity conditions with the Newton differential-arclength homotopy-continuation method, the radius of convergence to the maximum is greatly extended when $\lambda^0 > 0$. However, when $\lambda^0 < 0$, the maximum could not be achieved for any $\underline{x}^0$. Often the continuation method was unsuccessful in converging to the minimum, was attracted to an isola in t-space, or followed a branch along which t approached infinity. This may be due, in part, to the introduction of a singular point at $g_i = 0$, $\lambda_i = 0$.

This methodology was applied for the design optimization of a flowsheet that contains an aerobic fermenter in which *saccharomyces cerevisiae* grows in a sugar-cane molasses medium, as illustrated in Figure 10. Agrawal et al. (1982) modeled the reaction kinetics using a one-hump growth rate:

$$\mu\{S\} = kSe^{-S/K} \tag{39}$$

where μ is the specific growth rate (maximum at $S = K$) and S is the substrate concentration. Rather than model the mass transfer of oxygen, a variable yield coefficient:

$$Y\{S\} = \frac{\mu\{S\}}{\sigma\{S\}} = a + bS \tag{40}$$

was found to be necessary but not sufficient to reproduce the

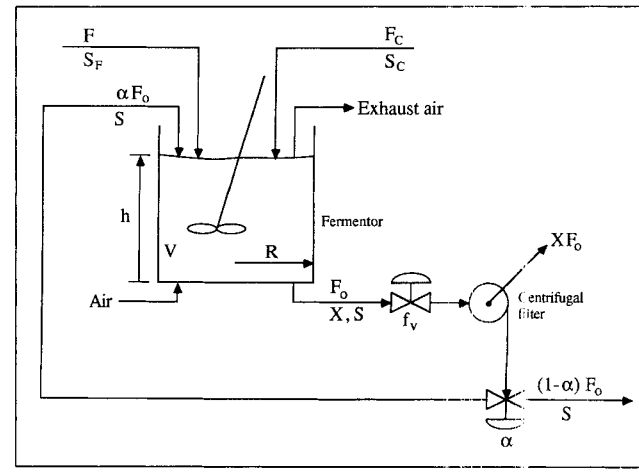


Figure 10. Fermentation process.

periodic behavior observed experimentally by Borzani et al. (1977). Note that σ is the substrate consumption rate.

When analyzing the reactor alone, Agrawal et al. identified regimes of hysteresis and periodic operation. Figure 11a shows the nonlinear steady-state and periodic branches of a solution diagram when $\gamma = K/S_F = 0.40$ and $\beta = a/(bS_F) = 0.10$ are shown. Note that the stable steady state that yields the highest cell mass occurs at the Hopf bifurcation point, where $Da = \mu\{S_F\}\, V/F = 0.6170$. Beyond that, the steady-state attractors are unstable and the periodic attractors are stable with large periods, corresponding to the experimental observations.

In the design study, Brengel and Seider (1991) maximized the venture profit of the flowsheet by adjusting the design variables (h, X, S, α, F, F_c, F_V, and R). When $\gamma = 0.4$ and $\beta = 0.1$, the maximum venture profit was located at $Da = 0.5597$, an unstable steady state. Figure 11b illustrates the iteration history of the methodology for several starting points. When convergence was obtained, less than ten iterations were required. More complete results are presented and discussed by the authors. Note the divergence from point E. Thus, convergence cannot be guaranteed for all starting points, even when a global convergence algorithm is used.

This strategy has shown good potential but, as suggested by the example above, there are several unresolved issues associated with its implementation. One involves the initial values λ^0 and g^0, when utilizing a Newton-based algorithm to solve the revised stationarity conditions (Eqs. 30a,b,d, and 38). It can be shown that when $\lambda^0 < 0$, $g^0 < 0$, and $2g^0 - \lambda^0 > 0$, a Newton-based algorithm will move λ and g in the wrong directions (i.e., decrease them). For all other λ^0 and g^0, a Newton-based adjustment moves λ and g in acceptable directions. This is particularly important during the final Newton-Raphson iterations of the homotopy-continuation algorithm with $t = 1$. To avoid this, the values of λ_i and g_i are monitored during the Newton-Raphson iterations. When $\lambda_i < 0$, $g_i < 0$, and $2g_i - \lambda_i > 0$, λ_i is arbitrarily adjusted to a small positive value, Λ. This methodology was very successful in improving the convergence properties of the Newton-Raphson method. A second issue concerns the function θ, for which Vasudevan et al. (1989) suggest $\theta = z^3$ as a better formulation. However, the convergence properties for this formulation appear to be more difficult to characterize and, in limited test, its performance was far poorer.

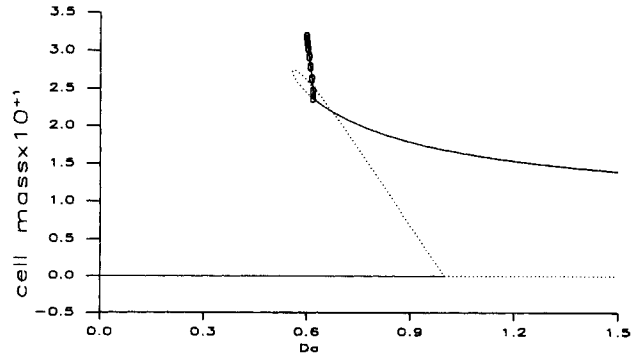
Relaxation Strategy. An alternate approach to satisfying the complementary slackness equations is to introduce relaxation parameters:

$$g_i\lambda_i = r_i \qquad \forall i \tag{41}$$

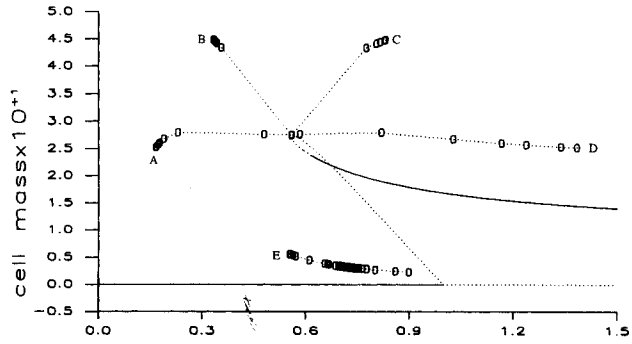
and to solve the revised K-T equations with progressively smaller values of r_i. This strategy, which was applied to solve bilevel programming problems (BLPPs; Clark and Westerberg, 1990), is discussed later in connection with the nonnegativity constraints (see the section on Phase and Chemical Equilibrium).

Active Set Strategy. Clark and Westerberg (1990) also apply a strategy that involves the assumption that certain of the inequality constraints are active. The K-T equations are solved for this active set and an approach is suggested for adjusting the active set, when necessary. As above, the strategy was applied to solve BLPPs and is discussed in the section on Phase and Chemical Equilibrium.

An active set strategy is implemented, as well, by Lucia and



a. Steady state (— stable, ... unstable) and periodic attractors of cell mass as a function of the Damkohler number



b. Iteration history (projected onto the solution diagram) for design optimization from five starting points

Figure 11. Solution diagrams for fermentation reactor with $\gamma = 0.4$ and $\beta = 0.1$.

Xu (1990) for the linear inequality constraints in a QP. For sparse QP problems, they report computation times between 1 and 15% of those for the VE06AD routine in the Harwell library. With this strategy, and other improvements, a much more efficient SQP algorithm is obtained.

Global optimization

As indicated above, complex nonlinearities in the process equality constraints often lead to multiple solutions, which can result in local optima, corresponding to qualitatively different operating regimes. To reduce the incidence of convergence to a local optimum, decomposition algorithms are being developed to locate the global optimum with a high degree of probability. These include the use of Benders decomposition (Geoffrion, 1972), in which complicating variables are fixed and the NLP is solved to locate upper bounds on the minimum. Then, a reduced master problem is solved to adjust the complicating variables and determine lower bounds on the minimum. When applied iteratively, this strategy adjust the bounds to locate a stationary point but, on its own, is *not* designed to locate the global optimum. However, with transformations designed to keep both the primal and reduced master subproblems convex, the global optimum has been determined far more reliably by Floudas et al. (1989). These authors have applied this approach for the calculation of phase and chemical equilibria, as described in the next section (Paules and Floudas, 1989).

In a related approach, Kocis and Grossmann (1987, 1988, 1989) formulate the master problem based upon a linearization of the constraints and the objective function. For nonconvex MINLP problems, the NLP is solved and the nonconvexities are identified with local and global tests (phase I). Then the invalid approximations to the nonconvex functions are relaxed and a new master problem is formulated and solved (phase II). These two phases are repeated in their outer approximation/equality relaxation algorithm until no improvement in the solution is obtained.

These global optimization strategies have great potential, but need to be tested more extensively and compared with more heuristic-oriented strategies that have been applied, in some cases, with great success (e.g., see the section on Phase and Chemical Equilibrium).

Optimal control

The optimal control problem (OCP), in which a functional is optimized subject to dynamic constraints, is probably the most difficult optimization carried out by design engineers. It often arises in the design of batch processes, the operation of semicontinuous processes, and the start-up of continuous processes. In these problems, the impact of complex nonlinearities, such as arise in catalytic reactors and phase equilibria, is the most varied, and depends greatly on the initial and boundary conditions. Here, the possibilities for multiple steady-states, periodic, and strange attractors can be anticipated.

This section begins with a brief review of the finite element methods being utilized to solve the OCP. Then, it reviews several examples that involve complex nonlinearities, with emphasis on convergence difficulties and the need for improved solution methods.

For the OCP, where the constraints are DAEs, Renfro et al. (1987) utilize global spline collocation (Villadsen and Michelsen, 1978) to approximate the ODEs, which is also referred to as orthogonal collocation on finite elements (Carey and Finlayson, 1975). The control variables are held constant over each finite element and continuity of the dependent variables is enforced at the interfaces between the finite elements. Special attention is devoted to determining whether or not first derivative continuity of the dependent variables is appropriate at the interfaces. With the ODEs replaced by polynomial approximations over the finite elements, the resulting NLP is solved using SQP.

In parallel, Vasantharajan et al. (1988) also utilized global spline optimization. These authors employ a Lagrange polynomial approximation for the control variables over each finite element (rather than hold the control variables constant) and do not enforce first-derivative continuity of the dependent variable at the element interfaces. They introduce an algorithm for adaptively positioning the finite elements during the optimization to minimize the largest residual at the midpoints of the elements. This so-called equidistribution method is being extended to adaptively adjust the number of finite elements. The paper also identifies problems in obtaining solutions for systems having an index greater than 2.

An excellent application of these methodologies is provided by Cuthrell and Biegler (1989) for a fed-batch reactor to produce penicillin. The problem involves adjusting the feed rate of substrate and the batch time to maximize the production of penicillin. Both the growth rate of the cells and the production rate of penicillin exhibit substrate inhibition at higher concentrations. These sources of nonlinearities suggest that the solutions are not unique and that the global minimum may not be achieved. In fact, the paper indicates that "because the objective functions are almost identical, this seems to suggest that the optimal control profile before the singular arc may be nonunique." From the designer's perspective, this insensitivity of the objective function to the control profiles is reassuring, although not likely for nonlinear reactors in general.

Although the equidistribution method works well for many systems, serious convergence difficulties have been encountered when solving boundary-value problems with steep composition fronts whose position is unknown. In one study, Koster (1990) documents these difficulties for bacterial chemotaxis in a confined region. The study involves the maximization of the cell mass subject to two coupled, highly-nonlinear ODEs (mass balances for the cells and substrate).

Clearly, the optimal control of systems that exhibit multiple steady states and oscillatory behavior is difficult to achieve. These problems are well-documented by Matsubara et al. (1986) who show how the bang-bang control of the dilution rate to a chemostat with a mixed culture can involve secondary bifurcations along a periodic branch.

Singular optimal control problems present many challenges and unresolved issues. In one strategy, Menawat et al. (1987) maximize the production of baker's yeast in a fed-batch reactor by controlling the substrate feed rate. They obtain convergence to the singular optimal control problem by solving a sequence of nonsingular problems that approach singularity.

Phase and Chemical Equilibrium

A primary concern in the design and control of many chemical processes is the phase distribution at equilibrium. Whereas robust algorithms are widely available for simple vapor-liquid equilibria, complications arise near phase boundaries, when a vapor and two liquid phases are possible, in the vicinity of critical points, in the presence of chemical reactions, etc. The phase equilibrium model, with or without chemical reactions, is an NLP (MINLP when binary variables represent the existence or nonexistence of the phases, as shown in the subsection on Global Convergence Strategies). At a given T and P, the phase distribution and compositions are determined by minimizing the Gibbs free energy subject to the mass balance constraints. Hence, the primary focus of this section is on the NLP and the difficulties in obtaining solutions in the vicinity of high-order singular points and limit points, often associated with nonideal solutions and at elevated pressures in the retrograde region. These usually arise near two- and three-phase critical points, near phase boundaries, and with chemical reaction, when the phase distribution is uncertain. A related focus is on the stability of the phase distribution at minimum G, which to exist at equilibrium, must be stable. Yet, another focus is on the superposition of design optimization. As designs vary, so do the equilibria of the process streams and vessels, and it becomes important to coordinate the design and equilibrium optimizations for the efficiency and reliability of the calculations.

To set the stage, the general NLP is presented and the well-recognized methodologies are briefly reviewed, with emphasis on those methods that are in active use. Note that these are covered more extensively in an excellent review article by Heide-

mann (1983). Then, several recent developments are considered along with promising new directions.

Nonlinear program

At equilibrium, with T and P given, G is minimized, where

$$G\{\underline{n}\} \equiv \sum_{\ell=1}^{P}\sum_{j=1}^{C} n_{j\ell}\,\bar{G}_{j\ell} = \sum_{\ell=1}^{P}\sum_{j=1}^{C} n_{j\ell}\left(G^0_{j\ell} + RT\ln\frac{\bar{f}_{j\ell}}{f^0_{j\ell}}\right) \tag{42}$$

and $n_{j\ell}$ and $\bar{G}_{j\ell}$ are the moles and partial molal Gibbs free energy (chemical potential) of species j in phase ℓ, C and P are the numbers of species and phases, $\bar{f}_{j\ell}$ is the fugacity of species j in phase ℓ, $G^0_{j\ell}$ is the Gibbs free energy of formation of species j in its standard state for phase ℓ, and $f^0_{j\ell}$ is the associated standard-state fugacity. The mixture fugacities are often expressed as:

$$\bar{f}_{j\ell} = \phi_{j\ell}\, y_{j\ell}\, P \tag{43}$$

where ϕ and y are the fugacity coefficients and mole fractions for species in the vapor or liquid phases, and

$$\bar{f}_{j\ell} = \gamma_{j\ell}\, x_{j\ell}\, f_{j\ell} \tag{44}$$

where γ, x, and f are the activity coefficients, mole fractions, and pure liquid fugacities for the species in the liquid phases.

