Transient Chemical Reaction Analysis by Orthogonal Collocation

NOBLE B. FERGUSON AND BRUCE A. FINLAYSON

Department of Chemical Engineering, University of Washington, Seattle, Washington 98105 (USA)

(Received: 5 July, 1970)

ABSTRACT

Models of packed-bed chemical reactors most frequently account for the diffusion of mass and energy within catalyst particles. The orthogonal collocation method is developed for transient, nonlinear problems of this type. A sequence of approximate solutions is proved to converge to the exact solution. A stability criterion is presented for estimating the maximum step size to use in the integration.

The orthogonal collocation method is applied to linear transient diffusion and gives accuracy to six significant figures for dimensionless times greater than 0.1 using six expansion functions. The method is then applied to nonlinear diffusion and reaction problems which have multiple solutions. Eight to twelve expansion functions are required to give temperatures with accuracies from 0.03% to 0.1% and heat flux at the boundary of the catalyst pellet within 1%. Jacobi polynomials are preferred expansion functions for boundary conditions of the first kind and Legendre polynomials are recommended for boundary conditions of the third kind. Comparison to two finite difference methods indicates that the collocation method is from four to forty times as fast for comparable accuracy.

The orthogonal collocation method is developed for nonlinear, parabolic partial differential equations. To illustrate the method we study the unsteady diffusion of mass and energy within a catalyst particle. Due to the nonlinear dependence of reaction rate on temperature, the coupling between mass and energy transport can yield unusual behavior: for example, the maximum temperature achieved during a transient can exceed the maximum steady-state temperature. This problem arises in some models of chemical reactors, McGuire and Lapidus,¹ where the primary quantity of interest is the flux of mass and energy to and from the catalyst. We thus compare the accuracy of different calculation methods by comparing the flux. Furthermore, a reactor model consists of several such problems, such as the 75 catalyst particles used by McGuire and Lapidus. Thus the time savings described below for a single particle are multiplied several fold for the reactor model.

The collocation method is one of several Methods of Weighted Residuals. In these methods the unknown solution is expanded in a series of known functions with arbitrary coefficients. These coefficients are chosen to give the best fit to the differential equation according to several possible criteria.^{2,3,4} For problems involving chemical reactions with an Arrhenius temperature dependence, only the collocation method is feasible, since the other methods require evaluation of complicated integrals involving exponential functions. (Various guadrature schemes could be used, however.) In the collocation method the differential equation is satisfied only at discrete points, called collocation points. The choice of these collocation points remained somewhat arbitrary until the work of Villadsen and Stewart,⁵ who firmly established the choice of collocation points as roots of appropriate orthogonal polynomials. The polynomials are specifically designed for problems of the type treated below. They also solved for the solution at the collocation points rather than for the arbitrary coefficients in the expansion, and this simplified the solution. More recent applications include the work of Stewart and Villadsen⁶ to predict the occurrence of multiple steady-state solutions to the mass and energy balances in a catalyst particle, Livbjerg et al.⁷ to study the catalytic oxidation of SO₂, and McGowin and Perlmutter⁸ to delineate regions of asymptotic stability for problems with multiple solutions. The application of orthogonal collocation used here differs from the procedure presented by Villadsen and Stewart

The Chemical Engineering Journal (1) (1970)-© Elsevier Publishing Company Ltd, England-Printed in Great Britain

in a minor way in that different polynomials are used for problems with boundary conditions of the third kind,

We first outline the orthogonal collocation method for the transient problem and then develop a criterion for determining the stable step size in numerical calculations. The convergence of the method is proved, so that we know as we increase the number of expansion functions the exact solution is approached. Finally we apply the method to three problems to test its effectiveness and compare the numerical results with those obtained using the Crank–Nicholson finite-difference scheme and the recent approach of Liu.⁹

