Seader's correlation can be expressed as follows:

$$\frac{\text{CPU time for Lee-Edmister's correlation}}{\text{CPU time for Chao-Seader's correlation}} = NC^m$$

CPU means central processor unit, NC is number of components in the system. The power m ranges from 1.43 for a three-component system to 1.56 for a ten-component system. The larger the NC, the larger the m. However, m is not expected to be larger than 2. For practical application, these correlations may be employed for a calculation of a distillation tower. In most of cases, iteration is required. Therefore, computing time consumed by Lee-Edmister's correlation becomes very critical.

In short, Lee-Edmister's correlation may be better for certain ranges given as ranges of data in their appendix. However, computing time required is serious, especially for a multicomponent system with iteration. For most hydrocarbon systems, Chao-Seader's correlation may be adequate for a design purpose.

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Trajectory Optimization Techniques in Chemical Reaction Engineering. II. Comparison of the Methods

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Although the theory and practice of methods for solving two-point boundary-value problems in chemical reaction engineering is quite well developed (*1* to *9*, *11*, *13*), a critical appraisal of these methods along the lines of that in the aerospace context (*10*) is lacking.

For obvious reasons only control vector iteration, boundary value iteration, and quasilinearization (which is really a subset of the first) will be considered here. Most other methods are variations of these three types. Observations, comments, and criticisms of the methods will be largely based on direct experience with them, although some conclusions may also be drawn from the literature.

Following Tapley and Lewallen (*10*) comparison will now be made on the basis of the following criteria:

1. Simplicity of formulation and ease of programming
2. Computer storage requirements
3. Convergence sensitivity
4. Stability
5. Convergence time

RECAPITULATION IN BRIEF

A short review of the methods of Boundary Condition and Control Vector Iteration and Quasilinearization will serve to pinpoint the basic differences in concept between these methods.

In Boundary Condition Iteration (BCI) (*9*) one guesses the missing boundary conditions—for example, the initial values of the adjoint variables—and integrates to the other boundary condition (say, the final adjoint variables) and the actual boundary conditions together with the transversality condition to calculate a new guess of the missing boundary condition.

Control Vector Iteration (CVI) uses the known boundary conditions to integrate from both ends of the interval, and this then constitutes one iteration which permits calculation of $\partial H/\partial u$ (which, according to the necessary condition of Pontryagin's Maximum Principle must be zero at the optimum) to step towards the optimum. In first-variation methods, the control function is corrected by an amount proportional to $\partial H/\partial u$, generally $\propto \partial H/\partial u$. Second-variation methods use a second-order expansion of H around the optimum and integration of additional (Riccati) costate equations (classical second-variation method) or without these Riccati equations (direct second-variation method) to achieve second-order convergence.

Quasilinearization (*4*) is effectively a subset of CVI in that stipulated boundary conditions are used, and successive approximations to the optimal control function are obtained by linearizing state and adjoint equations and solving, using a Newton-Raphson-Kantorovich method in function space. The quasilinearization method used here is that of Lee (*13*).

It is apparent that the foregoing observations are dependent to some extent on the numerical method of integration used. This is especially true of convergence time and stability of integration. The technique used throughout, except where noted, is the predictor-corrector method of Crane and Klopfenstein (*12*), with the Runge-Kutta-Gill method for starting. The problem used as a basis for comparison of the various algorithms is the well-known consecutive reaction system

$$A \rightarrow B \rightarrow C \qquad (1)$$

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in which production of B is to be maximized in a plug-flow tubular reactor by control of the temperature. C is a waste product.

The state equations are

$$f = \frac{dx}{dt} = \begin{bmatrix} -k_1 & 0 \\ k_1 & -k_2 \end{bmatrix} x \qquad x(0) = x_0 \qquad (2)$$

where the state variables x_1 and x_2 denote molar species of A and B respectively.

The control variable appears in the rate constants k_i in Equation (2) in the form

$$ki = k_{i0} \exp(-Ei/RT) \qquad i = 1, 2 \qquad (3)$$

whence it can be seen that the control problem is very highly nonlinear.