The Gibbs free energy is minimized subject to mass balance constraints. For phase equilibrium, these are:

$$n^T_j = \sum_{\ell=1}^{P} n_{j\ell} \qquad j = 1, \ldots, C \tag{45}$$

and for phase and chemical equilibrium, the atom balances normally apply:

$$b_k = \sum_{\ell=1}^{P}\sum_{j=1}^{C} m_{jk}\, n_{j\ell} \qquad k = 1, \ldots, E \tag{46}$$

where n^T_j are the total moles of species j, b_k are the gram atoms of element k, m_{jk} are the number of atoms of element k in species j (an element of the atom matrix), and E is the number of elements. In addition, the feasible region is bordered by nonnegativity constraints:

$$n_{j\ell} \geq 0 \qquad j = 1,\ldots,C;\ \ell = 1,\ldots,P \tag{47}$$

Stationarity conditions

There are numerous approaches to locating the minimum G, subject to the equality and inequality constraints. For chemical and phase equilibrium, Smith and Missen (1982) review two principal formulations and several algorithms, and provide FORTRAN and BASIC computer programs.

In the classical approach, for chemical equilibrium in a single phase, R independent chemical reactions are determined and the mole numbers in Eq. 42 are replaced by:

$$n_j = n^0_j + \sum_{i=1}^{R} \nu_{ij}\xi_i \qquad j = 1, \ldots, C \tag{48}$$

where n^0_j is the initial moles of species j, ν_{ij} is the stoichiometric coefficient of species j in reaction i, and ξ_i is the extent of reaction i. With $\underline{\xi}$ as the independent variables, the stationarity conditions are:

$$\underline{\nabla G} = 0 \tag{49}$$

and the mass-action equations result:

$$K_i = \prod_{j=1}^{C}\left(\frac{f_j}{f^0_j}\right)^{\nu_{ij}} \qquad i = 1, \ldots, R \tag{50}$$

where $K_i = \exp\{-\Delta G^0_i/RT\}$ and ΔG^0_i is the Gibbs free energy of reaction with the species in their standard states.

Similarly, for phase equilibrium without chemical reaction, when the stationarity conditions are applied,

$$\bar{G}_{j1} = \bar{G}_{j2} = \ldots = \bar{G}_{j\ell}, \qquad \ell = 1, \ldots, P \tag{51}$$

The classical approach has been to introduce distribution coefficients; for example, for vapor/liquid equilibrium:

$$K_j \equiv \frac{y_j}{x_j} \qquad j = 1, \ldots, C \tag{52}$$

These are combined with the mass balances (Eq. 45) and solved using many of the strategies previously described for NLEs. Of special note are the "inside-out" algorithms in the ASPEN program (Boston and Britt, 1978) and the thermodynamically-consistent hybrid method (Lucia et al., 1985) mentioned above.

Many alternatives to these "K-value" approaches have been introduced. Often, they involve a quadratic or near quadratic approximation to G and the formation of the Lagrangian. The early methods did not include the nonnegativity constraints in the Lagrangian; for example, the Rand method (White et al., 1958; Dluzniewski and Adler, 1972) and the NASA method (Gordon and McBride, 1971). Also, for nonideal phases, they assumed that $\partial\phi_{j\ell}/\partial n_{j\ell} = \partial\gamma_{j\ell}/\partial n_{j\ell} = 0$ when computing the elements of the Hessian matrix of G ($\partial^2 G/\partial n_{j\ell}\partial n'_{j\ell}$; $j, j' = 1, \ldots, C$). Since these elements are only approximate, quadratic convergence was not obtained (Smith and Missen, 1982; Dluzniewski and Adler, 1972; Gautam and Seider, 1979). The promising new methods add the inequality constraints and their Kuhn-Tucker multipliers; for example, iterative quadratic programming (Gautam and Seider, 1979), an active set strategy (Clark and Westerberg, 1990; Clark, 1990), and a strategy using Benders decomposition (Paules and Floudas, 1989). The latter two will be discussed subsequently in this section.

Other methods have been recommended; for example, direct substitution with acceleration by the generalized dominant eigenvalue method (Michelsen, 1982b). The effectiveness and efficiency of all such methods, however, depends on many factors including the region of the phase diagram and the quality of the initialization, $n^0_{j\ell}$. Hence, the selection of the best convergence strategy is not straightforward. Only through

comparative testing can guidelines be proposed. This is an unresolved issue that deserves further study.

Singularities

Occurrences of singularities arise in many equilibrium formulations. First, and probably most obvious, is the singularity at a critical point, where two or more phases coalesce. For two-phase critical points, the singularity is expressed explicitly using the tangent plane distance function (Gibbs, 1873):

$$g\{\underline{y}\} = \frac{1}{RT}\sum_{j=1}^{C} y_j \left(\mu_j\{\underline{y}\} - \mu_j\{\underline{z}\}\right) \qquad (53)$$

where g is the dimensionless Gibbs free energy of mixing at composition $\underline{y}$ minus the linear approximation to the Gibbs free energy of mixing at composition $\underline{z}$ (the equation of a tangent hyperplane) and μ_j is the chemical potential of species j. Note that the graphical interpretations of $g\{\underline{y}\}$ by Baker et al. (1981) and Michelsen (1982a, 1984) are reviewed below. At a given $\underline{z}$ (the overall composition of a stream), Michelsen (1984) shows that a critical point occurs at $y = z$, for a binary mixture, when

$$g\{z\} = \left.\frac{dg}{dy}\right|_z = \left.\frac{d^2g}{dy^2}\right|_z = \left.\frac{d^3g}{dy^3}\right|_z = 0, \frac{d^4g}{dy^4} > 0 \qquad (54)$$

Comparable conditions are derived for multicomponent mixtures and an algorithm is presented to locate T_c and P_c where the second- and third-order terms are zero. In a similar algorithm, Heidemann and Khalil (1980) express the criticality conditions in terms of the tangent-plane distance from the Helmholtz free energy surface and adjust T and v (molar volume) to locate T_c and v_c. This approach is advantageous with pressure-explicit equations of state (e.g., Soave-Redlich-Kwong and Peng-Robinson) because P is a unique function of T and v. As T and P are adjusted in the Michelsen method, discrete jumps from one to three real roots of v can occur. Yet, very favorable speeds of convergence have been obtained using the Michelsen method. Clearly, this is another area that deserves comparative testing and further study.

Algorithms to locate tricritical points, where the fourth- and fifth-order terms are zero, are extremely difficult to formulate and implement without sizable precision losses. In one approach, Michelsen (1986) obtains good initializations by averaging the compositions at two-phase critical points along three-phase envelopes (at fixed composition) in the vicinity of the tricritical point. Although this represents an important advance, much work is needed to perfect this algorithm and introduce other techniques.

Simpler singularities, such as limit points, occur when tracing phase envelopes in the retrograde region for two-phase systems. In an unpublished paper (Cygnarowicz and Seider, 1986), the NLEs formulated by Michelsen (1980) were solved using the differential-arclength homotopy-continuation algorithm described above. Results for a natural gas mixture, computed using the Soave Redlich-Kwong equation, are shown in Figure 12. Note that the turning point algorithm successfully bypasses both limit points as well as the critical point. Initially, the dew point curve is traced beginning at the lowest P, with P as the

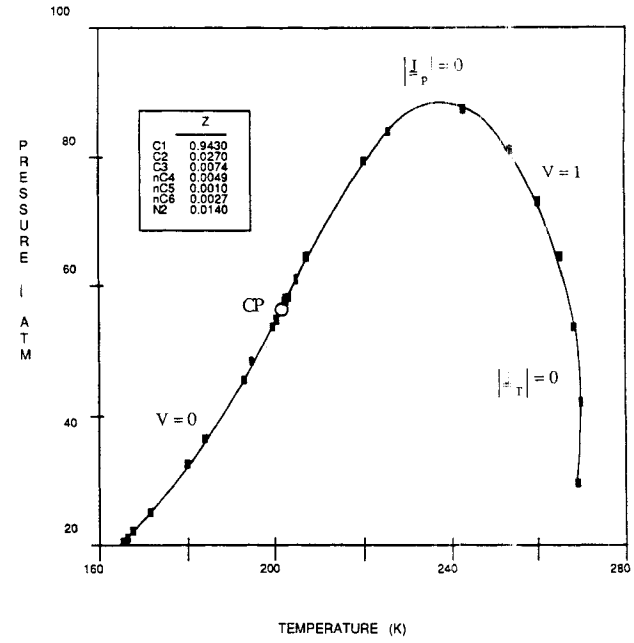


Figure 12. Phase envelope for seven-component hydrocarbon system.
$\underline{J}$ is a $(C+2) \times (C+2)$ Jacobian matrix

continuation variable. In the retrograde region, for $P > P_c$ along the dew point curve (vapor fraction, $V = 1$), two equilibrium solutions exist. When minimizing the utilities cost for a plant to dehydrate acetone using supercritical carbon dioxide, Cygnarowicz and Seider (1989) show how these two solutions lead to local and global minima. This might pose an excellent test problem for the global convergence strategies, such as the Benders decomposition with transformations to eliminate the nonconvexities in the primal and reduced master subproblems (Paules and Floudas, 1989). However, this method, which is discussed later in this section, has not been implemented for cubic equations of state because of the difficulties in locating suitable transformations.

Limit points have also been observed when tracing the VLE phase envelope (Kingsley and Lucia, 1987; Van Dongen et al., 1983). Kingsley and Lucia performed VLE calculations for a VLLE feed and computed three dew points, as illustrated in Figure 13 (points B, C, D). Two were located along the continuation path from B to D and the third along the path from A to C. Note, however, that the true solution lies along the VLLE branch between H and I. Similarly, Van Dongen et al. reported multiple VLE solutions for a LLE feed. In these, and other cases, when a VLE calculation is performed for a VLLE or LLE feed, multiple solutions often occur. Hence, before accepting a solution it is important to perform a stability check, perhaps using the Gibbs tangent plane criterion (see the next section).

In this regard, multiple solutions of the MESH equations that model azeotropic distillation towers have been reported (Magnussen et al., 1979; Kovach and Seider, 1987b; Kingsley and Lucia, 1988; Widagdo et al., 1989). However, in most cases, multiple solutions occurred when the trays contained one liquid phase and the reflux stream was specified. When the decanter was modeled at equilibrium (LLE), Prokopakis

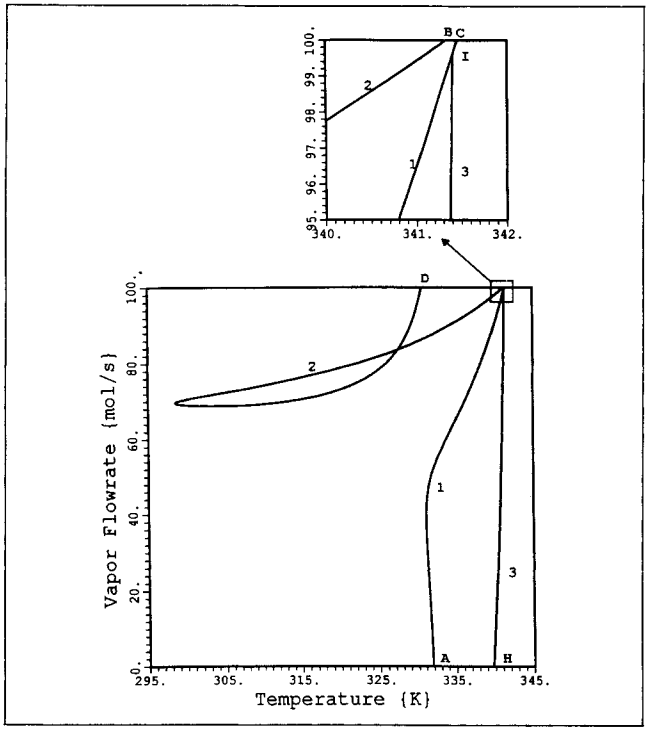


Figure 13. VL (1, 2) and VLL (3) branches for the ethanol-benzene-water system.
UNIQUAC parameters reduced from vapor-liquid equilibrium data.

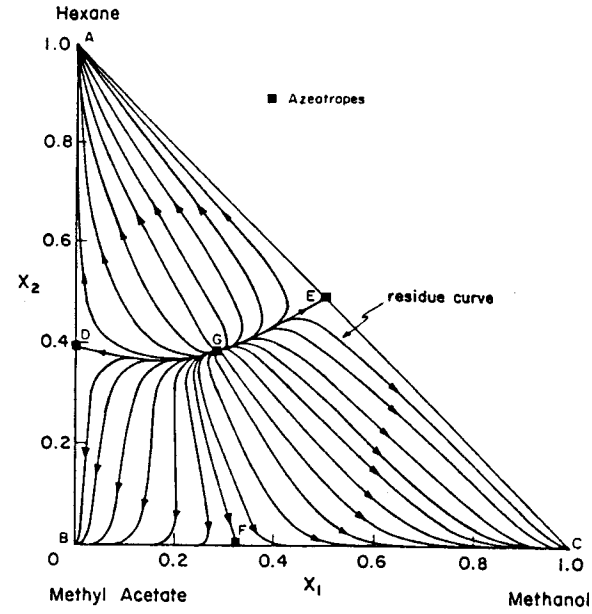


Figure 14. Residue curve map for methanol-hexane-methyl acetate system at 1 atm.
Arrows point in the direction of increasing time (and temperature)
Reprinted with permission from Van Dongen and Doherty, (1985)

and Seider (1983a) did not obtain multiple solutions. Widagdo et al. (1989) observed multiple solutions as two liquid phases were added to a tray by adjusting the aqueous reflux ratio.

These results led Sridhar and Lucia (1989a) to seek uniqueness criteria. First, the authors demonstrated that multistage separators, involving VLE on the stages, for binary, nonazeotropic mixtures at specified temperatures and pressures, have unique solutions. At specified T and P, for each stage, the energy balance can be omitted and the phase equilibrium equations and mass balances are written in a fixed point form. The authors apply the contraction mapping theorem (Ortega and Rheinboldt, 1970, p. 120) to prove that the fixed-point formula converges to a unique solution. Similarly it is shown that specifications of Q and P for each stage lead to unique solutions. Uniqueness criteria for multicomponent mixtures and more practical specifications are being considered (Sridhar and Lucia, 1989b). However, uniqueness criteria for systems with phase separation remain to be established. In this regard, it remains to be determined whether multiplicity can occur when *all* of the trays in a heterogeneous azeotropic distillation tower contain two liquid phases. Multiplicity is not likely, as it appears to be related to the improper calculation of VLE when a vapor and two liquid phases occur on a tray.

