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A Coordinate-Transformation Method for the Numerical Solution of Nonlinear Minimum-Time Control Problems

A new method is presented for the numerical solution of nonlinear minimum-time control problems where at least one of the state variables is monotone. A coordinate transformation converts the problem with fixed end point and free end time to one of free end point and fixed end time. The transformed problem can be solved efficiently by the use of the gradient method with penalty functions to force the system to achieve target values of state variables. Application of the method is illustrated by the synthesis of a minimum-time temperature path for the thermally initiated bulk polymerization of styrene.

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SCOPE

In the optimization of chemical processes, one is often interested in finding the minimum-time control which takes the system from a given initial state to a desired end state in the minimum time under a set of constraints. For linear systems, methods of solution are available, and the minimum-time control is usually of the bang-bang type, in which the controls assume either their maximum or minimum values. For chemical process systems described by nonlinear models there is no general method of solution.

The method proposed herein may be applied to any nonlinear system in which at least one of the state variables is monotone. It converts the original fixed-end-point, free-end-time problem to a free-end-point, fixed-end-time problem through a coordinate transformation. The method of steepest descent of the Hamiltonian may be used to obtain a numerical solution; a penalty function technique forces the system to achieve target values of the state variables at the end of the interval.

The method is illustrated to calculate the minimum-time temperature path for the thermally initiated bulk polymerization of styrene. It is easy to implement with a computational algorithm and is reliable in giving convergent solutions. The method provides a useful tool for understanding the nature of optimal processes.

CONCLUSIONS AND SIGNIFICANCE

The method described herein may be used to determine the optimal operation of a batch process or the best way of changing a continuous process from one steady state to another. The problem is to find the variation in one or more control variables that will force the system from its initial state to a specified final state in the minimum time. For systems described by nonlinear dynamic models, there is no general method of solving for the minimum time control. If any of the dependent variables, such as the conversion of reactant in a chemical reactor, is monotone (that is, its rate of change does not change sign), a powerful numerical method described in this paper can be used to solve the problem. The method is illustrated to find the temperature path for the bulk polymerization of styrene that results in specified number-average and weight-average molecular weights at 80% conversion with minimum reaction time. This is one of the few successful applications of optimal control to a practical problem of industrial importance in the chemical industry.

STATEMENT OF THE PROBLEM

Consider an n^{th} order dynamic system represented by a set of ordinary differential equations

$$\dot{\mathbf{x}}(t) = \mathbf{f}[\mathbf{x}, \mathbf{u}(t)] \qquad (1)$$

where $\mathbf{x}$ is the n vector of state variables $(x_1, x_2, \ldots x_n)$, and $\mathbf{u}$ is the m vector of control functions $[u_1(t), u_2(t), \ldots u_m(t)]$. The minimum-time control problem is to find values of the control functions $u_j(t)$ which take the system from a given initial state

$$\mathbf{x}(t_o) = \mathbf{x}_o \qquad (2)$$

to a desired end state

$$\mathbf{x}(t_f) = \mathbf{x}_f \qquad (3)$$

in a minimum length of time, while the control functions are constrained between lower and upper limits:

$$\mathbf{u}_{\min} \leq \mathbf{u}(t) \leq \mathbf{u}_{\max} \qquad (4)$$

We assume that the system is controllable, that is, that there is at least one set of control functions, within the constraints, which can take the system to the desired end point in a finite time. We assume also that there exists a unique minimum-time control $\mathbf{u}^*(t)$.

The minimum-time control problem is referred to as a fixed-end-point, free-end-time problem because all of the state variables are specified at the end of the interval, but the length of the interval is unspecified and is, in fact, to be minimized by an optimal choice of the control functions $\mathbf{u}(t)$.

NECESSARY CONDITIONS

According to Pontryagin's maximum principle (Pontryagin, et al., 1962), the minimum-time control $\mathbf{u}^*(t)$ satisfies the following necessary conditions. First, the Hamiltonian function is defined by

$$H(\mathbf{x}, \mathbf{p}, \mathbf{u}) = 1 + \mathbf{p} \cdot \mathbf{f} \qquad (5)$$

where $\mathbf{p}$ is the n vector of costate variables which, along the minimum-time path, satisfies the costate differential equation

$$\dot{\mathbf{p}}^*(t) = -\frac{\partial H}{\partial \mathbf{x}}(\mathbf{x}^*, \mathbf{p}^*, \mathbf{u}^*) \qquad (6)$$

where $\mathbf{x}^*$ is the optimal state path which satisfies Equation (1) with the minimum-time control $\mathbf{u}^*$. Along the optimal state path, the Hamiltonian function H has an absolute minimum value with respect to $\mathbf{u}$ as constrained by (4); that is

$$H(\mathbf{x}^*, \mathbf{p}^*, \mathbf{u}^*) \leq H(\mathbf{x}^*, \mathbf{p}^*, \mathbf{u}) \qquad (7)$$

Furthermore, for the minimum-time control, it is necessary that

$$H(\mathbf{x}^*, \mathbf{p}^*, \mathbf{u}^*) = 0 \qquad (8)$$

To solve the minimum-time control problem, one must find a set of optimal control functions $\mathbf{u}^*(t)$ and costate variables $\mathbf{p}^*(t)$ such that Equations (1) to (8) are satisfied. In most practical problems associated with chemical processes, obtaining solutions which satisfy the necessary conditions is a formidable task.