ORTHOGONAL COLLOCATION METHOD

In the method of weighted residuals the unknown solution is expanded in terms of known expansion functions with arbitrary coefficients, *e.g.*

$$T(x,t) = T(1,t) + (1-x^2) \sum_{i=1}^{n} a_i(t) P_{i-1}(x^2) \quad (1)$$

A similar equation is used for concentration. The expansion functions, P_i , must be specified and the unknown coefficients $a_i(t)$ are determined by satisfying the differential equation in some average or pointwise sense ^(2,3,4). Here we take the P_i to be orthogonal polynomials defined by the relation

$$\int_{0}^{1} \rho(x^{2}) P_{i}(x^{2}) P_{j}(x^{2}) x^{a-1} \, \mathrm{d}x = C_{i} \, \delta_{ij} \qquad (2)$$

The choice of a = 1, 2, or 3 corresponds to planar, cylindrical or spherical geometry. The choice of $\rho(x^2) = (1 - x^2), 1$, or $(1 - x^2)^{-\frac{1}{2}}$ will be referred to here as giving rise to Jacobi, Legendre or Chebycheff polynomials. The roots to these polynomials are well-tabulated to thirty significant figures.¹⁰

A typical differential equation treated below is

$$\frac{N_1}{4}\frac{\partial T}{\partial t} - \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial T}{\partial x}\right) - \delta\beta c \exp\left\{\gamma(1-1/T)\right\} = 0 \qquad (3)$$

Using the form of expansion represented in eqn. (1), the various spatial and time derivatives in eqn. (3) can be written as

$$\frac{\partial T(x,t)}{\partial t}\Big|_{x_j} = \frac{dT(1,t)}{dt} + (1-x_j^2) \sum_{i=1}^n \frac{da_i}{dt} P_{i-1}(x_j^2) = \frac{dT_j}{dt}$$
$$\frac{\partial T(x,t)}{\partial x}\Big|_{x_j} = \sum_{i=1}^n a_i(t) \frac{\partial}{\partial x} [(1-x^2)P_{i-1}(x^2)]\Big|_{x_j} = \sum_{i=1}^{n+1} A_{ji}T_i(t)$$
$$\nabla^2 T(x,t)\Big|_{x_j} = \sum_{i=1}^n a_i(t) \nabla^2 [(1-x^2)P_{i-1}(x^2)]\Big|_{x_j} = \sum_{i=1}^{n+1} B_{ji}T_i(t)$$
(4)

where $T_j(t) = T(x_j, t)$ is the approximate solution at the collocation point, x_j . The matrices A and B can be found easily using the algorithm described by Villadsen and Stewart.⁵ One needs only the collocation points, which are available.¹⁰ The orthogonal collocation method applied to eqn. (3) gives the equations

$$\frac{N_1}{4} \frac{dT_j}{dt} = \sum_{i=1}^{n+1} B_{ji} T_i + \delta \beta c_j \exp\{\gamma (1 - 1/T_j)\}$$
 5)

which are solved numerically to find the solution $T_j(t)$. The solution for values of x between the collocation points can be found from eqn. (1) if needed. If the boundary conditions are of the first kind, the function T(1, t) in eqn. (1) is known. If the

boundary condition is of the third kind, eqn. (4) can be used.

$$\left. -\frac{\partial T}{\partial x} \right|_{x=1} = \left. -\sum_{i=1}^{n+1} A_{n+1,i} T_i = \frac{\mathrm{Nu}}{2} \left(T_{n+1} - g(t) \right) \, (6) \right.$$

Note that the n + 1 - st collocation point is x = 1. Computer codes are much simpler to write in terms of the pointwise values of the solution, leading to eqn. (5), than in terms of the coefficients $a_i(t)$.