In all of the previous studies, however, it is important to note that the liquid flow rates have been expressed on a molar basis. Recently, Jacobsen and Skogestad (1990) observed that valves and pumps control mass or volumetric flow rates (not molar flow rates). Using these process inputs, they demonstrated conditions under which the relationship between the molar and mass flow rates is sufficiently nonlinear to account for multiple steady states in the operation of *all* distillation towers, not just those involving highly nonideal, azeotropic solutions.

Azeotropic Mixtures. At an azeotrope, two phases share the same compositions, e.g., $x_i = y_i$, $i = 1, \ldots, C$, and a first-order singularity is exhibited. Furthermore, many azeotropic mixtures are complex combinations of binary, ternary, ..., azeotropes, and when phase-splitting occurs, heterogeneous azeotropes are even more complex.

When minimizing the Gibbs free energy for azeotropic mixtures, the solution space is extremely nonlinear. As mentioned above, for systems that can form a second liquid phase, multiple steady-state solutions have been computed.

The more complex equilibria associated with azeotropic mixtures were first interpreted clearly by Doherty and Perkins (1978), who presented residue curve maps (RCM) for simple distillations (single-stage batch distillation with continuous removal of vapor). Figure 14 is an RCM for the homogeneous azeotropic mixture hexane-methanol-methyl acetate. Note the three low-boiling binary azeotropes at D, E, and F, and the low-boiling ternary azeotrope at G. Furthermore, three distinct regions of operation exist. When the feed composition lies within *ADGE*, the vessel concentrates in hexane; when within *BDGF*, in methyl acetate; and when within *CEGF*, in methanol. These simple distillation regions are shown by Van Dongen and Doherty (1985) to bound the compositions of azeotropic distillation towers; that is, when the feed compositions lie within *ADGE*, all of the tray compositions lie within this region. This paper is the first of several that introduce novel design procedures for homogeneous azeotropic distillation towers.

Singularities were also encountered by Kovach and Seider (1987b) and Widagdo et al. (1989) when the aqueous reflux ratio was varied in a heterogeneous azeotropic distillation tower

to dehydrate secbutanol. With an equilibrium-stage model, limit points were observed as the second liquid phase was introduced on the trays, with regions of steady-state multiplicity demonstrated.

Reactive Azeotropes. A more rigorous definition of an azeotrope is a mixture whose phases exhibit no changes in composition during vaporization or condensation (Rowlinson, 1969). For phase change with:

$$\frac{dx_i}{dt} = \frac{dy_i}{dt} = 0, \qquad i = 1,...,C \tag{55}$$

in the presence of a homogeneous chemical reaction, $\Sigma \nu_i A_i = 0$, at equilibrium, Barbosa and Doherty (1988a) derive the conditions that characterize a reactive azeotrope:

$$\frac{y_i - x_i}{\nu_i - x_i \nu_T} = \frac{d\xi}{dV} = \kappa \qquad i = 1,...,C \tag{56}$$

where x_i, y_i, and ν_i are the liquid and vapor mole fractions and the stoichiometric coefficient of species i, $\nu_T = \Sigma_i \nu_i$, ξ is the extent of the reaction, V is the moles of vapor, and κ is a constant.

In a subsequent paper, Barbosa and Doherty (1988b) show that the mass balances for simple distillation in the presence of chemical reaction are:

$$\frac{dX_i}{d\tau} = X_i - Y_i \qquad i = 1,...,C-1;\ i \neq k \tag{57a}$$

where

$$X_i = \left(\frac{x_i}{\nu_i} - \frac{x_k}{\nu_k}\right) \Big/ (\nu_k - \nu_T x_k) \tag{57b}$$

$$Y_i = \left(\frac{y_i}{\nu_i} - \frac{y_k}{\nu_k}\right) \Big/ (\nu_k - \nu_T y_k) \tag{57c}$$

$$\tau = \frac{V}{H}\left(\frac{\nu_k - \nu_T y_k}{\nu_k - \nu_T x_k}\right) t \tag{57d}$$

H is the molar liquid holdup in the still, and k denotes a reference species. Note that Eq. 57a corresponds to the mass balances without chemical reaction (Doherty and Perkins, 1978):

$$\frac{dx_i}{d\zeta} = x_i - y_i, \qquad i = 1,...,C \tag{58}$$

where ζ is a dimensionless time variable. When Eq. 58 is expressed in terms of the transformation variables, X_i, Y_i, and τ, at long times,

$$X_i = Y_i \qquad i = 1,...,C \tag{59}$$

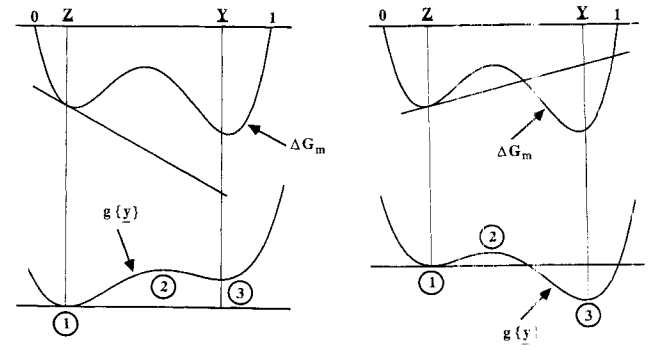
define the steady-state attractor and are the conditions derived for a reactive azeotrope (Eq. 56). Barbosa and Doherty proceed to integrate Eq. 57 and show the influence of the chemical reaction on the residue curve maps.

Finally, the authors (Barbosa and Doherty, 1988c) derive the equations for continuous distillation with reaction in towers having a single feed stream, and show that these equations, when expressed using the transformation variables, X_i and Y_i, are much simpler than when expressed using mole fraction variables, x_i and y_i. Furthermore, they derive an algorithm for the determination of the minimum reflux ratio that is comparable with those for distillation towers without reaction.

Phase stability analysis

To obtain the global minimum in the Gibbs free energy, the phase distribution must be correct. If $G_{\min}^{VL} < G_{\min}^{VLL}$, the VLL solution is unstable, and if $G_{\min}^{VLL} < G_{\min}^{VL}$, the VL solution is unstable. Hence, it is important to check the stability of the phases at $G_{\min}$.

Michelsen (1982a) accomplishes this by application of the Gibbs tangent plane criterion. It is postulated that an infinitesimal phase, of composition $\underline{y}$, is split from the existing phases at $G_{\min}$. If any composition $\underline{y}$ can be found where G is reduced, the original phases are unstable. The Gibbs free energy difference is simply the tangent plane distance (Eq. 53), as illustrated schematically for a binary mixture in Figure 15. For a stable phase, at composition z, the three stationary points have $g\{y_{sp}\} \geq 0$. However, for an unstable phase, at least one of the stationary points has $g\{y_{sp}\} < 0$. In the Michelsen approach, the stationarity conditions are solved in an attempt to locate all of the stationary points. When a composition y is found where $g\{y\} < 0$, instability exists and, as illustrated in Figure 15b, y provides a good initialization for the new phase. Then, G is minimized for the new phase distribution. Michelsen has demonstrated that the combined algorithm is particularly effective for locating small phases near phase boundaries and in the close proximity of critical points. Unfortunately, however, the failure to locate y at which $g\{y\} < 0$, does not guarantee that the phase distribution is stable. This is the primary limitation of the tangent-plane stability analysis. Three alternative approaches, previously introduced in the section on nonlinear programming, have recently been introduced to handle the nonnegativity constraints. These include an application of Benders decomposition, the active set strategy, and a relaxation strategy. All three are discussed in the sections that follow, although quantitative comparisons of their per-



a. Stable *b. Unstable*

Figure 15. Gibbs free energy of mixing and tangent plane distance for a binary mixture.
Z is mole fraction in the initial phase.

formance with the Michelsen algorithm have not been prepared.

Global convergence strategies

In a recent development, Paules and Floudas (1989) have applied the algorithm of Floudas et al. (1989) to seek the global minimum Gibbs free energy. The NLP is augmented with binary variables to represent the existence or nonexistence of the phases, resulting in the following mixed-integer nonlinear program (MINLP):

$$\underset{\underline{n}}{\text{Minimize}}\ G\{\underline{n}\} = \sum_{\ell=1}^{P}\sum_{j=1}^{C} n_{j\ell}\left(G^o_{j\ell} + RT\ln\frac{\bar{f}_{j\ell}}{f^o_{j\ell}}\right) \tag{60}$$

ST:
Phase and chem. equil.

$$b_k = \sum_{\ell=1}^{P}\sum_{j=1}^{C} m_{jk}\, n_{j\ell} \qquad k = 1,\ldots,E$$

or phase equil. alone

$$n_j^T = \sum_{\ell=1}^{P} n_{j\ell} \qquad j = 1,\ldots,C$$

$$n_{j\ell} \le \Omega_j y_{j\ell} \qquad j = 1,\ldots,C$$

$$\left.\begin{aligned} y_{j\ell} &\le y_\ell \\ n_{j\ell} &\ge 0 \end{aligned}\right\} \qquad j=1,\ldots,C;\ \ell=1,\ldots,P$$

$$y_{j\ell}, y_\ell \in \{0,1\}$$

where $y_{j\ell}$ is unity when species j exists in phase ℓ (otherwise, zero) and y_ℓ is unity when phase ℓ exists (otherwise, zero). For phase equilibrium only, $\Omega_j = n_j^T$ and for phase and chemical equilibrium, Ω_j is a sufficiently large constant.

In Benders decomposition, the binary variables are the complicating variables. These are fixed (corresponding to a specific phase distribution) and the resulting NLP (primal problem) is solved for an upper bound on the minimum of G. At this solution, the constraints of the reduced master problem (RMP) are augmented. Then, the RMP is solved to locate a new lower bound for G and its associated binary variables. The nonconvexities in the objective function, however, can lead to a local $G_{\min}$. To improve the reliability in locating the global $G_{\min}$, Paules and Floudas introduce variable transformations in the nonconvex expressions for the liquid-phase activity coefficients. These are included in the set of complicating variables and render both the primal and reduced master problems convex. The resulting subproblems are solved for their global solutions, but the global optimum of the MINLP cannot be guaranteed due to "the potential transfer of nonconvexities through the Kuhn-Tucker multipliers." This approach has the potential to significantly improve the reliability of the algorithms for phase and chemical equilibrium. The successes documented by the authors suggest that the algorithm is worthy of extensive testing.

In summary, this global optimization approach appears to improve the reliability of the NLP strategies to locate the global $g_{\min}$. For systems that can be expected to exhibit three or more phases at equilibrium, the role of stability analysis should continue to be important. In our experience, minimization algorithms can delete a phase prematurely, even with very good composition guesses. To be successful, these algorithms need to reinitialize the phase. Thus far, the tangent plane analysis has been quite successful for phase reinitialization and the success of this global optimization strategy has not been reported.

Bilevel design strategies

The phase and chemical equilibrium problem with the design objective function and design constraints superimposed is a bilevel programming problem (BLPP), which can be expressed without integer variables as:

$$\underset{\underline{x}}{\text{Minimize}} \quad C\{\underline{x},\underline{n}\} \tag{61a}$$

$$\text{ST:} \quad \underline{h}\{\underline{x},\underline{n}\} = 0 \tag{61b}$$

$$\underline{g}\{\underline{x},\underline{n}\} \le 0 \tag{61c}$$

$$\underset{\underline{n}}{\text{Minimize}} \quad G\{\underline{x},\underline{n}\} \tag{61d}$$

$$\text{ST:} \quad \underline{\hat{h}}\{\underline{x},\underline{n}\} = 0 \tag{61e}$$

$$\underline{\hat{g}}\{\underline{x},\underline{n}\} \le 0 \tag{61f}$$

where C is the cost objective, $\underline{n}$ are the mole numbers, and $\underline{x}$ are the remaining process variables, $\underline{g}$ and $\underline{h}$ are design constraints, G is the Gibbs free energy, $\underline{\hat{h}}$ are the mass balances (e.g., Eq. 45 or 46), and $\underline{\hat{g}}$ are the nonnegativity constraints (Eq. 47).

Recently, Clark and Westerberg (1990) introduced active set and relaxation strategies to solve BLPPs and these strategies were applied by Clark (1990) to solve Eq. 61. In the active set strategy, an arbitrary set of binding constraints is selected and the Lagrangian of the inner problem is formulated:

$$L_{\text{inn}} = G + \sum_j \pi_j \hat{h}_j + \sum_{j,\ell\in A} \lambda_{j\ell}\, n_{j\ell} \tag{62}$$

Note that only the active inequalities (A) are included. Then, Eq. 62 is differentiated to give the K-T conditions for the inner problem:

$$\underline{\nabla_n L_{\text{inn}}} = \underline{\nabla_n G} + \sum_j \pi_j \underline{\nabla_n \hat{h}_j} + \sum_{j,\ell\in A} \lambda_{j\ell}\, \underline{e}_{j\ell} \tag{63a}$$

$$\underline{\hat{h}} = 0 \tag{63b}$$

$$n_{j\ell} = \delta \qquad j,\ell\in A \tag{63c}$$

$$\lambda_{j\ell} \ge 0 \qquad j,\ell\in A \tag{63d}$$

where δ is a small positive number that keeps the chemical potential bounded as $n_{j\ell} \to 0$ and $\underline{e}_j$ is the jth unit vector. The

inner NLP is replaced by Eq. 63, along with the nonnegativity constraints:

$$n_{j\ell} \geq \delta \qquad j,\ell \in I \tag{64}$$

where I denotes the set of inactive constraints. With Eqs. 63 and 64, the outer problem becomes a single-level NLP. At the solution, if $\lambda_{j\ell} = 0$ $(j,\ell \in A)$, the associated constraint is a candidate to be removed from A, and if $n_{j\ell} = \delta$ $(j,\ell \in I)$, the constraint is a candidate to be added. The new active set is determined based upon the gradient of the Lagrangian of the single-level NLP. At a stationary point, the gradient of this outer Lagrangian is zero. New multipliers (so-called outer multipliers) are computed assuming the inner problem remains optimal. The signs of these so-called shadow prices indicate whether the outer objective, C, can be reduced by adding a constraint to A or removing a constraint from A.

In the relaxation strategy, the complementary slackness conditions are replaced by:

$$n_{j\ell}\,\lambda_{j\ell} \leq r \qquad j = 1,\ldots,C;\ \ell = 1,\ldots,P \tag{65}$$

and the single-level NLP is solved for several decreasing values of r, where $r \geq 0$. The effect of r is to replace the true feasible region with a smooth approximation, avoiding the problem of nondifferentiability at the intersection of constraints. Of course, as $r \to 0$ the true feasible region is approached continuously without discontinuities in the first derivatives.

Clark (1990) utilizes these methods to optimize the design for an aniline process. As the flash temperature, reactor conversion, and the hydrogen/nitrobenzene ratio in the feed are varied to maximize the venture profit, the phase distribution in the flash vessel shifts between VL and VLL. Results are presented, but unfortunately, limited performance information is provided. Much more extensive testing is needed to determine the effectiveness of these methods.