METHODS OF SOLUTION

For linear systems, methods of solution to the minimum-time control problems are well known (See, for example, Neustadt, 1960; Eaton, 1962; Knudsen, 1964; Athans and Falb, 1966.) In most linear systems, the minimum-time control is of the bang-bang type, in which the control functions are at their upper or lower bounds. The solution procedure in this case consists of establishing the points where the controls are switched from one extreme to the other so that the Hamiltonian is minimized.

Some nonlinear systems call for bang-bang controls as the solution to the minimum-time control problem. In a single exothermic reaction, for example, the minimum-time temperature path is simply the highest temperature allowable. For many nonlinear systems, as demonstrated by the example in this paper, the minimum-time control is not of the bang-bang type. If none of the control functions lies at the upper or lower bound along the optimal path, the necessary condition of Equation (7) requires that

$$\frac{\partial H}{\partial \mathbf{u}}(\mathbf{x}^*, \mathbf{p}^*, \mathbf{u}^*) = 0 \qquad (9)$$

$$\frac{\partial^2 H}{\partial \mathbf{u}^2}(\mathbf{x}^*, \mathbf{p}^*, \mathbf{u}^*) : \text{positive definite} \qquad (10)$$

If Equation (9) yields an explicit expression of $\mathbf{u}^*$ in terms of $\mathbf{x}^*$ and $\mathbf{p}^*$, then $\mathbf{u}^*$ can be eliminated from Equations (1) and (6) and an algorithm based upon Newton's method (Athans, 1968) can be applied iteratively to establish $\mathbf{x}^*(t)$ and $\mathbf{p}^*(t)$ which satisfy (9). When nonlinearity of the system equations does not allow this, however, the Athans algorithm cannot be applied. For such nonlinear systems, there is no method, known to the authors, for finding the minimum-time controls. It is for such nonlinear systems that we propose a new numerical method of iterative solution for the minimum-time control.

COORDINATE-TRANSFORMATION METHOD

A powerful numerical technique exists for solving free-end-point, fixed-end-time problems based upon the gradient method (Athans, 1968). This technique, referred to as the "Method of Steepest Descent of the Hamiltonian," is described in Appendix A. The penalty function technique (Kelley, 1962; Bryson and Denham, 1964; Lele and Jacobson, 1969; Balakrishnan, 1968; Fiaco and McCormick, 1967) can be used to force state variables to specified values at the end of the interval.

The coordinate transformation proposed herein converts the minimum-time control problem to an equivalent free-end-point, fixed-end-time problem. It is applicable to systems where at least one state variable is monotone; that is, its time derivative does not change sign during the time interval of interest. In chemical reactors the conversion of a reactant is often a monotone variable.

First, the state variable vector

$$\mathbf{x} = (x_1, x_2, \ldots x_n) \qquad (11)$$

is rearranged, if necessary, such that x_1 is the monotone state variable which will be used as the new independent variable. We assume that the problem has been reformulated, if necessary, so that x_1 and x_1 are both positive. We then make the coordinate transformation:

$$\tau \leftarrow x_1, \quad y_1 \leftarrow t, \quad y_i \leftarrow x_i \quad (i > 1) \qquad (12)$$

As a result, we have the system equation

$$\dot{y}(\tau) = dy/d\tau = \mathbf{F}(\mathbf{y}, \mathbf{u}, \tau) \qquad (13)$$

where

$$F_1 = 1/f_1, \quad F_i = f_i/f_1 \quad (i > 1) \qquad (14)$$

The initial and terminal conditions are

$$y_1(\tau_o) = t_o, \quad y_i(\tau_o) = x_{i_o} \quad (i > 1) \qquad (15)$$

$$y_1(\tau_f) = \text{free}, \quad y_i(\tau_f) = x_{if} \quad (i > 1) \qquad (16)$$

$$\tau_o = x_{1_o}, \quad \tau_f = x_{1f} \quad (\text{fixed}) \qquad (17)$$

We now convert the original fixed-end-point, free-end-time, minimum-time control problem to a free-end-point, fixed-end-time, terminal penalty minimization problem posed as follows. Given a set of system equations

$$\dot{\mathbf{y}}(\tau) = \mathbf{F}(\mathbf{y}, \mathbf{u}, \tau) \qquad (18)$$

with

$$\mathbf{y}(\tau_o) = \mathbf{y}_o, \quad \mathbf{y}(\tau_f) : \text{free}, \quad \tau_f : \text{fixed}$$

establish the optimal control $\mathbf{u}^*(\tau)$ $[\mathbf{u}_{\min} \leq \mathbf{u}^*(\tau) \leq \mathbf{u}_{\max}]$ which minimizes the terminal penalty function

$$J = y_1^2(\tau_f) + \gamma_k \sum_{i=2}^{n} w_i[y_i(\tau_f) - x_{if}]^2 \qquad (19)$$