The adjoint or costate equations are

$$\frac{d\lambda}{dt} = \begin{bmatrix} k_1 & -k_1 \\ 0 & k_2 \end{bmatrix} \lambda \qquad \lambda(t_f) = \lambda_f \qquad (4)$$

The constants and initial and final conditions are

$$k_{10} = 0.535 \times 10^{11} \text{ min}^{-1} \qquad E_1 = 18 \text{ kcal/mole}$$
$$k_{20} = 0.461 \times 10^{18} \text{ min}^{-1} \qquad E_2 = 30 \text{ kcal/mole} \qquad (5)$$

and

$$t_f = 10 \text{ min}, \quad x_{10} = 0.95 \text{ moles/l.}, \quad x_{20} = 0.05 \text{ moles/l.} \qquad (6)$$

It should be noted that the conclusions drawn in this study are dependent on the nature of this particular problem; therefore, they are not completely general but are merely intended as a guide for the chemical reaction engineer.

SIMPLICITY OF FORMULATION

From the integration standpoint, quasilinearization is theoretically the simplest method since it is only required to integrate in a forward direction. However, the effort required to implement reverse integration for other methods is a minor consideration compared with other difficulties, as explained below.

One must consider the two subclasses of CVI and the three types of BCI methods for discussion purposes. Since only the state and adjoint equations and the derivatives $\partial H/\partial u$ are required for first variation CVI, this is the simplest to formulate. The BCI method of a previous paper (9) is equally facile but may only be used when $\partial H/\partial u = 0$ is explicitly soluble for u as a function of the state and adjoint functions. The other methods require more partial derivatives, and although it becomes difficult to measure precisely the "simplicity of formulation" the GBCI method (9), both second variation CVI methods (11) and Horn's method (9) are all relatively simple as compared with quasilinearization. The use of the latter even for the comparatively simple problem considered in previous papers (9, 11) requires a large number of partial derivatives.

Implementation and programming are easiest for Horn's method, which requires forward integration only of the $n + r$ differential equations. The BCI method requires only reverse integration of $2n$ differential equations together with the use of r algebraic equations for the optimal control. The GBCI method requires reverse integration of $2n + r$ differential equations. These two methods are only slightly more difficult to use than Horn's method.

Quasilinearization and CVI are more or less equal in difficulty of programming while second-variation CVI is more difficult if the algorithm of Padmanabhan and Bankoff (8) is used. For CVI methods as a whole, determination of the parameters $\epsilon^{(j)}$, ϵ_s, and ϵ_r require some a priori definition and while this is also true for BCI methods the choice is less critical there. This is the major drawback of CVI methods. Padmanabhan and Bankoff (8) have indicated that "choice of a suitable contraction factor $\epsilon^{(j)}$ was found to be highly critical ... After several trials a variable $\epsilon^{(j)}$ given by $\epsilon^{(j)} = (j/j + 10)^4$ was found to give fairly rapid convergence. It is apparent that the matter of choosing the right $\epsilon^{(j)}$ is still an art." There is a certain amount of trade-off between ease of programming and convergence rates when using automatic stepsize ($\epsilon^{(j)}$) adjustment as detailed in a previous paper (11) than attempting to fit $\epsilon^{(j)}$ as a function of the iteration number j. The former approach is preferable because of the great saving in human time and effort.

COMPUTER STORAGE REQUIREMENTS

Storage for all the BCI methods will always be negligible compared with that necessary for CVI and quasilinearization. For the data of Lee (13) 2,340 storage locations are required by quasilinearization, even for this simple problem where $n = 2$, $r = 1$ for n homogeneous solutions. Using the suggestion of Kenneth and Taylor (15) this could be reduced to 520 only if the convergence criterion on temperature (which requires particular and homogeneous solutions to compute state and adjoint variables and hence temperature) can be dispensed with. For an integration stepsize of 0.1 the second-variation CVI method requires 1,100 locations compared with 1,700 for the direct second-variation method and only 600 for the first-variation method. However, the major advantage of the CVI methods is integration stability and this facilitates an integration stepsize increase to 0.25 minutes so that storage is reduced to 250, 680, and 150 locations for second-variations, direct second-variations, and first-variation methods respectively. Nevertheless, all the results of this study are for a stepsize of 0.1 minutes, except where otherwise stated. It is, therefore, clear that quasilinearization makes the most severe demands on storage facilities while storage requirements for the CVI methods are moderate.

CONVERGENCE SENSITIVITY

The theory of quasilinearization and of CVI methods requires that the initial approximation be sufficiently close to the solution. This is borne out by the fact that initial approximations $x_1^{(0)} = x_{10}$, $x_2^{(0)} = x_{20}$, $\lambda^{(0)} = \lambda_f$ are not good enough (13, 14) to obtain convergence. Instead the initial control function must be chosen, the initial approximation being found by forward integration of the state equations followed by reverse integration of the adjoint equations. Lapidus and Luus (2, 6) have noted that for CVI the initial approximation must be close enough to the solution for convergence to the guaranteed. No success has hitherto been reported for any initial guess other than the straight line approximations of Fine and Bankoff (1) for the control function:

$$T(t) = 360 - 2t$$

or that of Lee (15)

$$T(t) = \begin{cases} 360 - 5t & 0 \leq t \leq 4 \\ 350 - 4/6t & 4 \leq t \leq 10 \end{cases}$$

The first variation method is uneconomical for wild initial approximations. The fact that an initial control function must be assumed for CVI methods is a drawback.