Thus far, emphasis has been placed on the singularities associated with phase uncertainty, leading to potential problems in the implementation of bilevel design strategies. Before summarizing and introducing the section on Process Flowsheet Analysis, an important branch of nonlinear analysis, geometric theory, is reviewed, as it applies to the design of distillation towers.

Geometric theory

In recent work, Doherty and coworkers have applied geometric theory for the solution of problems involving nonlinear ODEs and phase equilibrium. This theory, which is based on topological concepts, was discussed by Lefschetz (1962) and Arnold (1973) in two books on the solution of ODEs. In this section, applications of the theory are reviewed for the generation of residue curve maps (RCM) and for the design of distillation towers involving nonideal multicomponent solutions. New insights are presented for sketching RCMs, based on few data and for locating the minimum reflux ratio. These are particularly effective in the early design stages of distillation towers involving azeotropic solutions.

Residue Curve Maps. As mentioned in the section on Azeotropic Mixtures, RCMs can be generated in simple distillation experiments (see Figure 14). However, when data are unavailable, early in a design, Doherty (1990) has introduced a qualitative method for sketching an RCM. First, the boiling points of the pure species are entered at the vertices. Then, the boiling points of the binary azeotropes are positioned along the edges, with the boiling points of the ternary azeotropes positioned in the concentration space. The topological sink-source principle is applied to show the direction of the concentration trajectories along the edges and along residue curves, which are positioned qualitatively between the vertices and the azeotropic points. Douglas (1988) shows an application of this methodology to the design of a distillation tower.

Nonideal Multicomponent Distillation. Before presenting the application of geometric theory, the work of Levy et al. (1985) is reviewed. These authors introduced a boundary-value design procedure (BVDP) to determine the minimum reflux ratio, given C of the distillate and bottoms mole fractions, $\underline{x}_D$ and $\underline{x}_B$, for ternary azeotropic solutions with no heat effects, where C is the number of chemical species. Assuming constant molal overflow, component balances are written for stages in the rectifying and stripping sections:

Rectifying Section

$$\underline{y}^r_{m+1} = \frac{r}{r+1}\,\underline{x}^r_m + \frac{1}{r+1}\,\underline{x}_D \qquad m = 0,1,\ldots,M \tag{66a}$$

$$\underline{x}^r_o = \underline{x}_D \tag{66b}$$

Stripping Section

$$\underline{x}^s_{n+1} = \frac{s}{s+1}\,\underline{y}^s_n + \frac{1}{s+1}\,\underline{x}_B \qquad n = 0,1,\ldots,N \tag{67a}$$

$$\underline{x}^s_o = \underline{x}_B \tag{67b}$$

where the rectifying and stripping sections contain M and N stages, r and s are the reflux ratios in these sections, $\underline{y}^r_m$ is the vector of vapor mole fractions in the rectifying section on stage m, and $\underline{x}^s_n$ is the vector of liquid mole fractions in the stripping section on stage n. These difference equations define the operating lines. At the feed stage, additional equations apply:

Overall Material Balance

$$\frac{x_{F,i} - x_{B,i}}{x_{F,1} - x_{B,1}} = \frac{x_{F,i} - x_{D,i}}{x_{F,1} - x_{D,1}} \qquad i = 2,\ldots,C-1 \tag{68}$$

Overall Energy Balance

$$s = (r+q)\left[\frac{x_{B,1} - x_{F,1}}{x_{F,1} - x_{D,1}}\right] + q - 1 \tag{69}$$

Feed Stage Continuity

$$\underline{x}^r_M = \underline{x}^s_N \tag{70}$$

where $\underline{x}_F$ is a vector of feed mole fractions and q is the feed quality.

To determine the minimum reflux ratio, the difference equations (Eqs. 66–67) are expressed as ODEs in the continuous variables, $\hat{\underline{x}}^r$, $\hat{\underline{x}}^s$, $\hat{\underline{y}}^r$, $\hat{\underline{y}}^s$.

$$\frac{d\hat{\underline{x}}^r}{dh} = \frac{r}{r+1}\,\hat{\underline{x}}^r + \frac{1}{r+1}\,\underline{x}_D - \hat{\underline{y}}^r = 0 \tag{71}$$

$$\frac{d\hat{\underline{x}}^s}{dh} = \frac{s}{s+1}\,\hat{\underline{y}}^s + \frac{1}{s+1}\,\underline{x}_B - \hat{\underline{x}}^s = 0 \tag{72}$$

where h is the elevation in the tower. When $d\underline{\hat{x}}^r/dh = d\underline{\hat{x}}^s/dh = 0$, Eqs. 71 and 72 apply to locate the two fixed (pinch) points (for a ternary system). First, Eq. 68 is solved for the unknown $\underline{x}_D$ and $\underline{x}_B$. Then, r is assumed, Eq. 69 is solved for s, and Eqs. 71 and 72 are solved (with $\hat{y}_i^r = K_i\hat{x}_i^r$ and $\hat{y}_i^s = K_i\hat{x}_i^s$; see Eq. 52) for the fixed points, $\underline{\hat{x}}^r$, $\underline{\hat{x}}^s$. When $\underline{\hat{x}}^r = \underline{\hat{x}}^s$, r and s are minimized, corresponding to N, $M \to \infty$.

Julka and Doherty (1990a) extended this methodology to apply for multicomponent systems ($C \geq 4$). For a quaternary system, four fixed points ($\underline{\hat{x}}_1^r$, $\underline{\hat{x}}_2^r$, $\underline{\hat{x}}_3^r$, $\underline{\hat{x}}_1^s$) are computed, all of which lie in the same plane, as illustrated in Figure 16. The curve between $\underline{x}_B$ and $\underline{\hat{x}}_1^s$ is the operating line in the stripping section. Vectors can be defined between $\underline{x}_F$ and the four fixed points:

$$\begin{aligned} \underline{d}_1 &= \underline{\hat{x}}_1^r - \underline{x}_F \\ \underline{d}_2 &= \underline{\hat{x}}_2^r - \underline{x}_F \\ \underline{d}_3 &= \underline{\hat{x}}_3^r - \underline{x}_F \\ \underline{d}_4 &= \underline{\hat{x}}_1^s - \underline{x}_F \end{aligned} \tag{73}$$

The authors show that at the minimum reflux these vectors lie in the same plane:

$$\det\{\underline{d}_i, \underline{d}_j, \underline{d}_k\} = 0 \qquad i, j, k \in \{1,2,3,4\} \tag{74}$$

and the volume defined by $\underline{d}_i$, $\underline{d}_j$, and $\underline{d}_k$ is zero. Thus, at the minimum reflux ratio, the fixed points satisfy the zero-volume formula, and Eq. 74 replaces Eq. 70. In this manner, geometric theory is applied to determine the minimum reflux ratio.

For solutions with heat effects, Knight and Doherty (1986) extended the methodology of Levy et al. (1985). A similar strategy can be applied for multicomponent systems ($C \geq 4$).

Recently, Julka and Doherty (1990b) presented a continuation strategy, using the AUTO program (Doedel, 1986), for locating all of the fixed points. To perfect this methodology for $C \geq 5$, where the tetrahedron cannot be displayed (see Figure 16), a strategy for selecting the permutations of vectors in the zero-volume formula (Eq. 74) is needed. Furthermore, the zero-volume formula provides an exact solution when the relative volatilities of the species are constant throughout the column. For azeotropic towers, the authors contend that this is a reasonable assumption, a contention that needs better verification.

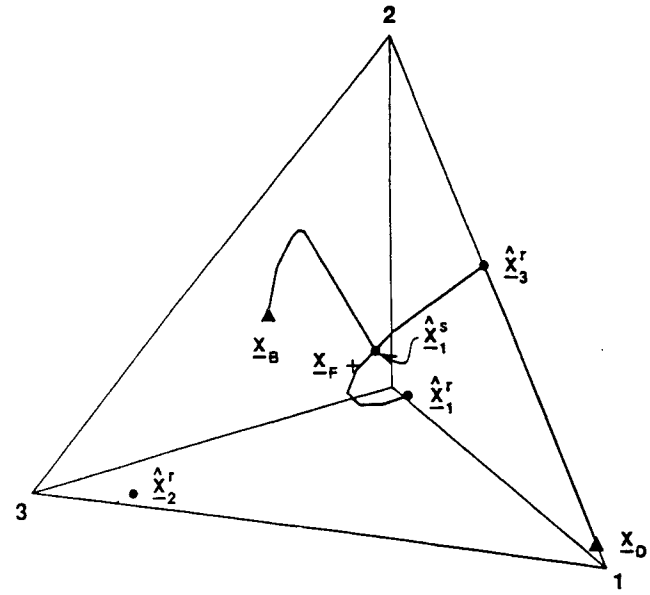


Figure 16. Isometric view of the fixed (pinch) points and operating lines for a quaternary distillation tower
Reprinted with permission from Pergamon Press (Julka and Doherty, 1990a).

Summary

Processes that involve phase equilibria, where the phase distribution is uncertain, can be difficult to characterize as their design and input parameters vary. Their models often become singular when phases coalesce. Furthermore, local minima in the Gibbs free energy with the wrong phase distribution are likely to arise. Several approaches designed to locate the global minimum more reliably were reviewed in this section. They utilize the latest methods for solving NLP and MINLP problems (reviewed in the previous section). Their effectiveness needs to be further tested in comparison with the repeated use of minimization and stability analysis.

In process units and flowsheets, phase uncertainties occur in many streams (as the operating parameters are adjusted), and related singularities and near singularities are often encountered. These can pose problems for the most widely used simulation programs, even when their phase equilibrium procedures are well developed. The next section addresses these problems and the problems experienced by the newer, more experimental packages, which have less extensive facilities and often encounter convergence difficulties and failures when their models involve nonideal phase and chemical equilibria.

Process Flowsheet Analysis

In recent years, steady-state simulators have undergone extensive improvements and are commonly used for the design and operation of many continuous processes. Often, they are accompanied by dynamic simulators, such as SPEEDUP, which are becoming widely available to simulate the responses to disturbances and setpoint changes, and to study start-up and shut-down strategies, among a growing list of applications. This rapid growth, together with faster and more interactive computers having larger memories, is stimulating the creation of new architectures and algorithms for the simulation of process flowsheets. When evaluating these architectures, it is important to assess the sources of the nonlinearities—those discussed above and those introduced through recycle. Consequently, in this section, the two principal architectures, sequential modular and equation-oriented, are reviewed, with emphasis on their strengths and weaknesses for processes that involve complex nonlinearities.

Impact of recycle

In flowsheet analysis, it is well recognized that recycle streams complicate the solution of the equations. However, their impact on the nonlinear responses of the unit processes is more difficult to characterize, as illustrated in the following examples.

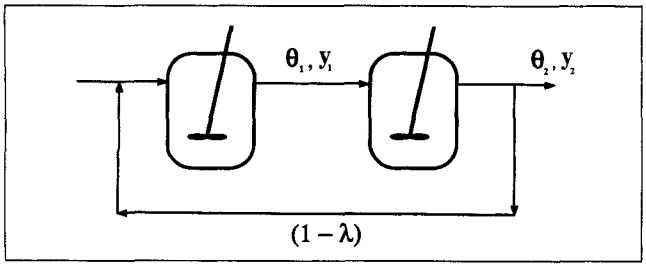


Figure 17. Two diabatic CSTRs with recycle.

Consider the addition of a recycle stream to two diabatic CSTRs in series (see Figure 17) which greatly simplifies the solution space, as shown in Fig. 18, for the conversion of $A \rightarrow B$ in a first-order, exothermic reaction. Without recycle ($\lambda = 1$), the solution diagram exhibits up to five steady-state solutions and periodic branches arise from three Hopf bifurcation points (Kubicek et al., 1980; Kubicek and Marek, 1983). As the fraction recycled is increased to 0.5, only unique steady-state solutions exist. In this case, recycle dampens the propagation of nonlinearities.

In a related study, Gawdzik and Berezowski (1987) examined the effect of recycle on an adiabatic PFTR that converts CO, CO_2, and H_2 to methanol in two exothermic reactions,

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

as illustrated in Figure 19. Their results, in Figure 20, also demonstrate that the occurrence of multiple steady-state attractors is inhibited as the fraction recycled increases.

However, when added to other unit processes, recycle streams introduce steady-state multiplicity. Consider, for example, the thermally-coupled distillation towers studied by Chavez C. et

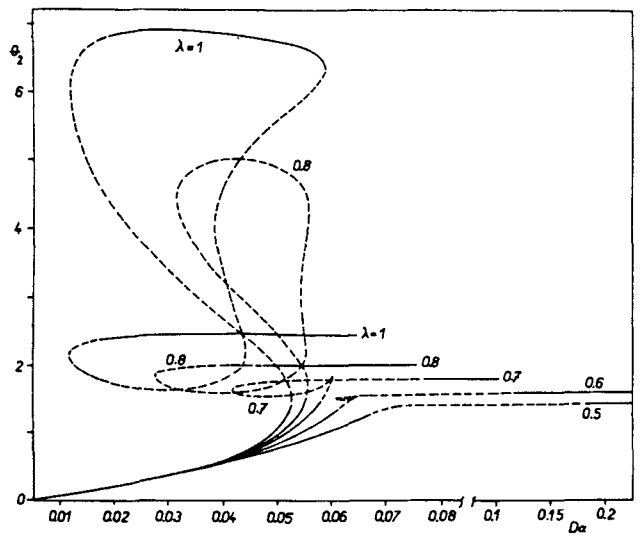


Figure 18. Dimensionless product temperature as a function of Damkohler number and recycle fraction

Reprinted with permission from Pergamon Press (Kubicek et al., 1987).