The problem, eqn. (3), has been reduced to a set of ordinary differential equations, eqn. (5), which can be integrated numerically using any standard method of integration. A simple explicit marching scheme would use in place of (5)

$$\frac{N_1}{4}\frac{\mathrm{d}T_j}{\mathrm{d}t} \cong \frac{N_1}{4}\frac{T_{j,e+1} - T_{j,e}}{\Delta t} = \sum_{i=1}^{n+1} B_{ji}T_{i,e} + f_{j,e} \quad (7)$$

Finite difference methods lead to an identical equation except that the matrix B has a tri-diagonal form (for central, second-order difference schemes). In the orthogonal collocation method each element of B_{ii} is non-zero. One might expect then that for the same n, the collocation method would require the longest computation time. The advantage of the collocation method is that a much smaller n may be used since the solution at each point is influenced directly by the value at all the collocation points, as is the case for the exact solution, instead of depending directly on only neighboring grid points, as is the case in second-order finite difference schemes. In this respect, then, the collocation method can be viewed as a very high order difference equation. The collocation method has the added advantage of permitting the boundary conditions to influence the expansion functions, as in eqn. (1). The preference for one method over the other must then be based on computational experience giving the values of n and Δt necessary for an accurate solution. These matters are discussed below.

Several methods are available for integrating the system of first-order ordinary differential equations. Because of the exponential nonlinearity, it is desirable to evaluate the right-hand side as few times as possible. For this reason Hamming's method, which is an explicit, four-point method of fifth-order truncation error and requires two evaluations per time step, is preferable to the usual Runge-Kutta scheme, which requires four evaluations of the nonlinear right-hand-side per time step. Hamming's method and the modified Euler method are used below. The modified Euler method requires two evaluations per time step* but permits a larger step size than Hamming's method. Other methods may be equally suitable. Villadsen and Sorensen¹¹ report a collocation method for integrating in time as well as position and implicit methods are also possible. We do not present an exhaustive comparison of methods to integrate the ordinary differential equations, but we find that Euler's modified method is very suitable.

NUMERICAL STABILITY

We next consider the stability of methods to numerically integrate eqns. (5) and deduce a stable step size. For simplicity consider the system of equations

$$\frac{\mathrm{d}T_j}{\mathrm{d}t} = \sum_{i=1}^n N_{ji}T_i + f(T_j) + G(t) \tag{8}$$

$$N_{ji} = B_{ji} - \frac{A_{n+1,i}B_{j,n+1}}{(Nu/2) + A_{n+1,n+1}}$$
(9)

The term G(t) arises because of the boundary conditions. Let y_j be the numerically calculated value of T_j and define the error $e_j = T_j - y_j$. We assume the error is small so that we can expand the nonlinear term in a Taylor series, keeping only first-order terms, to obtain the following equations governing the error:

$$\frac{d\overline{e}}{dt} = \overline{\overline{D}}\overline{e}$$

$$\overline{e} = \{e_j\}, \ \overline{\overline{D}} = \{D_{ji}\}$$
(10)

$$D_{ji} = \begin{cases} N_{ji} & j \neq i \\ N_{ji} + \frac{\partial f}{\partial y_j} \Big|_{yj} & j = i \end{cases} \quad i, j = 1, \dots, n$$

The integration method used is Euler's modified method which is a predictor-corrector method.¹² To study the growth of the error we define the natural norms

$$\|\bar{x}\|_{\infty} = \max_{i} |x_{i}|$$
$$\|\bar{\overline{D}}\|_{\infty} \equiv \max_{x} \frac{\|\bar{\overline{D}}\bar{x}\|_{\infty}}{\|\bar{x}\|_{\infty}} = \max_{j} \sum_{k=1}^{n} |D_{jk}| \quad (11)$$

