Trajectory Optimization Techniques in Chemical Reaction Engineering:

I. Boundary Condition Iteration Methods

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A new generalization of boundary condition iteration (BCI) methods is developed, based on a suggestion of Denn and Aris. This simplifies to Horn's equation for up to two state equations and to previous boundary iteration methods when $\partial H/\partial \vec{u} = \vec{0}$ is explicitly soluble for $\vec{u}_{opt}$ as a function of the constants, the state and the adjoint variables. The new general method is also applicable when this latter function is unobtainable.

Distinct improvement in the convergence rates of the existing BCI methods has been obtained through the introduction of a correction specific to each state variable.

A convergence procedure for use with Horn's equation is proposed and the resultant algorithm has desirable properties.

The quest for optimal design and control of chemical process plant has attracted much attention in recent years. In particular the optimal control of continuous systems and the concomitant two-point boundary value problem has been the subject of many publications; see Bankoff (*14* to *16*), Lee (*8*), Lapidus (*4*), among others. These studies can be classified into three major methods: control vector iteration, boundary value iteration (BCI), and quasilinearization. It is beyond the scope of the present paper to compare all these methods in depth, and this must be left for a subsequent paper. The object of this paper is not only to compare existing BCI methods but also to introduce a new general algorithm.

The major advantages of boundary iteration are low storage requirements and programming simplicity. Although control signal iteration has been used by most workers, little attention has been given to the BCI method despite these inherent advantages. Denn and Aris (*1*) have formulated an iterative technique for the BCI method but their approach employs the same correction for each state variable. Lapidus and Luus (*4*) have discussed the inadequacies of this latter procedure but as yet an improvement remains to be published. Furthermore the method fails when the equation

$$\frac{\partial H}{\partial \vec{u}} = \vec{0} \tag{1}$$

is not explicitly soluble for closed-form functions of the state and adjoint variables. Denn and Aris (*1*) have thus suggested a technique of avoiding this difficulty, namely, differentiating Equation (1) totally with respect to time and obtaining a differential equation $d\vec{u}/d\tau = \vec{U}(\vec{x}, \vec{u}, \vec{\lambda})$ which can be solved together with the state and adjoint equations.

Horn (2) and Aris (3) have demonstrated that one may eliminate the adjoint variables for $n = 2$. This simple and efficient method is a subset of the general method which will now be derived.

GENERAL ALGORITHM FOR BOUNDARY CONDITION ITERATION

A dynamic system of n state variables $\vec{x}$ and r controls $\vec{u}$ is described by the state equation

$$\frac{d\vec{x}}{d\tau} = \vec{f}(\vec{x}, \vec{u}, \tau) \tag{2}$$

where τ denotes space or chronological time. The necessary condition for an extremum of the objective functional

$$J = \vec{c}^{\,t}\vec{x}(\tau_f) \tag{3}$$

where $\vec{c}$ is an n dimensional constant vector, is that the Hamiltonian

$$H = \vec{\lambda}^{\,t}\vec{f} \tag{4}$$

be extremized, the n dimensional adjoint vector $\vec{\lambda}$ being specified by the equation

$$\frac{d\vec{\lambda}}{d\tau} = -\frac{\partial H}{\partial \vec{x}} = -\vec{\lambda}^{\,t}\left[\frac{\partial \vec{f}^{\,t}}{\partial \vec{x}}\right]^{t} \tag{5}$$

subject to the final conditions

$$\vec{\lambda}(\tau_f) = \left[\frac{\partial J}{\partial \vec{x}}\right]_f = \vec{c} \tag{6}$$

In weak form the extremization of the Hamiltonian reduces to Equation (1).