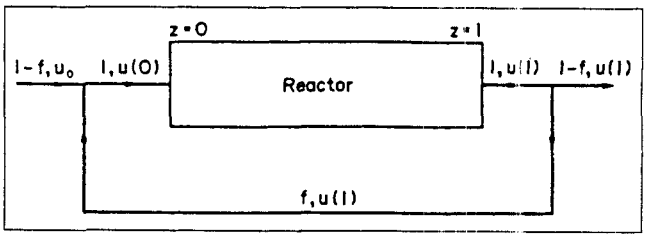


Figure 19. Recirculation about an adiabatic PFTR to produce methanol.

u, dimensionless temperature; f, product fraction

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al. (1986). These authors obtained multiple steady-state solutions of the MESH equations for three configurations, one of which is illustrated in Figure 21a. For this Petlyuk system, they computed four sets of interlink flow rates over a sizable range of the reflux ratio. Calculations were performed for the separation of a benzene-toluene-*o*-xylene system, with the following specifications: 95% molar purity of benzene in the distillate, 90% toluene in the middle product, 95% *o*-xylene in 380 kmol/h of the bottoms stream, and the reflux ratio (4.525–5.75). As shown in Figure 21b, the flow rates of the liquid interlink streams are significantly displaced. However, the flow rates of the distillate and middle product, the boil-up, and the condenser load, are negligibly different at each reflux ratio. It is noteworthy that Lin et al. (1987) subsequently located all of the steady-state solutions from a single starting

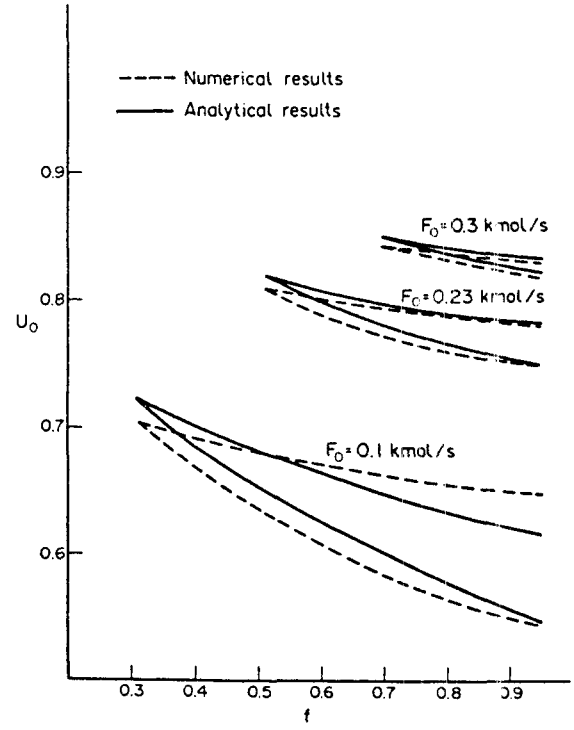

Figure 20. Adiabatic PFTF with recycle; regions of multiple steady states.

U_0, feed temperature (dimensionless); F_0, flowrate; f, product fraction

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point using homotopy continuation. Unfortunately, the studies of Chavez C. et al. and Lin et al., did not include checks on the stability of the solutions and provided no experimental verification of the multiple solutions. For design calculations (to size the towers properly), it is important to recognize that multiple solutions are possible, to locate the solutions when they exist, to check for stability, and to perform dynamic simulations.

In general, the degree of backmixing is important in most chemical processes. At the microscopic level, internal recirculation can significantly influence the rates of heat and mass transfer and chemical reaction, whereas at the macroscopic level external recirculation (as illustrated above) can play an important role. These two perspectives are thoroughly reviewed by the Russian authors Kafarov et al. (1985a,b). Their work suggests that microscopic analysis may help to explain the impact of recycle on the nonlinear behavior of the unit processes.

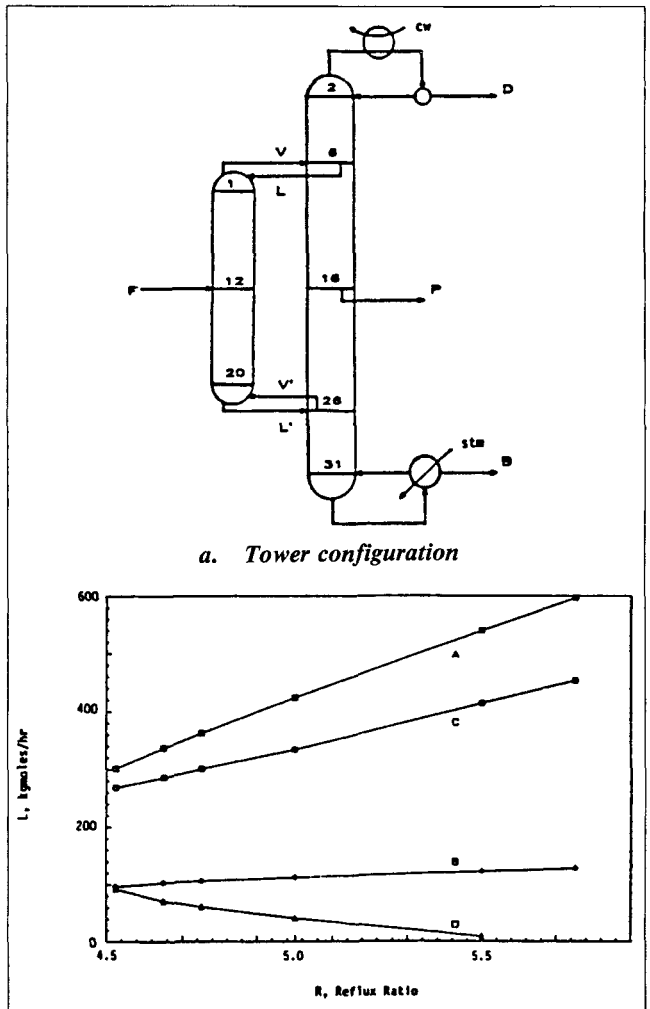
Multilevel analysis

The models of process flowsheets can often be conveniently decomposed into a tree of submodels. Such a tree can be important conceptually, as well as in the practical implementation of flowsheet simulators, when the flowsheets involve streams with two or more phases at equilibrium, exothermic reactors, autocatalytic reactors, separators with two or more phases that approach equilibrium, and so on. At the lowest level are the NLPs that minimize the Gibbs free energy (at phase equilibrium), as required for many of the process streams. At a higher level are the single-stage reactor and separator models. These are often connected at the flowsheet level to form more complex structures, such as multistage towers with reaction. At the highest level, cost models can be incorporated in an MINLP to optimize an economic objective function.

The ability of a flowsheet simulator to solve the full MINLP efficiently and reliably depends, of course, on the complexity of its subproblems. Often the phase distribution is uncertain in the process streams or the unit processes. This can occur near phase boundaries, in the critical region, etc. Here, the subproblem is highly nonlinear, has a complex solution space (singularities, multiple solutions, etc.), and hence the solution of the full MINLP is more difficult to achieve. This also occurs with nonlinear reactors and complex recycle structures. These, indeed, are the problems that are most difficult to solve using the commercial process simulators. They are excluded from the test problems used to evaluate the new equation-based simulators, probably because they elude even the most advanced solvers. This observation is supported in the next section, which is devoted to the decomposition strategies that underlie the commercial simulators and the most advanced prototypes currently being developed.

Decomposition strategies

Process flowsheets often incorporate many unit processes, in some cases several hundred, integrated with many recycle streams. Consequently, the design problem, which usually involves an economic objective function, is often solved subject to many suboptimization problems and constraints. For steady-state analysis, the entire system [expressed using the stationarity (K-T) conditions] can be on the order of several thousand



a. Tower configuration

b. Interlink liquid flow rate as a function of reflux ratio

Figure 21. Petlyuk system.
Reprinted with permission from Chavez C. et al. (1986).

NLEs. These nonlinear systems have large, sparse Jacobian matrices, and hence, it becomes imperative to store their matrices efficiently, with minimal requirements for storing and retrieving the individual elements, and to utilize efficient matrix inversion techniques. See, for example, the approaches by Stadtherr and Hilton (1982), Stadtherr and Wood (1984a,b), and Stadtherr and Vegeais (1985).

The bulk of the decomposition strategies deal with the representation and processing of the Jacobian matrix in Newton-based algorithms. However, the simplest and most widely-used decomposition strategy involves algorithms or procedures to solve the subproblems associated with each unit process. This is reviewed first.

Much has been written on decomposition strategies for flowsheet analysis in process design. The principal objective in this section is to examine the strengths and limitations of these strategies for flowsheets with complex nonlinearities. To facilitate this examination, their distinctive features are reviewed briefly.

Unit Procedures. Most of the commercial process simu-

lators contain a large library of well-tested FORTRAN subroutines or procedures to solve the subproblems associated with the unit processes (e.g., ASPEN PLUS, FLOWTRAN, PROCESS, DESIGN II, CHEMCAD, and HYSIM). Most of the procedures determine the product streams, given the feed streams and parameters for the unit processes. HYSIM procedures, however, are unique in their implementation of a so-called partial information flow, in which specifications are permitted for the feed and product streams and the unknowns in all of the streams are determined.

The use of subroutines or procedures has been termed the sequential modular approach (SMA), which when implemented to solve the system of steady-state subproblems associated with a recycle loop, requires *tears* (guesses) for the recycle stream and a so-called recycle convergence algorithm (e.g., Wegstein's method). In recent years, much has been done to implement an improved representation of multiphase streams, including solids, to permit more flexible programming with FORTRAN statements, to more efficiently solve combined recycle and control problems, etc. However, the strength of these simulators continues to lie in their algorithms for solving the nonlinear subproblems. Much emphasis has been placed on the determination of the proper phase distribution at equilibrium, for processes involving highly non-ideal solutions and at elevated pressures in the critical region. One less known simulator, SEPSIM (Anderson and Fredenslund, 1987), implements the tangent-plane analysis, described above, to determine the stability of the phase distribution at G_{min}.

Recently, successive quadratic programming (SQP) has been implemented to solve the recycle and design optimization problems simultaneously. This has been described, in a comprehensive review of chemical process simulation by Biegler (1989). The algorithm, developed by Lang and Biegler (1987), is briefly reviewed here. For the process flowsheet in Figure 22a, the design optimization problem is:

$$\underset{\underline{x},\underline{y}}{\text{Minimize}} \quad F\{\underline{x},\underline{y}\} \tag{75a}$$

$$\text{ST:} \quad \underline{g}\{\underline{x},\underline{y}\} \le 0 \tag{75b}$$

$$\underline{c}\{\underline{x},\underline{y}\} = 0 \tag{75c}$$

$$\underline{h}\{\underline{x},\underline{y}\} = \underline{y} - \underline{w}\{\underline{x},\underline{y}\} = 0 \tag{75d}$$

where $\underline{x}$ is the vector of design variables and Eq. 75d are the so-called tear constraints, involving $\underline{y}$, the vector of tear variables. The solution, for a single design variable, is illustrated in Figures 22b and 22c. Note that for each $\underline{x}$, the equality constraints can be solved in a feasible path strategy, which requires a complete simulation for each vector of guesses, $\underline{x}^{(k)}$. In the Lang and Biegler strategy, the constraints are linearized and the following quadratic program:

$$\underset{\underline{d}}{\text{Minimize}} \quad \nabla \underline{F}\{\underline{x}^{(k)},\underline{y}^{(k)}\}^T\underline{d} + (1/2)\underline{d}^T\underline{\underline{C}}\,\underline{d} \tag{76a}$$

$$\text{ST:} \quad \underline{g}\{\underline{x}^{(k)},\underline{y}^{(k)}\} + \nabla \underline{g}\{\underline{x}^{(k)},\underline{y}^{(k)}\}^T\underline{d} \le 0 \tag{76b}$$

$$\underline{c}\{\underline{x}^{(k)},\underline{y}^{(k)}\} + \nabla \underline{c}\{\underline{x}^{(k)},\underline{y}^{(k)}\}^T\underline{d} = 0 \tag{76c}$$

$$\underline{h}\{\underline{x}^{(k)},\underline{y}^{(k)}\} + \nabla \underline{h}\{\underline{x}^{(k)},\underline{y}^{(k)}\}^T\underline{d} = 0 \tag{76d}$$

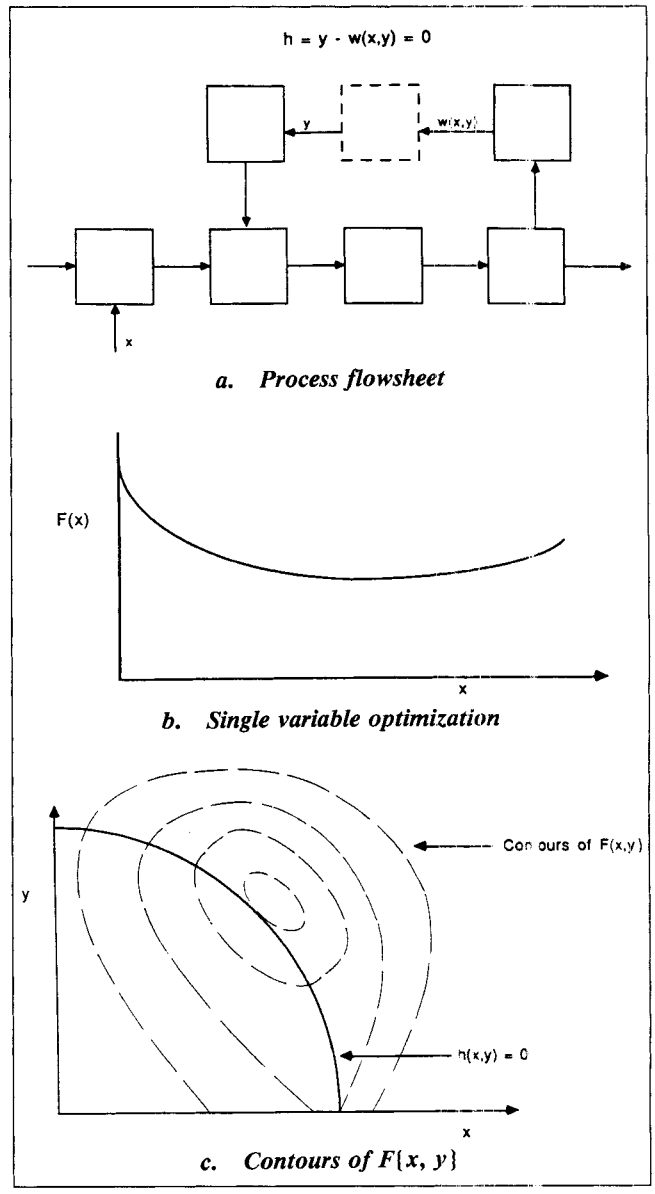
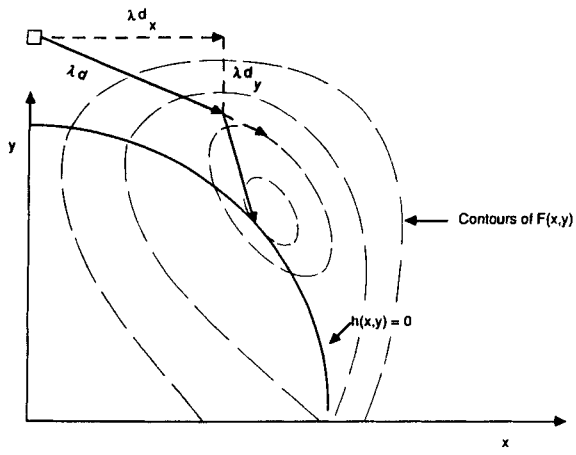


Figure 22. Design optimization of a process flowsheet.
Reprinted with permission from Seader et al. (1987).

is solved for iteration k, where $\underline{d} = [\underline{\Delta x}\,\underline{\Delta y}]^T$ is the vector of changes in the design and tear variables and $\underline{\underline{C}}$ is an approximation to the Hessian of the Lagrangian of Eq. 75. As illustrated in Figure 23, SQP implements an infeasible path strategy; that is, both $\underline{x}$ and $\underline{y}$ are adjusted simultaneously. This implementation is far more efficient, as demonstrated for two sample problems in *FLOWTRAN Simulation—An Introduction* (Seader et al., 1987).