A sequence of problems is solved with values of γ_k progressively increasing as $k = 0, 1, \ldots$. The values of $y_i(\tau_f)$ converge to x_{if} while $y_1(\tau_f)$ (the real terminal time) is minimized. In cases where the control variables satisfy the conditions which were investigated by Lele and Jacobson (1969), convergence of the iterative solution to the final minimum-time control is better assured.

The iterative solution to the new optimal control problem can be obtained efficiently by application of the gradient algorithm. When a convergent solution is obtained with a reasonably large value of γ_k, the optimal state path can be transformed back to the minimum-time state path by use of Equation (12).

Thus, the coordinate-transformation method requires that at least one of the state variables in the original system equation be monotone with respect to time. But, once the equations are transformed, application of the penalty function technique in combination with the gradient method enables one to obtain a solution easily and efficiently.

FORMULATION OF THE EXAMPLE PROBLEM FOR STYRENE POLYMERIZATION IN BULK

We will demonstrate the application of the method to determine the minimum-time temperature path for thermally initiated bulk polymerization of styrene. The process is widely used in industry for the production of general purpose polystyrene. The problem is to establish the reactant temperature path which gives a desired conversion of monomer to polymer with desired end values of the number-average and weight-average chain lengths in a minimum time. In a batch process, this temperature path would be the time change of the reactant temperature in the reactor, and in a continuous process, it would be the sequence of temperature which the reactant is to follow in its flow through a continuous reactor.

When the state of system is represented by the monomer weight fraction m, number-average chain length $\bar{x}_n$, and weight-average chain length x_w, the system dynamics is represented by the following three equations for the industrially important temperature range of 100° to 200°C (Kwon, 1970):

$$\frac{dm}{dt} = f_m = -\frac{M_m}{\rho} k_M [M_e]^2 \qquad (20)$$

$$\frac{d\bar{x}_n}{dt} = f_n = \frac{f_m}{W_b + (1 - m)}\left[\bar{x}_n\left(\frac{\bar{x}_n}{\bar{x}_n{}^0} - 1\right)\right] \qquad (21)$$

$$\frac{d\bar{x}_w}{dt} = f_w = \frac{f_m}{W_b + (1 - m)}[x_w - \bar{x}_w{}^0] \qquad (22)$$

with

$$m(t_o) = m_o; \quad \bar{x}_n(t_o) = \bar{x}_{n_o}; \quad \bar{x}_w(t_o) = \bar{x}_{w_o} \qquad (23)$$

$$m(t_f) = m_f; \quad \bar{x}_n(t_f) = \bar{x}_{nf}; \quad \bar{x}_w(t_f) = \bar{x}_{wf} \qquad (24)$$

W_b is the amount of base polymer, which is an imaginary amount of polymer with the average chain lengths of $\bar{x}_{nf}$ and $\bar{x}_{wf}$ assumed to exist initially in the system. This quantity is introduced to avoid indeterminate values of f_n and f_w at $m = 1$. Derivations of Equations (21) and (22) are based on a continuous blending model (Kwon and Evans, 1973).

The reactant density changes considerably during the reaction as a function of monomer conversion and the reaction temperature; it is approximated by

$$\rho = \frac{1}{\dfrac{m}{r_1 + r_2 T_c} + \dfrac{1-m}{r_3 + r_4 T_c}} \qquad (25)$$

The overall polymerization rate constant is an Arrhenius function of temperature

$$k_M = A_M \exp\left(-E_M/RT\right) \qquad (26)$$

The effective monomer concentration is represented in terms of monomer activity in the polymer-monomer solution:

$$[M_e] = [M_o]\, a \qquad (27)$$

where $[M_o]$ is the molar concentration of pure monomer at the current temperature, and a is the monomer activity which is approximated by the Flory equation (Flory, 1953):

$$\ln a = \ln m + (1 - m) + \chi(1 - m)^2 \qquad (28)$$

Values of $\bar{x}_n^0$ and $\bar{x}_w^0$ are approximated as the function of reaction temperature as follows (Kwon, 1970):

$$\bar{x}_w^0 = A_w \exp\left(B/T\right) \qquad (29)$$

$$\bar{x}_n^0 = \bar{x}_w^0/2 \qquad (30)$$

Now, the problem is to find $T(t)$ which takes the system from the given initial state $[m_o, x_{n_o}, x_{w_o}]$ to the desired fixed end point $[m_f, \bar{x}_{nf}, \bar{x}_{wf}]$ in a minimum time. The temperature path is constrained to a range bounded by the lowest and highest temperatures allowed; that is,

$$T_{\min} \leqq T(t) \leqq T_{\max} \qquad (31)$$

Values of the key parameters related to the system equations are shown in Appendix B. For this system, it has been shown (Kwon, 1970) that the system is controllable if the maximum allowable temperature $T_{\max}$ and the minimum allowable temperature $T_{\min}$ are such that $T_{\min} \leqq T_L \leqq T_H \leqq T_{\max}$, where T_H and T_L are determinate limits dependent on the values of $\bar{x}_{nf}$ and $\bar{x}_{wf}$.