If Equation (1) is differentiated with respect to time, then

$$\frac{d}{d\tau}\left[\frac{\partial H}{\partial \vec{u}}\right] = \vec{0}$$

or

$$\frac{d}{d\tau}\left[\vec{\lambda}^{\,t}\left[\frac{\partial \vec{f}^{\,t}}{\partial \vec{u}}\right]^{t}\right] = \vec{0}$$

and hence

$$\frac{d\vec{\lambda}^t}{d\tau}\left[\frac{\partial \vec{f}^t}{\partial \vec{u}}\right]^t + \left[\frac{\partial^2 H}{\partial \vec{u}^2}\frac{d\vec{u}}{d\tau}\right]^t + \left[\frac{\partial^2 H}{\partial \vec{u}\,\partial \vec{x}}\frac{d\vec{x}}{d\tau}\right]^t = \vec{0}$$

resulting in

$$\frac{d\vec{u}}{d\tau} = \left[\frac{\partial^2 H}{\partial \vec{u}^2}\right]^{-1}\left[\left[\frac{\partial H}{\partial \vec{x}}\right]^t\left[\frac{\partial \vec{f}^t}{\partial \vec{u}}\right]^t - \vec{f}^t\left[\frac{\partial^2 H}{\partial \vec{x}\,\partial \vec{u}}\right]\right]^t \quad (7)$$

by substitution from Equations (1) and (4); see reference *11*. Equation (7) is the general equation for the entire class of methods.

HORN'S METHOD

Equation (7) reduces to Horn's equation since, if one utilizes Equation (1) for $n = 2$, $r = 1$ to give

$$\frac{\partial H}{\partial \vec{u}} = \frac{\partial H}{\partial u} = \lambda_1\frac{\partial f_1}{\partial u} + \lambda_2\frac{\partial f_2}{\partial u} = 0$$

then

$$\lambda_2 = -\lambda_1\left[\frac{\partial f_1}{\partial u}\right] \Big/ \left[\frac{\partial f_2}{\partial u}\right] = -\lambda_1 Z \qquad \frac{\partial f_2}{\partial u} \neq 0 \quad (8)$$

Differentiating the former equation totally with respect to time, one may obtain with some manipulation

$$\frac{du}{d\tau} = \left[\frac{\partial f_1}{\partial x_2} - \frac{\partial f_2}{\partial x_1}Z^2 + \left[\frac{\partial f_1}{\partial x_1} - \frac{\partial f_2}{\partial x_2}\right]Z - f_1\frac{\partial Z}{\partial x_1} - f_2\frac{\partial Z}{\partial x_2}\right] \Big/ \frac{\partial Z}{\partial u} \quad (9)$$

(Horn's equation) which may also be obtained directly by substitution of Equation (8) in Equation (7). Thus we are able to reduce the system of n $(= 2)$ differential equations and r $(= 1)$ algebraic equations in function space given by $\dfrac{\partial H}{\partial \vec{u}} = \vec{0}$ to $n + r$ differential equations (2) and (9). The initial values $\vec{x}_0$ are known; $\vec{u}_0$ however is not known and may be selected freely. The final condition imposed in Equation (9) is given by

$$\left.\frac{\partial H}{\partial \vec{u}}\right|_{\tau_f} = \vec{0} \quad (10)$$

Since a family of curves is generated according to the assumed initial values of $\vec{u}_0$ it becomes necessary to select the best optimal policy from among the set—a point to be discussed later.

BOUNDARY CONDITION ITERATION METHODS

One method of utilizing Equation (7) involves a procedure similar to that of Denn and Aris (*1*), in which the final state vector $\vec{x}(\tau_f)$ and the final control vector $\vec{u}(\tau_f)$ are assumed. Equations (2), (5), and (7) are then integrated backward in time to the initial state. By successive trial the calculated $\vec{x}(\tau_0)$ is adjusted until a specified degree of convergence is achieved. The reasons for backward integration are discussed by Lapidus and Luus (*4*). The main advantages are increased stability of numerical integration and the greater ease of guessing the final values of the state variables rather than the initial values of the adjoint variables.

Denn and Aris (*1*) have also derived the correction to the assumed guess in the following equation:

$$\vec{x}_f^{(j+1)} - \vec{x}_f^{(j)} = \delta\vec{x}(\tau_f) = \vec{\lambda}^t(\tau_0)\,\delta\vec{x}(\tau_0) = \vec{\lambda}^t(\tau_0)\left(\vec{x}^{(j+1)}(\tau_0) - \vec{x}^{(j)}(\tau_0)\right) \quad (11)$$

where the j superscripts refer to the iteration number. The inherent weakness of this method results from its use of the same correction for each state variable.