The reliability of the SQP algorithm is, of course, dependent on the nonlinear unit processes and the recycle structure. When multiple solutions exist for the subproblems, local solutions can be obtained for the nonconvex NLPs and care must be exercised to locate the global optimum. This is demonstrated by Cygnarowicz and Seider (1989), who obtained local and global minima in the utilities cost for a process to extract



Figures 23. Infeasible path strategy using SQP.
Reprinted with permission from Seader et al. (1987).

acetone using carbon dioxide in the retrograde region. They used the SCOPT program, developed by Lang and Biegler, with the SEPSIM system to implement the infeasible path strategy. The local and global optima were computed with two different initializations.

In summary, simulators that utilize unit procedures are often more reliable in avoiding the singularities in nonlinear processes, but they may not locate the global optimum. With the incorporation of tools for homotopy continuation, bifurcation analysis, and global optimization, more incidences of local and global optima are likely to be reported. The aniline process (Clark, 1990), referred to above, is a prime candidate, with local optima likely to be associated with the two phase distributions in the flash separator (VL and VLL).

Simultaneous Equations. The simplest alternative to a library of subroutines and procedures for the unit processes, is a library of subproblems. In the so-called equation-oriented simulators, the subproblems have been expressed as equation sets, with procedures used to compute thermophysical properties, such as the density of a stream. These may be expanded eventually to include an MINLP for each subproblem.

Given the process flowsheet, the subproblems (in the form of equation sets) are currently assembled to form a complete set of equations for the flowsheet. When available, analytical expressions for the first partial derivatives are also assembled to form the Jacobian matrix, or alternatively, code is installed for the numerical evaluation of the Jacobian elements. In addition, design constraints and specifications are easily added, this being a principal advantage of the equation-oriented simulators.

For the most part, Newton-based methods have been utilized to solve the large set of equations simultaneously. Several methods (discussed in the section on Local Convergence Algorithms) have been proposed and tested, including: a hybrid algorithm that blends a quasi-Newton method and the steepest descent method in an implementation of Powell's dogleg method (Stadtherr and Hilton, 1982; Chen and Stadtherr, 1981); Schubert's quasi-Newton method (Mah and Lin, 1980); the hybrid quasi-Newton update implemented with Schubert's method (Westman et al., 1984; see Eq. 6). In one study, Bogle and Perkins (1988) selected a scale-invariant implementation of Schubert's method for use within SPEEDUP (Pantelides, 1988). This method was utilized to solve four flowsheet problems containing between 50 and 200 unknowns. The problems involved mass balances only [one included nonlinear reaction rate expressions, and one (the Cavett process) used procedures to model the flash drums]. Similarly, Zitney and Stadtherr (1988) tested a prototype program, SEQUEL-II, that implements five variants for the evaluation of the sparse Jacobian matrices. Their four flowsheet problems also involve material balances with recycle. Conversions are specified in the ethylene and ammonia reactors. Temperatures and pressures are specified in the flash drums of the Cavett process, which involve nearly ideal liquid phases.

It is also noteworthy that Gupta et al. (1984) tested SPEEDUP with mixed results. For the Cavett problem, a heat exchanger network, and a five-stage absorber, they found that SPEEDUP easily obtained solutions with poor initial guesses. However, when they used the rigorous distillation model from Exxon's COPE as a procedure to solve a separation problem involving three towers with recycle, SPEEDUP was unsuccessful.

In summary, the simultaneous equation approach, as reported in the literature, has been only partially successful. Successes have been reported for models involving material balances and simple nonlinearities. To our knowledge, the models have not included diabatic and autocatalytic reactors nor phase equilibrium with uncertain phase distributions (e.g., heterogeneous azeotropic distillation towers; Kovach and Seider, 1987a,b). For these processes, multiple steady-state solutions can be expected and more reliable solution methods may be necessary.

It seems clear that the equation-oriented simulators need facilities to deal with the singularities at limit and real bifurcation points and to determine the proper phase distribution at equilibrium. Homotopy-continuation methods, with stability analysis, are needed to locate multiple solutions and determine their stability. For phase equilibrium, some means of incorporating the algorithms to locate $G_{\min}$ (described in the previous section) needs to be formulated. The equation-oriented simulators have the greatest potential to provide global solutions. However, these problems must be overcome before their potential can be realized.

These problems are further complicated when an objective function and inequality constraints are added to the equality constraints assembled for the flowsheet. While several strategies have been proposed for solving the NLP:

$$\underset{\underline{p}}{\text{Minimize}} \quad f\{\underline{x}, \underline{p}\} \tag{77a}$$

$$\text{ST:} \qquad \underline{h}\{\underline{x}, \underline{p}\} = 0 \tag{77b}$$

$$\underline{g}\{\underline{x}, \underline{p}\} \geq 0 \tag{77c}$$

these do not deal with the singularities at limit and real bifurcation points or address the problem of locating the proper phase distribution in streams at equilibrium. Here, $\underline{x}$ is a vector of n problem variables (typically, $n > 1{,}000$), $\underline{p}$ is a vector of ρ decision variables (typically, $\rho \leq 10$), $\underline{h}$ is a vector of n equality constraints, and $\underline{g}$ is a vector of m inequality constraints.

When implementing SQP, the QP solved during each iteration is:

$$\underset{\underline{d}}{\text{Minimize}} \quad \underline{\nabla f}^T \underline{d} + (1/2)\underline{d}^T \underline{\underline{C}}\, \underline{d} \tag{78a}$$

$$\text{ST:} \quad \underline{\underline{\nabla_x h}}\, \underline{\Delta x} + \underline{\underline{\nabla_p h}}\, \underline{\Delta p} = -\underline{h} \tag{78b}$$

$$\underline{\underline{\nabla_x g}}\, \underline{\Delta x} + \underline{\underline{\nabla_p g}}\, \underline{\Delta p} \geq -\underline{g} \tag{78c}$$

where $\underline{d} = [\underline{\Delta x}\ \underline{\Delta p}]^T$ and $\underline{\underline{C}}$ is an approximation to the Hessian of the Lagrangian of Eq. 77. For large n, this is a large QP, which led Berna et al. (1980) to show that an equivalent solution is obtained by solving the smaller QP:

$$\text{Minimize} \quad \underline{q}^T \underline{\Delta p} + (1/2)\underline{\Delta p}^T \underline{\underline{H}}\, \underline{\Delta p} \tag{79a}$$

$$\text{ST:} \quad \underline{\underline{Q}}^T \underline{\Delta p} \geq -\underline{\hat{g}} \tag{79b}$$

where $\underline{q}^T$, $\underline{\underline{H}}$, and $\underline{\underline{Q}}$ are functions of $\underline{\underline{C}}$, $\underline{\underline{\nabla h}}$, and $\underline{\underline{\nabla g}}$. This small QP is solved for $\underline{\Delta p}$ and $\underline{\lambda}$ (K-T multipliers). Then, $\underline{\Delta x}$ and $\underline{\pi}$ (Lagrange multipliers) are solved for by back-substitution.

Problems in storing the updates of the approximation to $\underline{\underline{C}}$, an $(n + \rho) \times (n + \rho)$ matrix, led Locke et al. (1983) to develop a strategy that updates $\underline{\underline{H}}$, which is only a $\rho \times \rho$ matrix. However, its performance results are mixed. To overcome these problems, Vasantharajan and Biegler (1988) developed range and null space projections that require fewer iterations for problems involving small flowsheets with few nonlinearities. Unfortunately, these have not been tested for large flowsheets with many nonlinearities.

SPEEDUP does not implement these decompositions. Instead, the full NLP is solved either using a feasible path strategy with SQP or an infeasible path strategy with MINOS. These are, of course, local convergence strategies and cannot be expected to perform well when unit processes with complex nonlinearities are prominent in the flowsheet.

Flowsheet dynamics

For the most part, dynamic simulations of process flowsheets are performed for continuous processes. Typical disturbances and setpoint changes are introduced and the simulations project the performance of different controller designs. Dynamic simulations are also used to study start-up and shut-down procedures, the responses to equipment failures, safe operating limits, continuous changes in operating parameters (such as catalyst activity and fouling factors), and other problems. These and other applications are reviewed by Hlavacek (1977, Part III), and Perkins and Sargent (1982).

Like their steady-state counterparts, the integration methods in the dynamic simulators, also reviewed in these papers, are referred to as modular or equation-oriented. In the modular approach, procedures are created to integrate the DAEs associated with each unit process, with care taken to select the numerical integrator best suited for each unit process. When stiffness is not encountered, explicit integrators are sufficient, and otherwise the semi-implicit and implicit methods may be necessary to permit practical time steps. The problem, of course, in implementing the modular approach involves the coordination of the integrations for fast- and slow-moving unit processes, especially when the dynamics are highly nonlinear and the recirculation of material and energy is sizable. This problem is also encountered when implementing the equation-oriented strategies, in which the DAEs for all of the unit processes are integrated simultaneously. To avoid integrating all of the DAEs with the smallest time step necessary to achieve error control, decomposition strategies have been developed.

The brief review of decomposition strategies that follows covers the principal approaches, but does not deal with their performance when complex nonlinearities exist. This is unfortunate because, in principle, each unit process can shift from steady to periodic to quasiperiodic, or even chaotic, attractors as parameters and manipulated variables are adjusted. The methods described have been tested for the efficient integration of slow- and fast-moving process units, but with simple nonlinearities, not involving the propagation of quasiperiodic or chaotic motion from process unit to process unit. This brief review is presented to establish the state of the art and the unresolved questions concerning the effectiveness of these techniques for highly nonlinear processes.

Unit Procedures. Several simulators, with libraries of procedures (or FORTRAN subroutines) to integrate the DAEs for the unit processes, have been developed over the past 20 years. These include DYFLO (Franks, 1972), DYNDSI (Patterson and Rozsa, 1980), and CAPES by Chiyoda Corporation (Biegler, 1989).

Two recent papers introduce coordination strategies that significantly advance the state of the art. In the Liu and Brosilow (1987) strategy, a time horizon is selected and the so-called interconnecting variables are assumed. All of the procedures for the unit processes are integrated in parallel to reach the time horizon. Then, the assumed and calculated values of the interconnecting variables are compared to produce error estimates, which are reduced by adjusting all of the interconnecting variables or the time horizon using a Newton-type method. Cook et al. (1987) show the fine performance of this coordinator for a five component (ethane, propene, propane, *i*-butane, and cis-butene-2), 29 stage distillation tower, with PI controllers, and for an atmospheric crude tower with four side strippers.

The second strategy, by Hillestad and Hertzberg (1988), represents the interconnecting variables with polynomials, which are fitted to the integrated solutions at several previous time steps and to the first derivatives at the current time. For each recycle loop, the unit process that receives the tear stream is integrated first over the designated time horizon, T. Its output variables at T, $\underline{y}\{T\}$, are compared with the polynomial estimates, $\underline{y}_p\{T\}$, and the polynomial coefficients are adjusted to eliminate the differences. If necessary, the time horizon is adjusted. Then the next unit process in the flowsheet is integrated, using the adjusted $\underline{y}_p\{t\}$ to represent its input variables. Integration proceeds from unit to unit and is completed for a given time horizon when the prescribed error tolerances are satisfied for the tear variables. For two simple flowsheets (two process units with recycle), the strategy is reported to reduce the computation time by more than 50%, as compared with the simultaneous integration of the DAEs using a common integrator.

In preparing the procedures for dynamic simulation of unit processes, it is often convenient to adapt a well-tested procedure for steady-state analysis. This was accomplished by Boston et al. (1981), who used the GEAR integrator to convert RADFRAC, the ASPEN program for solution of the MESH

equations, to BATCHFRAC for the simulation of batch distillation towers. Subsequently, Prokopakis and Seider (1983b) showed a similar method to prepare a procedure for continuous distillation towers. It is also noteworthy that Ponton (1983) utilized a first-order (Euler) integrator to convert from steady-state to dynamic procedures, but this approach is effective only for processes with simple and slow dynamics.

Simultaneous Equations. As previously discussed, in equation-oriented strategies the equations for each unit process are stored in a library of subproblems. These are collected, along with analytical expressions for the partial derivatives (when available), and integrated simultaneously, usually using a BDF integrator, such as DASSL. In this family, the most well-recognized simulators are SPEEDUP (Perkins and Sargent, 1982; Pantelides, 1988), QUASILIN (Hutchison et al., 1986a,b; Smith and Morton, 1988), DPS (Thambynayagam et al., 1981), DIVA (Holl et al., 1988), and DYNSIM (Gani et al., 1990).

Unfortunately, in these simulators the advantage that design constraints and specifications are easily added is balanced by the disadvantage that the time step for the integration must be sufficiently small to accurately track the most rapidly changing variable. To avoid the unnecessary function and partial derivative evaluations for those ODEs having slow rates of change, strategies are being developed to integrate the slow moving ODEs only when necessary. See, for example, the strategies of Kuru and Westerberg (1985) and Prokopakis and Seider (1983b).

Nonlinear Programming. To our knowledge, optimal control techniques are just beginning to be applied to process flowsheets, with just one PhD Thesis (Renfro, 1986) describing the dynamic optimization of an ammonia synthesis loop. Rather, computing systems are being developed for supervisory control; that is, optimization of the operating variables for steady-state operation. One such system, PROCAM, has been applied for the optimization of a plant for the recovery of nitrogen from natural gas (Fisher et al., 1990). In principle, after new temperature and pressure setpoints are computed, a dynamic simulator can project the performance of the plant in transition and check its controllability about the new steady state. Facilities for supervisory control and dynamic simulation are provided in SPEEDUP.

Nonlinear Predictive Control

Thus far, recurring nonlinearities in the design of chemical processes have been examined, with emphasis on open-loop operation (e.g., multiple steady-state, periodic, and strange attractors) and local and global economic optima. Another important consideration deals with satisfying the design specifications in the face of disturbances; that is, the impact of nonlinearities on process control.

Most chemical processes are regulated with simple PID controllers. While these often successfully reject disturbances and permit operation at unstable steady states (Chang and Chen, 1984), PID controllers often need retuning after small excursions in the operating parameters. The more recently developed model predictive controllers (MPCs), in which a digital computer model of the process resides in the control loop, often provide better disturbance rejections and require far less tuning. Hence, MPCs can be effective in the early stages of process design because they provide a measure of the inherent controllability of the process. That is, in principle and in practice, MPCs provide both better control and a means of assessing the controllability of the process in the early design stages.