If it is not necessary to satisfy the final conditions of the two average chain lengths, the minimum-time temperature path would be the maximum allowable temperature, obviously. Because of the constraints on final chain lengths, however, the maximum allowable temperature can not be used freely. And, as there are many possible temperature paths which will take the system to the desired end point, we seek to find the one which will finish the reaction in a minimum length of time.

The incentive for establishing a minimum-time temperature path for this process stems from the fact that, in view of the large volumes of production involved in industry, even a small gain in reaction time could significantly reduce the production cost. The tower process (Smith, 1964), for example, requires about 70 hours of residence time to achieve 35 percent conversion from monomer. Reduction of this residence time by a few percent (5 percent, for instance, corresponds to 3.5 hours) would result in a considerable savings of the equipment and operating costs.

The state variables are scaled so that their numerical magnitudes at the terminal state are of the same order:

$$x_1 = 1 - m, \quad x_2 = \bar{x}_n/\bar{x}_{nf}, \quad x_3 = \bar{x}_w/\bar{x}_{wf} \qquad (32)$$

A dimensionless time is defined as

$$t^* = t/\tilde{t} \qquad (33)$$

where $\tilde{t}$ is defined as

$$\tilde{t} = -1/f_m(m = 1, T = T_{\text{ref}}) \qquad (34)$$

with the reference temperature T_{ref} given by the relation

$$\bar{x}_{wf} = A_w \exp\left(B/T_{\text{ref}}\right) \qquad (35)$$

This scale factor for time makes the minimum time of order unity.

With the scaled state variables, Equations (20) to (22) can be written as

$$\begin{aligned} \dot{x}_1(t^*) = f_1 = C_1 \left[\frac{1 - x_1}{r_1 + r_2 T_c} + \frac{x_1}{r_3 + r_4 T_c}\right] \\ \cdot \exp\left(-E_M/T\right) \cdot (r_1 + r_2 T_c)^2 \\ \cdot \exp\left[2(\ln(1 - x_1) + x_1 + \chi x_1^2)\right] \end{aligned} \qquad (36)$$

$$\dot{x}_2(t^*) = f_2 = \frac{f_1 x_2}{W_b + x_1}\left[1 - C_2 x_2 \exp\left(-B/T\right)\right. \qquad (37)$$

$$\dot{x}_3(t^*) = f_3 = \frac{f_1}{W_b + x_1}\left[C_3 \exp(B/T) - x_3\right] \qquad (38)$$

where C_1, C_2, and C_3 are constants. A dimensionless temperature is defined by

$$u = (T - T_b)/\tilde{T} \qquad (39)$$

The system equations are then in the form

$$\dot{\mathbf{x}}(t^*) = \mathbf{f}(\mathbf{x}, u) \qquad (40)$$

with

$$\mathbf{x}(0) = \mathbf{x}_o, \quad \mathbf{x}(t_f^*) = \mathbf{x}_f \qquad (41)$$

Let us consider, for example, polymerization of pure monomer to an 80 percent conversion with $\bar{x}_{nf} = 700$ and $\bar{x}_{wf} = 1\,500$. For the initial conditions of $\bar{x}_n$ and $\bar{x}_w$, we assume that W_b weight parts of polymer with $\bar{x}_n = 700$ and $\bar{x}_w = 1\,500$ are initially present in addition to the monomer and that the newly formed polymer is blended into this polymer. Then the initial and final conditions are

$$\mathbf{x}_o = \begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix} \quad \mathbf{x}_f = \begin{bmatrix} 0.8 \\ 1 \\ 1 \end{bmatrix} \qquad (42)$$

SOLUTION OF THE EXAMPLE PROBLEM

To apply the coordinate-transformation method, we make the coordinate transformation

$$\tau \leftarrow x_1, \quad y_1 \leftarrow t^*, \quad y_2 \leftarrow x_2, \quad y_3 \leftarrow x_3 \qquad (43)$$

The transformed equations are

$$\dot{\mathbf{y}}(\tau) = \mathbf{F}(\mathbf{y}, u, \tau) = \begin{bmatrix} 1/f_1 \\ f_2/f_1 \\ f_3/f_1 \end{bmatrix} \qquad (44)$$

For the new system equations, the initial and terminal conditions are

$$\begin{aligned} \mathbf{y}(0) &= \begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix} \qquad && \mathbf{y}_f : \text{free} \\ \tau_o &= 0 && \tau_f = 0.8 \text{ (fixed)} \end{aligned} \qquad (45)$$

and the terminal penalty function to be minimized is

$$J = y_{1f}^2 + \gamma_k\left[(y_{2f} - x_{2f})^2 + (y_{3f} - x_{3f})^2\right] \qquad (46)$$

with weighting coefficients of unity applied to each variable.