A more general approach which appears to work better is to utilize the Euclidean norm $\|\vec{x}\| = \sqrt{\vec{x}^t\vec{x}}$ of the errors

$$e = \|\vec{x}(\tau_0) - \vec{x}_0\| \quad (12)$$

and

$$e_i = (x_i(\tau_0) - x_{i0})^2$$

If a Newton-Raphson type correction

$$\delta x_i(\tau_f) = \epsilon\left[\frac{\partial e_i}{\partial x_i}\right]^{-1} \quad e_i = \epsilon/2\; e_i^{1/2} \quad (i = 1, 2 \ldots n) \quad (13)$$

is used, where x_i denotes $x_i(\tau_0)$, convergence may be quadratic.

In practice the damping factor $0 < \epsilon \leq 1$ is required to ensure suitable convergence properties, but when $\epsilon = 0.05$, as is sometimes the case, the convergence may not be quadratic.

APPLICATION TO REACTOR OPTIMIZATION: HORN'S METHOD

As a means of comparison we will now consider the widely used example of consecutive reactions

$$A \rightarrow B \rightarrow C \quad (14)$$

taking place in a tubular reactor for which plug flow is assumed. It is desired to maximize the conversion of species B by choice of the best temperature profile wherein C is considered to be a waste product. Examples of this reaction system are to be found in pyrolytic reactions (*13*), in the saponification of lactides and esters of polyalcohols (*9*), and other examples cited by Frost and Pearson (*10*).

Since $r = 1$ only one control need be considered—the temperature T. The state equations are

$$\frac{d\vec{x}}{d\tau} = \begin{bmatrix} -k_1 & 0 \\ k_1 & -k_2 \end{bmatrix}\vec{x} = \vec{f} \qquad \vec{x}(0) = \vec{x}_0 \quad (15)$$

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

The specific reaction rate constants are exponential functions of the temperature, given by the equation of Arrhenius

$$k_i = k_{i0}\exp\left(-E_i/RT\right) \quad i = 1, 2 \quad (16)$$

The adjoint of Euler-Lagrange equations are

$$\frac{d\vec{\lambda}}{d\tau} = \begin{bmatrix} k_1 & -k_1 \\ 0 & k_2 \end{bmatrix} \vec{\lambda} \qquad \vec{\lambda}(\tau_f) = \vec{\lambda}_f = \vec{c} \tag{17}$$

Maximization of the Hamiltonian

$$H = \vec{\lambda}^t \vec{f} = -\lambda_1 k_1 x_1 + \lambda_2 (k_1 x_1 - k_2 x_2) \tag{18}$$

determines

$$\vec{c} = [\,0 \;\; 1\,]^t$$

It can be shown that Equation (9) yields

$$\frac{dT}{d\tau} = \frac{-RT^2 k_1 x_1}{E_2 x_2} \tag{19}$$

At this juncture it may be categorically stated that Equation (19) is sufficient for a stationary maximum of $x_2(\tau_f)$ only if $E_2 > E_1$. Note also that Equation (19) holds for the second-order system $2A \rightarrow B \rightarrow C$, assuming constant volume, except that the power of x_1 is 2, as might be expected from the kinetics.

Exploitation of Equation (1) leads to

$$\lambda_1 k_1 x_1 E_1 = \lambda_2 (k_1 x_1 E_1 - k_2 x_2 E_2)$$

and the final conditions $\vec{\lambda}_f = \vec{c}$ give

$$E_1 k_1 x_{1f} = E_2 k_2 x_{2f}$$

Casting this into the form of a Newton-Raphson method, one obtains

$$T_o^{(j+1)} = T_o^{(j)} - \epsilon \left[\frac{F}{\left[\frac{\partial F}{\partial T} \right]} \right] \tag{20}$$

where the following definitions apply:

$$F = 1 - \frac{k_1 E_1 x_{1f}}{(k_2 E_2 x_{2f})}$$

and

$$\frac{\partial F}{\partial T} = \frac{k_1 E_1 x_1 (E_1 - E_2)}{(RT^2 k_2 E_2 x_2)} \tag{21}$$