The first MPCs, which were developed for linear processes, improved upon PID controllers, but did not replace them in large numbers. Only recently have MPCs been extended for nonlinear processes, with the promise of providing substantially better control. Hence, it is the objective of this section to consider the departures of nonlinear MPCs, their potential for better control, and strategies for designing nonlinear processes that are easily controlled.

To set the stage, the section begins with a brief review of the MPC structure, including MPCs for linear processes. It is noteworthy that Bequette (1990) recently completed a review of nonlinear process control, which expands on many of the developments presented in this section.

MPC structure

In an MPC, the controller objective function, *CO* (defined below), is superimposed on the dynamic model of the process (Eq. 27), with the manipulated inputs selected by the designer. When the process and model are assumed to perform identically ($\underline{x} = \underline{\tilde{x}}$, where $\underline{\tilde{x}}$ are the model outputs), only setpoint changes and the impact of measured disturbances (analogous to start-up problems) can be investigated. Differences between the process and model outputs, that is, process/model mismatch, can arise through the inclusion of incorrect terms and parameters in the model, and unmeasured disturbances. The designer must anticipate the unmeasured disturbances, which the MPC estimates, while performing both servo- and regulatory control.

MPC algorithms solve an NLP that can be formulated as:

$$\underset{\underline{u},\underline{x},\underline{y}}{\text{Minimize}} \quad \text{CO}\{\underline{x},\underline{y},\underline{u},\underline{p}_c\} \tag{80a}$$

$$\text{ST:} \quad \underline{\dot{x}} = \underline{f}\{\underline{x},\underline{y},\underline{u},\underline{p}_c\} \quad \underline{x}\{t=0\} = \underline{x}_0, \quad \underline{y}\{t=0\} = \underline{y}_0, \; \underline{u}\{t=0\} = \underline{u}_0 \tag{80b}$$

$$\underline{h}\{\underline{x},\underline{y},\underline{u},\underline{p}_c\} = 0 \tag{80c}$$

$$\underline{g}_h\{\underline{x},\underline{y},\underline{u},\underline{p}_c\} \geq 0 \tag{80d}$$

$$\underline{u}^L \leq \underline{u} \leq \underline{u}^H \tag{80e}$$

where $\text{CO}\{\underline{u}, \underline{x}, \underline{y}\}$ is the control objective function (defined in Eq. 83a below), $\underline{x}$ and $\underline{y}$ are time dependent vectors of state and algebraic variables (process outputs), $\underline{u}$ are the manipulated inputs, $\underline{p}_c$ are the parameters of the control model, $\underline{g}_h$ (a subset of $\underline{g}$) are the "hard" inequality constraints that cannot be violated during transient operation, and $\underline{u}^H$ and $\underline{u}^L$ are upper and lower bounds on the physical limits of the manipulated inputs.

Linear Processes. The inclusion of a process model in the control loop was first proposed for chemical processes more than ten years ago. Among this new class of control structures were model algorithmic control (MAC) by Richalet et al. (1978), dynamic matrix control (DMC) by Cutler and Ramaker (1979), and the inferential control methodology of Brosilow and Tong

(1978). These single-input/single-output (SISO) algorithms relate the desired output to the manipulated input, through a linear model, and to unmeasured disturbances. They were unified and extended to multiple-input/multiple-output (MIMO) systems in the framework of internal model control (IMC) by Garcia and Morari (1982, 1985a,b). Subsequent algorithms within this class were extended to include linear constraints involving the inputs and outputs, and bounds on the inputs.

For linear systems, $\dot{\underline{x}} = \underline{f}\{\underline{x}, \underline{u}, \underline{p}_c\}$ can be written as:

$$\dot{\underline{x}} = \underline{\underline{A}}\,\underline{x} + \underline{\underline{B}}\,\underline{u} \qquad \underline{x}\{t=0\} = \underline{x}_0 \qquad \underline{u}\{t=0\} = \underline{u}_0 \tag{81}$$

Note that the algebraic variables, $\underline{y}$, have been omitted for simplicity. An explicit solution for $\underline{x}$ in terms of $\underline{u}$ can be found using the state transition matrix or by algebraic manipulation in the Laplace domain. This solution is then converted to a discrete form which is necessary to relate the inputs to the outputs at the discrete sampling instants. The resulting impulse response model is written as a summation of the previous N control actions multiplied by impulse response coefficients:

$$\underline{x}_{k+j} = \sum_{n=1}^{N} \underline{\underline{H}}_n \underline{u}_{k+j-n} \qquad j = 1,2,\ldots \tag{82}$$

where these coefficients, $h_{i\ell n}$, are the responses of output i at future times, $t = nT$, to a time-zero impulse of input ℓ, as shown in Figure 24, k is the index of the current sampling interval, T is the sampling time, and N is the order of the model. The IMC framework of Garcia and Morari (1982) is illustrated in Figure 25 for continuous (Laplace domain) transfer functions. $G\{s\}$, $\tilde{G}\{s\}$, $G_C\{s\}$, and $F\{s\}$ represent the process, model, controller, and filter transfer functions; $x\{s\}$, $\tilde{x}\{s\}$, $x^{SP}\{s\}$, are the process and model outputs and the setpoint value, $d\{s\}$ is the unmeasured disturbance, and $\tilde{d}\{s\}$ is an estimate of $d\{s\}$ plus the effect of process/model mismatch. Garcia and Morari (1982) show the relationship of these transfer functions, in the z domain, to the NLP, rewritten with $\underline{x}$, $\underline{\tilde{x}}$, $\underline{x}^{SP}$, $\underline{u}$, and $\underline{\tilde{d}}$ at the discrete sampling instants:

$$\underset{\underline{u}_k,\ldots,\underline{u}_{k+M-1}}{\text{Minimize}} \sum_{j=1}^{P} [\gamma_j^2 (\underline{x}^{SP}_{k+j} - \underline{x}_{k+j})^T \underline{\underline{C}} (\underline{x}^{SP}_{k+j} - \underline{x}_{k+j}) + \beta_j^2 (\underline{u}_{k+j-1} - \underline{u}_{k+j-2})^T \underline{\underline{D}} (\underline{u}_{k+j-1} - \underline{u}_{k+j-2})] \tag{83a}$$

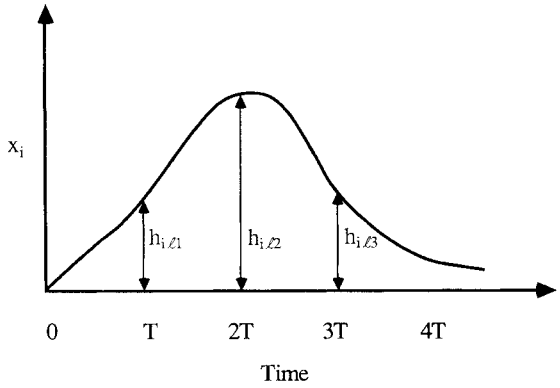


Figure 24. Response to a unit impulse.

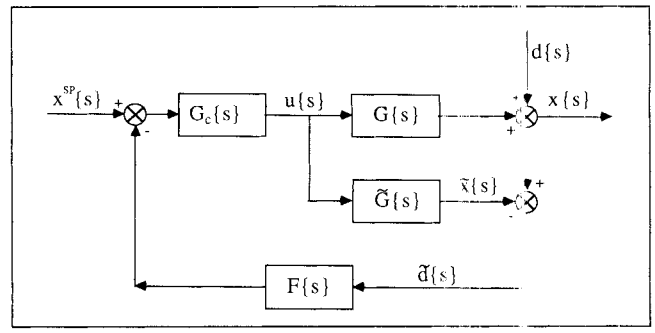


Figure 25. Block diagram for internal model control.

$$\text{ST:} \quad \underline{\tilde{x}}_{k+j} = \sum_{n=1}^{N} \underline{\underline{H}}_n \underline{u}_{k+j-n} + \underline{\tilde{d}}_k \qquad j = 1,\ldots,P \tag{83b}$$

$$\underline{x}\{t=0\} = \underline{x}_k, \; \underline{u}\{t=0\} = \underline{u}_k \tag{83c}$$

$$\underline{u}_{k+M} = \underline{u}_{k+M+1} = \ldots = \underline{u}_{k+P-1} = u_{k+M-1};$$

$$\beta_j = 0 \quad \forall_j > M \tag{83d}$$

where M is the manipulated variable horizon, P is the predicted output horizon, $\underline{c}$ is a vector of n weights on the state variables, $\underline{\underline{C}} = \text{diag}\,[\underline{c}]$, $\underline{d}$ is vector of m weights on the manipulated inputs, and $\underline{\underline{D}} = \text{diag}\,[\underline{d}]$. γ_j and β_j are weighting coefficients that are specific to each sampling instant over the predictive horizon. During the next sampling interval, only $\underline{u}_k$ is implemented. However, the values of $\underline{u}_{k+1}, \ldots, \underline{u}_{k+M-1}$ and $\underline{x}_{k+1}, \ldots, \underline{x}_{k+P}$ are useful in projecting the performance of the controlled system and providing early warnings when the system is approaching process design and operating constraints. Typical variations of the input and output variables, in response to a disturbance, are illustrated over the time horizons in Figure 26.

For unconstrained processes (without Eq. 80c,d,e), Garcia and Morari (1982) provide several theorems to relate the closed-loop stability to both the process and controller design. However, for constrained processes, no such theorems have been established.

Nonlinear Processes. As control theory evolved, research efforts began to address the problem of controlling nonlinear processes. The IMC framework was the basis for the earliest nonlinear control algorithms, including industrial model predictive control by Garcia and Prett (1986) and an algorithm by Economou et al. (1986) using operator theory. Other extensions for nonlinear systems include a Newton-based method by Li and Biegler (1988, 1989), universal dynamic matrix control (UDMC) by Morshedi (1986), collocation-based methods by Renfro et al. (1987) and Patwardhan et al. (1988), a nonlinear inferential algorithm by Parrish and Brosilow (1988), and a multistep nonlinear predictive controller by Brengel and Seider (1989).

Research has been slowed, however, by the inability to directly extend the results of linear control systems to nonlinear systems. Several workers have sought to circumvent the complexities of the nonlinear systems through transformations that convert general classes of nonlinear models to linear models. Recent work, with applications to chemical processes, includes

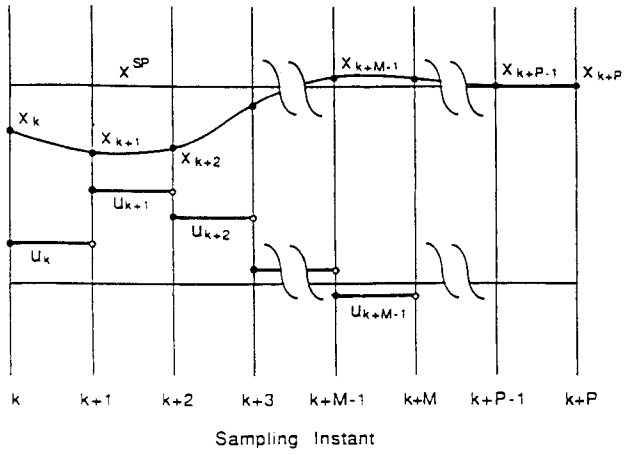


Figure 26. Output horizon *P* and input horizon *M* for model predictive control.
k, index of current sampling instant; *x*, *u*, output and input deviations from initial steady state

contributions by Hoo and Kantor (1985), Kravaris and Chung (1987), Kravaris and Palanki (1988), and Limqueco and Kantor (1988). However, when process constraints are present, unfortunately they retain the nonlinearities and this disadvantage counters the utility of this methodology. A general methodology is needed to transform both the dynamic model and the process constraints (linear and nonlinear) into linear ones.

Consider a linear MPC applied to a nonlinear process, with a linearization (or impulse response model, Eq. 82) prepared at the desired steady state. When large disturbances and setpoint changes are encountered, the linear approximations are usually very poor and the controller responses are degraded significantly. In some cases, the control system may be attracted to an alternate steady state.

While examples of such poor performance to our knowledge have not been published, several successes have been reported with nonlinear MPCs at both stable and unstable steady states. As an example, Brengel and Seider (1989) show the ability of their nonlinear MPC to reject disturbances when operating the fermentation process, Figure 11, at an unstable steady state near the turning point.

These results are important because, as pointed out by Seider et al. (1990), economic optima often lie near or within regions involving hysteresis and periodic or even chaotic behavior (e.g., the fermentation process). These controllers offer the potential to effectively operate near or within these regimes, which are characterized by greater sensitivities to modeling errors (process/model mismatch), disturbances, and changes in setpoints.

Dynamic Resiliency. Of great importance is the ability to describe the dynamic responses of MPCs when there are unknown, or even known, types of process/model mismatch. For this purpose, the eigenvalues and Condition Number of the Jacobian provide good measures of the stability or so-called dynamic resiliency of the MPCs (Morari, 1983). Much work has been done to characterize the dynamic resiliency for unconstrained, linear systems, but always under the assumption that the mismatch *cannot* be reduced. Furthermore, little or no work has been reported for constrained, nonlinear systems. It is our contention, however, that adaptive estimation techniques can and should be applied to reduce the amount of process/model mismatch, thereby increasing both the performance and stability of the MPCs. These techniques, which are beyond the scope of this paper, successfully reduced the process/model mismatch in the fermentation process described above.

With faster work stations, having larger memories, more rigorous process models are being developed that involve fewer parameters. In many cases, much of the process/model mismatch can be eliminated by adjusting these parameters. This is a promising approach for the control of processes with complex nonlinearities, whose models are developed as their designs are optimized, often using pilot plant data.

Coordination of design and control optimizations

Although controllability is important, some would suggest that it be assessed after the flowsheet is configured, when the tradeoffs between controllability and economy are better defined. There are examples (Palazoglu and Arkun, 1987; McAvoy, 1987), however, that illustrate how modifications in the flowsheet can improve its control characteristics. In these cases, and especially for processes that exhibit highly nonlinear behavior, it is desirable to evaluate controllability during design syntheses. Unfortunately, however, the heuristic-based synthesis strategies, which are prevalent in industry, usually do not involve process models and consequently are not well suited for this evaluation.

When complex nonlinearities are present, special care should be taken to avoid process designs that are prone to off-spec production (with economic losses), and safety and environmental complications. To accomplish this, it is desirable to examine the controller performance and reject designs that exhibit poor controllability as early as possible in the design stage.

Algorithmic methods that utilize process models for both design optimization and MPC evaluation have the potential to create more profitable designs, often near or within regimes having complex nonlinearities. In one approach, Brengel and Seider (1991) present a strategy for evaluating the MPC performance as the design optimization proceeds. In a prototype computing system, PRODOC, they simulate several disturbance scenarios and penalize the design objective for poor controllability, which results in decreased profitability due to off-spec production. It should be noted that much work remains to perfect these techniques.