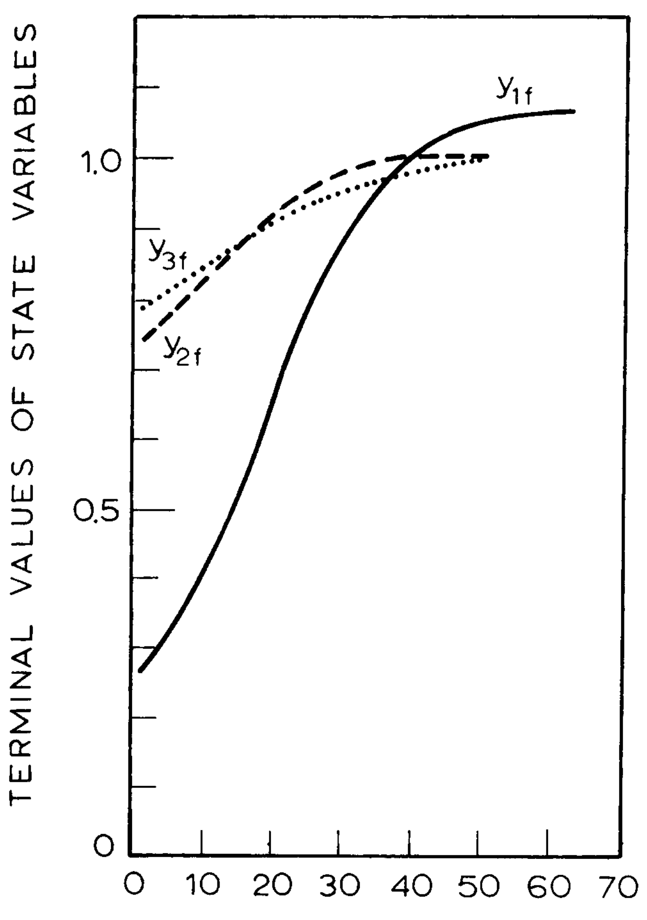

Fig. 1. Values of terminal state variables as functions of iteration number with penalty coefficients varied according to Equations (47) and (48).

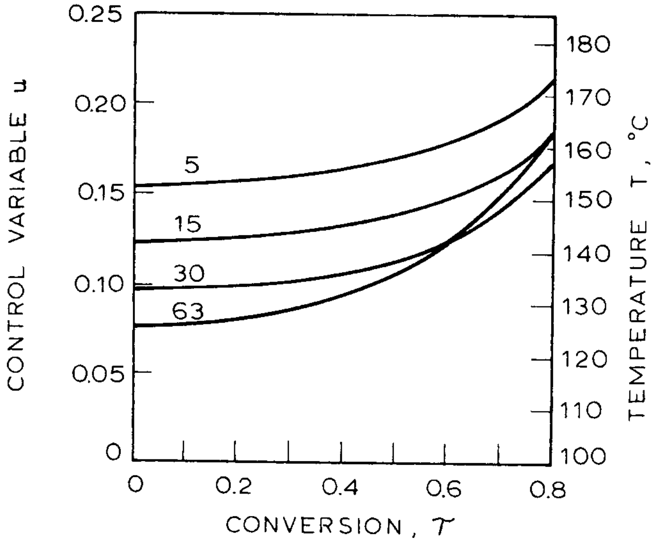

Fig. 2. Control variable (temperature) as a function of the independent variable (conversion) at various iterations.

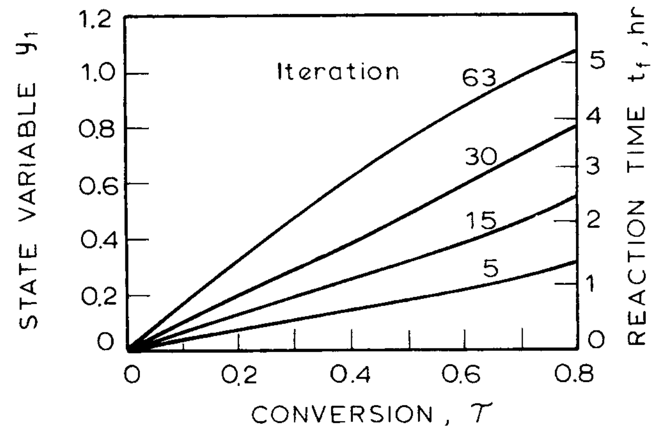

Fig. 3. Reaction time as a function of conversion at various iterations.