NUMERICAL RESULTS

In order to compare the foregoing and subsequent methods with existing methods, it will be worthwhile to use the data of Lee (*8*), where the following values are used:

$$k_{10} = 0.535 \times 10^{11} \text{ min.}^{-1} \quad E_1 = 18{,}000 \text{ cal./g.-mole}$$
$$k_{20} = 0.461 \times 10^{18} \text{ min.}^{-1} \quad E_2 = 30{,}000 \text{ cal./g.-mole} \tag{22}$$

and

$$\tau_f = 10 \text{ min.}, \quad x_{10} = 0.95 \text{ mole/liter}, \quad x_{20} = 0.05 \text{ mole/liter} \tag{23a}$$

$$\tau_f = 8 \text{ min.}, \quad x_{10} = 0.53 \text{ mole/liter}, \quad x_{20} = 0.43 \text{ mole/liter} \tag{23b}$$

The numerical method used consisted of a fourth-order Runge-Kutta-Gill integration for starting, followed by a fourth-order Adams-Moulton predictor-corrector, as developed by Crane and Klopfenstein (*12*). The step size used was always 0.1 min.

COMPUTATIONAL SCHEME 1: HORN'S METHOD

The following is an outline of the logic flow diagram:

1. Assume an initial temperature.
2. Integrate Equations (15) and (19) forward in time.
3. Using Equations (20) and (21) at $\tau = \tau_f$, compute a new initial temperature. If this differs from that of the previous iteration by more than a specified amount, return to step 2. X_{2f} may sometimes be less than that of the previous iteration, in which case reduction of ϵ may be required, such as halving it.

Convergence is assured and was generally obtained in less than ten iterations, provided that the temperature is kept below 400°K. (merely as a computational ploy to avoid overflow). The results obtained were virtually identical to those of Lee (*8*). As an example, using an initial guess of 345°K., $\epsilon = 0.05$, and the data of Equations (22) and (23*a*), convergence to $\delta T_0 = 10^{-5}$°K. was obtained in nine iterations (10 sec. of execution time on the IBM 7090 computer used throughout this study), while convergence to graphical indistinguishability was achieved in only five iterations. This compares favorably with Lee (*8*), who obtained convergence to 0.02°K. in seven iterations using quasilinearization with an isothermal initial profile of 340°K. Using the data in Equation (23*a*) convergence to 10^{-5} °K. was obtained in seven iterations (6.3 sec. of execution time) from initial guesses of 345°, 335°, and 330°K.

BOUNDARY CONDITION ITERATION (BCI)

In this case the iteration is on the final state variables, and not on the initial control as in Horn's method. Using Equations (12) and (13), one obtains

$$x_i^{(j+1)}(\tau_f) = x_i^{(j)}(\tau_f) - \epsilon \frac{e_i^{1/2}}{2} \tag{24}$$

where

$$e = \sqrt{e_1 + e_2}$$
$$e_i^{1/2} = x_i(0) - x_{i0}$$

Using Equation (1) one may obtain for the optimal temperature

$$T_{\text{opt}} = \frac{(E_2 - E_1)}{R \ln \left[\frac{x_1 k_{10} E_1 (\lambda_2 - \lambda_1)}{x_2 k_{20} E_2 \lambda_2} \right]} \tag{25}$$

COMPUTATIONAL SCHEME 2: BCI METHOD

The following is the computational procedure for the BCI method:

1. Guess the values of x_{1f} and x_{2f}.
2. Integrate Equations (15) and (17) backward in time, using Equation (25) for the temperature.
3. At $\tau = \tau_0$ compute new final values for x_1 and x_2 using Equation (24). When e is sufficiently small terminate the iteration; otherwise return to step 2. For the data (23*a*) it is found that $\epsilon = 0.05$ gives optimal convergence and whenever $e^{(j+1)} > e^{(j)}$ it may be necessary to halve ϵ.