By contrast, for all BCI methods only point values—the boundary conditions—need be guessed. Theoretically, BCI methods have limitless convergence envelopes, but this has only been verified for Horn's method. Since the major shortcoming of the BCI and GBCI methods is possible instability of numerical integration, this instability becomes evident for initial guesses too far from the solution. The high nonlinearity of the problem considered [that is, that of Lee (*13*)] is partially responsible. For initial guesses of $x_1^{(0)}(t_f) = 0.15$, and $x_2^{(0)}(t_f) = 0.70$ moles/l these methods yielded $x_1^{(0)}(t_0) = 0.445$, $x_2^{(0)}(t_0) = 0.499$ for the data of Lee (*13*). These represent 50% and 900% deviations from the true values. With Horn's method, using guesses as far away as 40°K when applied to the data of Lee (*13*) yielded convergence.

A wider range cannot be investigated since, for the data of Lee (*13*) the rate constants become too large for the computer to handle above 400°K.

Thus for all methods except Horn's method, a sufficiently close initial approximation must be made in order to achieve convergence. The nature of the initial guess varies among the methods but for the choice of point values for the BCI methods, in contrast with the necessity of a choice of a function for the other methods, renders the BCI methods easier to handle from this aspect.

INTEGRATION STABILITY

Integration stability is the most important advantage of CVI methods over BCI methods (excluding Horn's method, which is always stable except when the control vector function is very steep). Integration using the CK method was unstable with CVI methods. Integration with the RKG method, however, is stable. Quasilinearization requires the use of a smaller stepsize in the entrance region in spite of linearization of the state and adjoint system of differential equations.

CONVERGENCE TIME

The class of BCI methods has a distinct advantage over CVI and quasilinearization methods in speed in terms of computation time. Convergence criteria and initial guesses are different but nevertheless a good approximation to the optimum was obtained in only 13.6, 12.2, and 10 seconds for the BCI, GBCI, and Horn's methods respectively, using the CK integration method. Quasilinearization required 86 and 56 seconds for the RKG and CK integration methods respectively. A fair approximation to the optimal policy by first variation CVI methods required 87 and 43 seconds by Equations (7) and (8a) of Fine and Bankoff (*1*) respectively, using the RKG integration method which takes at most one and a half times as long as the CK method. The direct and classical second-variation CVI methods require 38 and 101 seconds of time respectively. Convergence rates for the CVI methods depend on the values of $\epsilon^{(0)}$. The values of $\epsilon^{(0)}$ used here are those which can be found in relatively few trials, perhaps 4.

DISCUSSION

There is no absolutely clear cut choice of method for the chemical reaction engineer when $n \neq mr$. BCI methods are fast but may not always be stable. CVI methods are slower, more difficult to program but perhaps more reliable. Quasilinearization is useful but is most difficult to formulate, requires the most storage, consumes the most computer time, and requires a good initial approximation. Lee (*4*) has shown how to avoid storage problems, but stability is often a difficulty in quasilinearization. Horn's method is applicable when $n = mr$ and if this equality is satisfied it is the obvious choice from every viewpoint except in its requiring several partial derivatives.

It is thus recommended that Horn's method be used whenever applicable. Otherwise BCI or GBCI methods should be tried and, if unstable, CVI methods should be used—preferably the direct second-variation method. A combination of first- and second-variation methods is a good choice here, and is discussed by Fine and Bankoff (*1*) and by Lapidus and Luus (*2*).

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NOTATION

H = Hamiltonian
j = iteration number
m = an integer such that $n/r = m$
n = number of components of state or adjoint vectors
r = number of components of control vector
T = temperature, °K
t = time, minutes
u = control variable column vector (r components)
x = state variable vector (n components)

Greek Letters

ϵ = stepsize, damping factor, convergence criterion
λ = adjoint variable column vector (n components)

Subscripts

c = convergence criterion
f = final
0 = initial
r = convergence criterion
s = stepsize control

Superscripts

(j) = iteration number
t = transposition operator

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