The iterative solution of the minimum-time temperature path is obtained as follows:

1. Assume an initial temperature path, $u(\tau)$ for $0 \leq \tau \leq \tau_f$. A constant value of 133°C was used initially which results in the desired end value of weight-average molecular weight.

2. Set the initial value of γ_1 to be a relatively small value ($\gamma_1 < 1.0$).

3. Increase the value of γ_k at each iteration and apply the gradient algorithm to minimize J (see Appendix A).

In the first trial, γ_1 was first set to 0.77 and was increased exponentially by the formula

$$\gamma_k = 0.77\,\alpha^{k-1} \tag{47}$$

$$\alpha = (10^4/0.77)^{1/60} \tag{48}$$

for iteration number $k \leq 60$ and $\alpha = 10^4$ for $k > 60$. The results are summarized in Figures 1 to 6.

Figure 1 shows convergence of the terminal state to the final one. Figure 2 shows the sequence of temperature paths converging to the minimum-time path. Figures 3 to 5 show the state variables as functions of iteration numbers.

The minimum-time temperature path shows a gradual rise of the polymerization temperature with the progress of conversion. This is the result of a compromise between the decrease of polymerization rate with the progress of conversion and the decrease of average molecular weights of the polymer formed with the increase of temperature. The minimum-time temperature path thus obtained is identical to that obtained by a nonlinear programming technique (Kwon et al., 1970).

Whether the established minimum-time state path satisfies the necessary conditions of Equations (6) to (10) was tested as follows: (1) determine, by trial and error, the terminal costate $\mathbf{p}(t_f)$; (2) integrate Equation (6), backward in time, to establish $\mathbf{p}(t)$; (3) compute H, $\partial H/\partial u$, and $\partial^2 H/\partial u^2$ and examine the values. When tested by this procedure, the minimum-time path established in this example satisfied the necessary conditions with a reasonable numerical accuracy. This guarantees that at least a local optimum was found.

The minimum time for 80% conversion from monomer to obtain a polymer of $\bar{x}_{nf} = 700$ and $\bar{x}_{wf} = 1\,500$ is about 5.2 hr. This compares very favorably with the 70 hr. required for 35% conversion in the tower process mentioned earlier. This result should justify further studies to see if realization of the minimum-time temperature path is practicable in industrial processes for styrene polymerization.

RATE OF THE STEPWISE INCREASE OF PENALTY COEFFICIENT γ_k

The rate of convergence to the solution depends on the manner of increasing the penalty coefficient γ_k. To find the effect of a faster rate of increasing γ_k, another solution was obtained with α of Equation (48) set to

$$\alpha = (10^4/0.77)^{1/10} \tag{49}$$

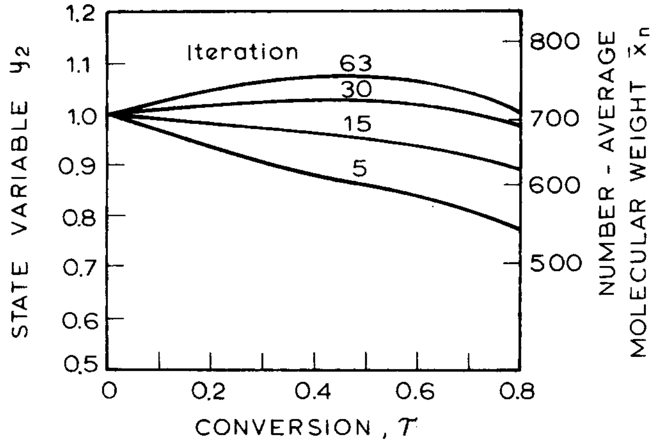

Fig. 4. Number-average chain length as a function of conversion at various iterations.

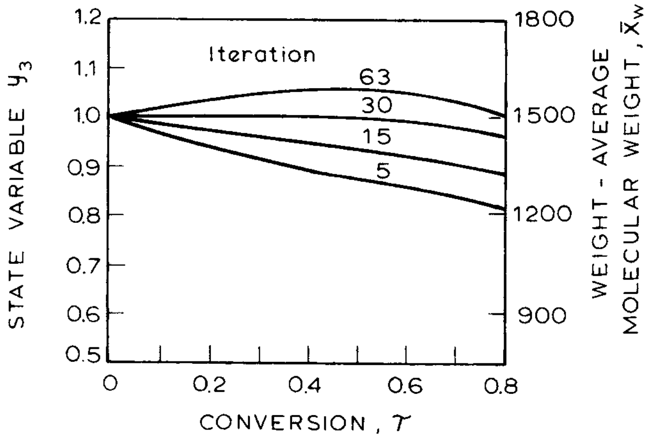

Fig. 5. Weight-average chain length as a function of conversion at various iterations.