This scheme should work for virtually any ϵ, $0 \leq \epsilon \leq 1$, since the halving technique will quickly reduce ϵ to a suitable size. Only three trials were required to find the optimum value of $\epsilon^{(0)}$. In view of this there seems to be little point in seeking the best $\epsilon^{(0)}$.

Using $\epsilon^{(0)} = 0.05$, the parameters of (22) and the data of (23*a*) and the initial guesses $x_1^{(0)}(\tau_f) = 0.15$, $x_2^{(0)}(\tau_f) = 0.70$ mole/liter, convergence to $e < 0.001$ mole/liter was obtained in eight iterations (13.6 sec. of execution time). The results were essentially those of Lee (*8*) except that the feed temperature $T(\tau_0)$ differed from that of Lee by 6.2°K. The error in the performance index $x_2(\tau_f)$ was only 2.1×10^{-4} mole/liter.

It should be noted that no convergence could be obtained by using the equation of Denn and Aris, namely, Equation (11) in lieu of Equation (24) and the same initial guesses.

GENERALIZED BOUNDARY CONDITION ITERATION (GBCI)

A variation of the foregoing method would be to use Equation (7) and to integrate the resulting equation

$$\frac{dT}{d\tau} = \frac{-RT^2k_1k_2x_1\lambda_2(E_2 - E_1)}{[k_2E_2^2x_2\lambda_2 - k_1E_1^2x_1(\lambda_2 - \lambda_1)]} \quad (26)$$

together with Equations (15) and (17). The root of $\partial H/\partial T = 0$ is used as a boundary condition for Equation (26). This generally may be found with a Newton-Raphson or bounded Wegstein method (*17, 18*). The former technique will be slower than the latter when the derivative $\partial^2 H/\partial T^2$ is complicated (*17, 18*).

SCHEME 3: GBCI METHOD

The following procedure is to be used:

1. Assume values of $\epsilon^{(0)}$, $x_{1f}^{(0)}$, $x_{2f}^{(0)}$, and $\overline{T}_f^{(0)}$.
2. Using $\overline{T}_f^{(j)}$ as an initial guess, find the zero ($T_f^{(j)}$) of $\partial H/\partial T$ by an above-mentioned method, say the bounded Wegstein method.
3. Integrate Equations (15), (17), and (26) backward with $x_{1f}^{(j)}$, $x_{2f}^{(j)}$, and $T_f^{(j)}$ as boundary conditions.
4. Proceed as in Scheme 2, step 3, except set $\overline{T}_f^{(j)} = T_f^{(j)}$.

Using initial guesses $\epsilon^{(0)} = 0.1$, $x_{1f}^{(0)} = 0.15$, $x_{2f}^{(0)} = 0.70$, and $\overline{T}_f^{(0)} = 340°$K., convergence to $e < 0.001$ was achieved in seven iterations (12.2 sec. of execution time). Here again the results were essentially those of Lee (*8*), $T(\tau_0)$ and x_{2f} differing by 0.45°K. and 0.00038 mole/liter, respectively.

DISCUSSION

In this paper we have considered a highly nonlinear problem and have analyzed its solution using the general class of boundary iteration techniques.

The bases for comparison of the methods are those of speed in terms of computation time, numerical stability, simplicity, and ease of programming.

Computation times required to achieve convergence for Horn's method, BCI, and GBCI were 5.5, 13.6, and 12.2 sec., respectively. The first method cannot be compared with the others in terms of speed because of the differences in the initial guesses.

Horn's method where it is applicable will almost always be stable except when the entrance profile is exceptionally steep, that is, as $X_{20} \rightarrow 0$ in the example. The other methods will be relatively stable. Horn's method seems to be rarely divergent. The convergence interval for the other methods is uncertain because of instability when the initial guess is too far from the solution.

For complicated state equations the derivation of the differential equations for the control vector from Equation (7) may be quite laborious. There is little to be gained from simplification of these equations.

Boundary iteration methods, however, are comparatively simple to use in that the iteration is not being undertaken in function space as is the case with control vector iteration, but merely on boundary values.

Boundary iteration methods require storage for only the n values of the initial state variables at the previous iteration, in strong contrast to the stringent requirements of other methods. Since integration in only one direction is necessary, programming is simple. Also it is not required to call from storage values of the state and adjoint functions at the previous iteration.