Uncertainty Analysis

As nonlinear predictive controllers are further developed, processes are being designed to operate nearer or within regimes characterized by hysteresis and periodic or even chaotic behavior. Since nonlinear processes are more sensitive to model uncertainties, it is important to check, in the design stage, that they have the ability to operate at various levels of capacity, with different feedstocks, variations in the ambient conditions, and changes in the process parameters (e.g., fouling of the heat exchangers). The ranges of conditions over which steady-state operation is feasible are a measure of the flexibility or static resiliency of the designs. On a smaller time scale, the ranges over which the process with its control system can reject disturbances and move smoothly between setpoints are meas-

ures of the dynamic resiliency of the designs, as discussed briefly in the previous section.

While the importance of flexibility analysis is generally acknowledged, thus far it has been attempted only for small portions of processes, and with significant restrictions. Consequently, there are many unresolved problems, especially in its application for processes with nonconvex feasible regions, which often arise when the inequality constraints contain complex nonlinearities. The methods for resiliency analysis involve a linearization about the desired steady state (Morari, 1983; Palazoglu et al., 1985). Since these methods have not yet been extended for processes with complex nonlinearities, they are not reviewed in this article. Furthermore, as noted in the previous section, parameter estimation techniques can be very effective in eliminating process/model mismatch, and hence the usual assumption of fixed mismatch appears to be too conservative.

In this section, the status of flexibility analysis is reviewed briefly, with emphasis on its limitations for process designs involving nonlinear inequalities.

Flexibility analysis

Grossmann et al. (1983) define two related design tasks for processes with uncertainty. The first is to design for the minimum cost, with the degree of flexibility specified. The second, which encompasses the first and is often preferred, is to design for an optimal degree of flexibility. It requires a multivalued objective in which the flexibility is traded off against the expected cost of the plant.

The general form of the NLP to achieve a minimum cost design under uncertainty is:

$$\underset{\underline{d},\underline{u}}{\text{Minimize}} \quad C\{\underline{d},\underline{u},\underline{x},\underline{p}\} \tag{84a}$$

$$\text{ST:} \quad \underline{h}\{\underline{d},\underline{u},\underline{x},\underline{p}\} = 0 \tag{84b}$$

$$\underline{g}\{\underline{d},\underline{u},\underline{x},\underline{p}\} \geq 0 \tag{84c}$$

$$\underline{p}^L \leq \underline{p} \leq \underline{p}^H \tag{84d}$$

where $\underline{d}$ are the design variables, $\underline{u}$ are the steady-state values of the control variables, $\underline{x}$ are the state variables, $\underline{p}$ are the r uncertain parameters that are expected to vary between $\underline{p}^L$ and $\underline{p}^H$ during operation, C is the cost objective function, $\underline{h}$ are the equalities that comprise the process model, and $\underline{g}$ are the inequality constraints that define the region of feasible operation. When Eq. 84b is solved for $\underline{x}$,

$$\underline{x} = \underline{x}\{\underline{d},\underline{u},\underline{p}\} \tag{85}$$

the region of feasible operation becomes:

$$\underline{g}\{\underline{d},\underline{u},\underline{x},\underline{p}\} = \underline{g}\{\underline{d},\underline{u},\underline{x}\{\underline{d},\underline{u},\underline{p}\},\underline{p}\} \equiv \underline{f}\{\underline{d},\underline{u},\underline{p}\} \geq 0 \tag{86}$$

This feasible region is illustrated in Figure 27 for the special case where the constraints confine a convex set. The region R is centered at the parameters of the nominal design, $\underline{p}^N$, and with $\delta = 1$, expands to $\underline{P}$, which encompasses the lower and upper bounds defined by Eq. 84d. The critical point, $\underline{p}^C$, is the extreme to which R can extend without violating the constraints. When $\delta = 1$ at $\underline{p}^C$, the design is considered to be flexible. Otherwise, δ is a measure of the flexibility, often referred to as the flexibility index. To minimize the cost of a design by adjusting $\underline{d}$, it is necessary to check that the full range of parameters lies in the feasible region and this involves locating $\underline{p}^C$. Alternatively, it is possible to minimize a combined objective function, which involves weighted contributions of the cost and the negative of the flexibility index.

Identification of the critical points, however, is nontrivial. Fortunately, as shown by Swaney and Grossmann (1985a), the NLP, Eq. 84, has the important property that when the constraints are jointly convex in $\underline{d}$ and $\underline{p}$, the critical point lies at one or several of the vertices of the hyperrectangle. For nonlinear processes, however, the feasible region is often nonconvex and this property does not apply. Here, a less stringent condition, proven by Swaney and Grossmann (1985a), is helpful; it requires the constraints to be convex only in the directions parallel to the $\underline{p}$ coordinates. When this restriction applies, the critical points are located within the finite set of vertices of $\underline{P}$. For this search, Swaney and Grossmann (1985b) suggest an implicit enumeration algorithm that requires far fewer eval-

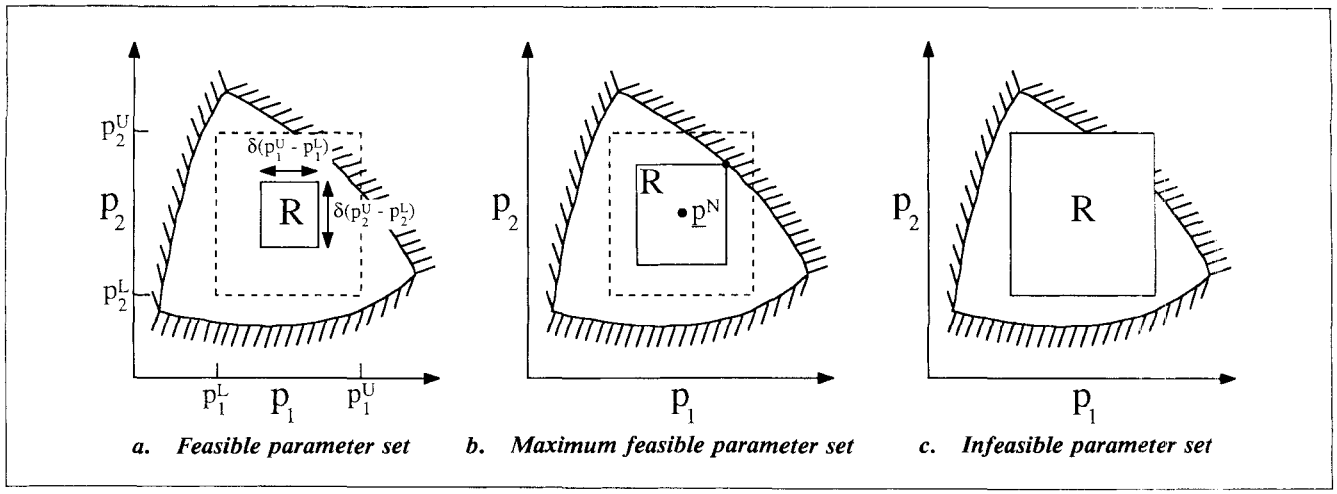


Figure 27. Critical points of inflexibility analysis.

uations than an exhaustive search of all 2^r vertices.

In general, however, the critical points do not lie at vertices of $\underline{P}$ and are more difficult to locate. In one approach, for the synthesis of flexible networks of heat exchangers, Floudas and Grossmann (1987) formulated a MINLP to locate nonvertex critical points. Pistikopoulos and Grossmann (1989a) extended this analysis for the optimal retrofit of designs having a desired flexibility. In a companion paper, these authors (Pistikopoulos and Grossmann, 1989b) generated a trade-off curve of the expected cost as a function of the flexibility which, coupled with an analysis of the expected revenues, provided the optimum level of flexibility for retrofits.

In summary, to assure the flexibility of a design, feasible operation is required for the full range of parameters envisioned by the designer. Work is underway to locate the critical points for nonconvex feasible regions, but much remains to be accomplished to avoid exhaustive checks of the entire feasible region.

Conclusions

This review has concentrated on process nonlinearities and their impact on the simulation and optimization of the designs for process units and flowsheets in both steady and dynamic operation. For processes with complex nonlinearities, especially, it has established the important role of the process model throughout the design process.

There is a rich literature of methodologies for analysis and solution strategies in each of these areas. In this review, emphasis has been placed on the methodologies and strategies that have, or have not, been successful for processes with complex nonlinearities. The sources of the nonlinearities were more clearly defined, and in every area the methodologies and strategies were reviewed with emphasis on their successes, failures, and unresolved issues in the solution of specific design problems.

The singularities that arise when phases coalesce or destabilize at equilibrium are often overlooked when simulating and optimizing process units and flowsheets. This review has drawn attention to the sources of these singularities, showed how they arise in azeotropic and reactive distillations and high pressure separations, and explained the numerical problems that occur in the simulation and optimization of these processes.

The many new approaches for nonlinear analysis in process design are a product of the widely available work stations that are doubling in speed annually. As demonstrated in this article, these are resulting in the preparation of better models at all stages of the design process. These models, in turn, are enhancing our understanding of the chemical processes and creating the need to confront their complex nonlinearities. To conclude this review, it is important to note that in the past, designers often intentionally avoided operation near or within regimes that involve hysteresis and periodic or even chaotic behavior. However, the results of research, in which new tools for nonlinear analysis, optimization, model predictive control, and so on, are being developed, are enabling engineers to prepare more economical designs that operate closer to or within these regimes. Seider et al. (1990) provide many examples of how these methods are contributing to the reduction of overdesign in process engineering.

Acknowledgment

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Acronyms

BDF = backward difference formula
BLPP = bilevel programming problem
BVDP = boundary-value design procedure
CO = controller objective function
DAE = differential/algebraic equations
DMC = dynamic matrix control
F-J = Fritz-John conditions
HBP = Hopf bifurcation point
IMC = internal model control
K-T = Kuhn-Tucker conditions or multiplier
LLE = liquid-liquid equilibrium
LSR = Liapunov-Schmidt reduction method
MAC = model algorithmic control
MESH = material balance, equilibrium, summation of mole fractions, and heat balance equations
MIMO = multiple-input/multiple-output
MINLP = mixed integer nonlinear program
MPC = model predictive control
NLE = nonlinear equation
NLP = nonlinear program
N-R = Newton-Raphson method
OCP = optimal control problem
ODE = ordinary differential equation
PI = proportional-integral control
PID = proportional-integral-derivative control
QP = quadratic program
RCM = residue curve map
RG = reduced gradient method
RMP = reduced master problem
SD = steepest descent method
SISO = single-input/single-output
SMA = sequential modular approach
SQP = successive quadratic programming
UDMC = universal dynamic matrix control
VLE = vapor-liquid equilibrium
VLLE = vapor-liquid-liquid equilibrium

Programs and Sources

Program		Source
ASPEN	advanced system for process engineering	Aspen Tech., Inc.
AUTO	continuation or bifurcation problems in ODEs	E. Doedel, Concordia Univ.
BATCHFRAC	batch distillation	Aspen Tech., Inc.
CAPES	computer-aided process engineering system	Chiyoda
CHEMCAD	steady-state simulation of process flowsheets	COADE, Inc.
CHESS	chemical engineering simulation system	R. L. Motard, Washington Univ.
COPE	steady-state simulation of process flowsheets	Exxon
CSMP	continuous system modeling program	IBM
DASSL	differential/algebraic simulation system language	L. Petzold, Lawrence Livermore Lab.
DASP3	dynamic analysis and simulation package	Aston University, United Kingdom

DERPAR	continuation of equilibrium solutions of ODEs	Kubicek and Marek (1983)
DERPER	continuation of periodic solutions of ODEs	Kubicek and Marek (1983)
DESIGN II	steady-state simulation and optimization of process flowsheets	ChemShare Corp.
DIVA	dynamic simulation of process flowsheets	University of Stuttgart, Holl et al. (1988)
DPS	*dynamic process simulator*	Thambynayagan et al. (1981)
DRIBLOCK	differential/algebraic equation solver	Mack (1986)
DYFLO	dynamic simulator of chemical processes	R. G . E. Franks, Dupont
DYNDSL	dynamic simulator of process flowsheets	Patterson and Rozsa (1980)
DYNSIM	dynamic simulation	Danmarks Tekniske Hojskole; Gani et al. (1990)
EISPACK	package for solving matrix eigenvalue problems	National Energy Software Center, Argonne Nat'l. Lab.
FLOWTRAN	flowsheet translator	Monsanto Co.
GEAR	ODE integrator	C. W. Gear, Univ. of Illinois
HOMPACK	Homotopy package	L. T. Watson, Virginia Polytech.
HYSIM	steady-state simulation of process flowsheets	Hyprotech, Inc.
LIMEX	differential/algebraic equation solver	Deuflhard and Nowak (1987)
LSODE	*ODE integrator (update of* GEAR program)	A. *Hindmarsh*, Lawrence Livermore Lab.
LSODI	integrator for implicit ODEs	A. Hindmarsh, Lawrence Livermore Lab.
MACSYMA	computer algebra system	M.I.T.; Symbolics, Inc.
MATHEMATICA	computer algebra system	Wolfram Research, Inc.
MIMIC	digital simulation language	Control Data Corp.
MINOS	modular in-core nonlinear optimization system	Stanford University
ODEPACK	ordinary differential equation package	A. Hindmarsh, Lawrence Livermore Lab.
OPT	successive quadratic programming system	L. T. Biegler, Carnegie-Mellon Univ.
PACER	process assembly case evaluator routine	P. T. Shannon, Dartmouth College
PEFLOQ	bifurcation analysis of periodic solutions of ODEs	Aluko and Chang (1984)
PITCON	continuation of equilibrium solutions	Rheinboldt and Burkhardt (1983)
PROCAM	process computer-aided manufacturing system	ChemShare Corp.
PROCESS	steady-state simulation and optimization of process flowsheets	Simulation Sciences, Inc.
PRODOC	process design, operations, and control system	University of Pennsylvania
QUASILIN	dynamic simulation of process flowsheets; steady-state optimization	Cambridge University
RADFRAC	multicomponent distillation	Aspen Tech, Inc.
REDUCE	computer algebra system	Stanford University, Univ. of Utah, Rand Corporation
SCOPT	simultaneous convergence and optimization of process flowsheets	L. T. Biegler, Carnegie-Mellon Univ.; Monsanto Co.
SEPSIM	steady-state simulation of separation flowsheets	A. Fredenslund, Danmarks Tekniske Hojsköle
SEQUEL-II	steady-state simulation of process flowsheets	Sun and Stadtherr (1988)
SPEEDUP	dynamic simulation of process flowsheets; steady-state optimization	Imperial College
VE06AD	quadratic program solver	Harwell library

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