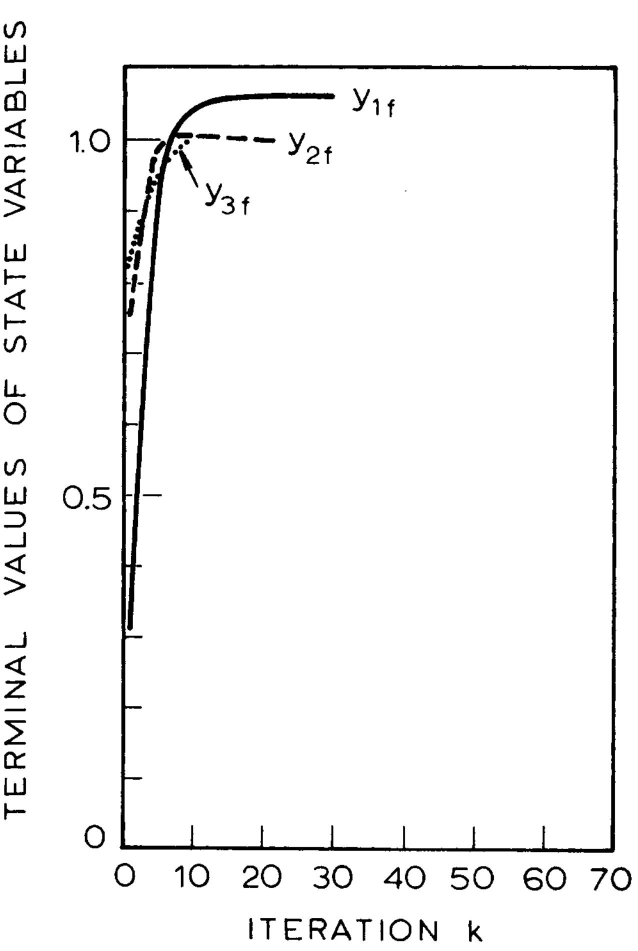

Fig. 6. Terminal state variables as functions of iteration number for accelerated increase of the penalty coefficient according to Equations (47) and (49).

for $k \leq 10$ and $\alpha = 10^4$ for $k > 10$. The results are shown in Figure 6. The convergence to the final optimal path was faster with the more rapid increase of γ_k. Thus, a higher rate of increasing the penalty coefficient accelerates convergence to the optimal path.

The use of penalty functions to solve constrained optimization problems may distort the response surface to introduce local optima not present in the original problem. It is important to start the iterations with a value of γ_k which is reasonably small, for example, $\gamma_k < 1$. When the iteration is started with a large value of γ_k, the solution obtained may converge to a local optimum which is not the minimum-time solution desired. The large value of γ_k tends to inhibit the adjustment of the control variables to reduce the terminal time because the penalty for violating the terminal conditions is greater than the benefits from reducing the time of operation.

The fact that the solution obtained agreed with the one obtained by nonlinear programming leads us to believe that a global optimum was found. In general, one should obtain a set of solutions with different choices for the initial control functions. If convergence to common optimal paths results, then one has greater confidence that it is the global optimum.

NOTATION

a = monomer activity
A_M = frequency factor in Arrhenius equation for the overall rate of polymerization
A_w, B = coefficients in the relation between $\bar{x}_w{}^0$ and T
C_1, C_2, C_3 = constants
E_M = activation energy of overall monomer reaction
$\mathbf{f}$, $\mathbf{F}$ = time derivative vectors of state variables
f_m, f_n, f_w = time derivatives of monomer fraction, number-average chain length and weight-average chain length
H = Hamiltonian function
J = objective function
k_M = overall polymerization rate constant
m = monomer weight fraction in the reactant
M_m = monomer molecular weight
$[M_e]$, $[M_o]$ = effective monomer concentration, pure monomer concentration in moles per unit volume
$\mathbf{p}$ = costate vector
R = gas constant
$r_1 - r_4$ = constants in density-temperature correlation
t, t^* = real time, scaled time
$\tilde{t}$ = time scale factor
T, T_c, T_b, T_{ref} = absolute temperature, temperature in °C, base temperature, and reference temperature
$\tilde{T}$ = temperature scale factor
$\mathbf{u}$, $\mathbf{u}^*$ = control variable vector, optimal control vector
W_b = weight parts of the base polymer
w_i = weighting coefficients applied to penalty terms
$\mathbf{x}$, $\mathbf{y}$ = state variable vectors
$\bar{x}_n$, $\bar{x}_w$ = number-average and weight-average chain lengths

Greek Letters

α = multiplying factor in increasing the penalty coefficient
γ_k = penalty coefficient applied at the k^{th} iteration

τ = time in the transformed coordinate system
ρ = reactant density
χ = polymer-monomer interaction parameter