Thus the desirability of eliminating the adjoint variables in Horn's method is clearly motivated by the ease of programming (readily performed on a digital-analog simulator), the rapidity of convergence, and the absence of numerical instability.

In larger scale problems one wishes to retain as many desirable features (enumerated above) of Horn's method as possible, but because one can no longer eliminate the adjoint equations one is forced to integrate backward, as dictated by stability. One must also sacrifice some of the simplicity of the iteration philosophy. Lapidus and Luus (*4*) have called the boundary iteration method the approximation-to-the-problem method and have discussed its shortcomings.

As will be discussed in a subsequent paper, the matter of finding a suitable ϵ for boundary iteration methods is a much easier and less costly task than for control iteration methods [compare Padmanabhan and Bankoff (*16*), who find that ϵ should be a function of the iteration number j].

The simplicity of BCI methods compared with alternative methods such as control iteration and quasilinearization is also a feature of the new GBCI approach. The latter converges more closely to the true solution than BCI methods. Horn's method requires the integration of $n + r$ differential equations, compared to $2n + r$ for GBCI and $2n$ differential equations plus r algebraic equations for BCI. It can thus be expected that Horn's method will be quicker in terms of computation time.

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NOTATION

$\vec{c}$ = column vector of constants as defined by Equations (3) and (6)
e = error as defined by Equation (12)
E = activation energy, cal./mole^{-1}
$\vec{f}$ = column vector of derivatives as defined by Equation (2)
F = function as defined by Equation (21)
H = Hamiltonian as defined by Equations (4) and (18)
J = performance index as defined by Equation (3)
k = specific reaction rate constant
k_{i0} = constant as defined by Equation (16)
n = number of state variables or equations
r = number of control variables
R = gas constant, cal./(deg.$^{-1}$)(mole^{-1})
T = temperature
$\vec{u}$ = control vector
$\vec{U}$ = vector of derivatives of controls u
$\vec{x}$ = vector of state variables or concentrations
Z = function as defined by Equation (8)

Greek Letters

δ = variation or perturbation operator
ϵ = damping factor
$\vec{\lambda}$ = vector of adjoint variables

τ = space time

Subscripts

f = final conditions
i = component of vector
o = initial conditions
opt = optimum

Superscripts

j = iteration number
t = transposition operator
$—$ = rough estimate
(0) = initial estimate

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Liquid Bridges Between Cylinders, in a Torus, and Between Spheres

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The stability of a capillary liquid bridge of given volume between two small, solid, equal, separated spheres is investigated by formulating and treating a minimum energy problem in the calculus of variations and by experiment. A conjecture is made that in the case of two solutions one and only one is minimizing, and that the case of one solution represents the limiting stable bridge. This theory agrees accurately with our stability experiments. Furthermore, it is possible to predict the cohesive force. For the case of spheres in contact, the theory presented here is in agreement with some experimental work and also with the theory of Fisher and calculations of cohesive force based on Melrose and Wallick's solution to the bridge problem. For the case of separated spheres, the agreement with the only available experimental data is excellent except for close separations.

Recently there has been a revival of interest in the classical problems (*4, 17*) concerning the configuration of a mass of liquid which bridges a gap between solid surfaces, being supported by capillary attraction. These liquid bridges are concepts in theories of oil recovery from porous media, adsorption hysteresis in porous adsorbents (*7*), capillary condensation (*13*), particle sedimentation (*18*), soil properties (*10*), and space exploration. At the present time very few exact solutions to liquid bridge problems have been obtained; for example, the cylinder between flat plates (*1*).

One system which has received considerable attention is that of two solid spheres, either in contact or slightly separated with a liquid bridge held between them by capillary attraction, under conditions where gravitational forces may be ignored. The force required to hold the spheres apart has been measured by Mason and Clark (*13*) as a function of separation, from contact until breakage of the liquid bridge. When the separation of the spheres is increased slowly, the meniscus displaces until a certain critical bridge configuration is attained, at which stage the bridge becomes unstable and snaps.

The neck diameter of this critical bridge is unquestion-

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