Subscripts

o = initial state
f = final state
min = minimum
max = maximum

Superscripts

o = values related to the polymer formed at the current temperature
$*$ = optimal path (except for t^* which is the scaled time)

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APPENDIX A: GRADIENT METHOD (STEEPEST DESCENT OF HAMILTONIAN) IN TRAJECTORY OPTIMIZATION (ATHANS, 1968)

System equation	$\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}, \mathbf{u})$
Initial condition	$\mathbf{x}(t_o) = \boldsymbol{\xi}$
Final condition	$\mathbf{x}(t_f)$: free
End time	t_f : fixed
Objective function	$J = K[\mathbf{x}(t_f)] + \int_{t_o}^{t_f} L(\mathbf{x}, \mathbf{u})\, dt$
Hamiltonian	$H = L(\mathbf{x}, \mathbf{u}) + \mathbf{p} \cdot \mathbf{f}$

Necessary conditions of optimality

$$\dot{\mathbf{x}}^* = \left.\frac{\partial H}{\partial \mathbf{p}}\right|_{*} \qquad \dot{\mathbf{p}}^* = -\left.\frac{\partial H}{\partial \mathbf{x}}\right|_{*}$$

$$\left.\frac{\partial H}{\partial \mathbf{u}}\right|_{*} = 0 \quad (\text{or } \mathbf{u}^* \text{ at the constraint limit})$$

$$\mathbf{x}^*(t_o) = \boldsymbol{\xi}$$

$$\mathbf{p}^*(t_f) = \left.\frac{\partial K[\mathbf{x}(t_f)]}{\partial \mathbf{x}(t_f)}\right|_{*}$$

Gradient Algorithm (i^{th} iteration)

1. Given i^{th} guess of $\mathbf{u}$, that is, $\mathbf{u}^i(t)$.
2. Determine $\mathbf{x}^i(t)$ by forward-in-time integration of $\dot{\mathbf{x}}^i(t) = \mathbf{f}(\mathbf{x}^i, \mathbf{u}^i)$ with $\mathbf{x}^i(t_o) = \boldsymbol{\xi}$.
3. Evaluate $\mathbf{p}^i(t_f) = \left.\frac{\partial K[\mathbf{x}(t_f)]}{\partial \mathbf{x}(t_f)}\right|_{\mathbf{x}^i(t_f)}$.
4. Determine $\mathbf{p}^i(t)$ by backward-in-time integration of
$$\dot{\mathbf{p}}^i = -\left.\frac{\partial H}{\partial \mathbf{x}}\right|_{\mathbf{x}^i, \mathbf{u}^i}$$
5. Evaluate H gradient $\mathbf{q}^i(t)$
$$\mathbf{q}^i(t) = \left.\frac{\partial H}{\partial \mathbf{u}}\right|_{\mathbf{u}^i, \mathbf{x}^i, \mathbf{p}^i}$$
6. Determine the best step size α^{*i} by
$$J(\alpha^{*i}) \leqq J(\alpha^i)$$

where

$$J(\alpha^i) = K[\mathbf{x}_{\alpha i}(t_f)] + \int_{t_o}^{t_f} L[\mathbf{x}_{\alpha i}(t),\ \mathbf{u}^i(t) - \alpha^i\, \mathbf{q}^i(t)]\, dt$$

in which $\mathbf{x}_{\alpha i}(t)$ is the solution of

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, \mathbf{u}^i - \alpha^i\, \mathbf{q}^i)\ ; \quad \mathbf{x}(t_o) = \boldsymbol{\xi}$$

7. Set $\mathbf{u}^{i+1} = \mathbf{u}^i - \alpha^{*i}\, \mathbf{q}^i(t)$
8. Stop when the maximum of $||\mathbf{u}^{i+1} - \mathbf{u}^i||$ in the time range of $t_o - t_f$ is less than a small value ϵ.

For the example, the integrations in steps 2 and 4 were performed by Euler's method with a step size of 0.01 in the independent variable conversion. In the search for α^* at a given iteration, an initial trial value of α was selected to give a maximum adjustment of u corresponding to 2°C. If this brought an improvement in cost function, α was doubled and the cost function recomputed. If it did not bring an improvement, α was divided by four and the cost function recomputed. This step taking was continued, with the same gradient, until α was less than a prescribed small value (for example, 0.001). The α^* is the sum of these steps taken with the same gradient.

APPENDIX B: PARAMETERS OF SYSTEM EQUATIONS FOR THE THERMALLY INITIATED BULK POLYMERIZATION OF STYRENE

A_M = 4.266×10^5 liter/g mole · s
E_M = 20.207 kcal/mole
r_1 = 0.9328 g/cc
r_3 = 1.0902 g/cc
χ = 0.33
W_b = 1 (for this example)
A_w = 0.033454
B = 4364.6 °K
r_2 = -8.7902×10^{-4} g/cc · °C
r_4 = -5.9×10^{-4} g/cc · °C
M_m = 104

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