By applying Euler's modified method to eqn. (10) and requiring that the error die out in time it can be shown that a sufficient condition for numerical stability is

$$h\left\|\overline{\bar{D}} + \frac{h}{2}\,\overline{\bar{D}}^2 + \frac{h^2}{2}\,\overline{\bar{D}}'\overline{\bar{D}}\right\|_{\infty} \le 2 \qquad (12)$$

where $h = \Delta t$. For the linear diffusion problem $D_{ji} = N_{ji}$ and to first order eqn. (12) becomes

$$h\|\overline{N}\|_{\infty} \le 2 \tag{13}$$

Values of this norm are shown in Fig. 1 for several different polynomials. Smaller values of Δt must be used as we change from Jacobi to Legendre to Chebycheff polynomials. Note also the rapid decrease of stable step size as *n* increases. Equation (9) and Fig. 1 show that as the Nusselt number is decreased from infinity (boundary condition of the first kind), the stable step size increases. If N_{ij} is positive definite the use of the Euclidean norm would replace $||N||_{\infty}$ in eqn. (13) by the maximum eigenvalue of $[N_{ij}]$. Computation of the eigenvalues for Jacobi polynomials, n = 6, shows the maximum eigenvalue is 1200 for Nu = ∞ and 600 for Nu = $55 \cdot 3$.

When the reaction term is present, it is difficult to predict how the stability changes because $[D_{ij}]$

^{*} The modified Euler method is an iterative method. We use only two steps in the iteration so that it is essentially a predictor — corrector method.



Fig. 1. Matrix norm of eqn. (13) versus n.

depends on the solution $y_j(t)$. It is possible to check such a criteria as (12) to guard against error growth and to use an efficient size of Δt . For the applications discussed here, which have a Lewis number near one, the stable step size was predicted from eqn. (13). With small Lewis numbers, the temperature dominates the stability through the exponential nonlinearity.

CONVERGENCE

We prove convergence of the orthogonal collocation method by relating it to the Galerkin method, whose convergence has been studied. For linear problems Villadsen and Stewart⁵ have shown that the orthogonal collocation and Galerkin methods yield identical results.

For the nonlinear problem, eqns. (15, 16) below, Finlayson¹³ has shown that the Galerkin method converges to a weak solution as n approaches infinity. The quadrature involved in the Galerkin method is exact if the integrand is a polynomial of degree no greater than n - 1 in x^2 . In this case the exponential function in the reaction rate term is not such a polynomial so that the quadrature is approximate. The quadrature error approaches zero, however, as the number of quadrature points, m, increases (provided the integrand is continuous, as is the case here). The number of quadrature points increases as *n* is increased, since $m \ge n$. Thus in the limit $n \to \infty$ the quadrature is exact and the collocation and Galerkin solutions coincide. Since the Galerkin method converges, so must the orthogonal collocation method converge.

APPLICATIONS

Linear diffusion

We first apply orthogonal collocation to the unsteady-state diffusion in a slab. Liu⁹ has previously

compared finite difference methods for this problem.

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} \tag{14}$$

$$\frac{\partial u}{\partial x}(0,t) = 0, \quad u(1,t) = 1, \quad u(x,0) = 0$$

The Jacobi polynomials and Hamming's predictormodifier-corrector method¹² were used.

The value of concentration at the collocation point was compared to the exact value given by an infinite series and the errors are shown in Table 1. A threeterm expansion is accurate within 0.02% and a sixterm expansion gives six digit accuracy. For smaller times than those shown some error occurs due to the discontinuous initial conditions, as in finite difference methods. The computation times can be reduced by using another method of integrating ODE. It was also found that one can use a step size relatively close to that predicted by an equation similar to (13), applicable to Hamming's method.

It is clear from Table 1 that the orthogonal collocation method can give accurate results. Comparison with the calculations reported by Liu⁹ shows that the collocation solution is more accurate than finite difference solutions which use three to twelve times as many spatial grid points.

TABLE 1 POINTWISE ERROR FOR LINEAR DIFFUSION PROBLEM

n	Computation time (Sec on IBM 7094)	Δt	$\frac{\frac{1}{n}\sum_{i=1}^{n} \tilde{u}(xi, t) - u(xi, t) }{t = 0.1}$	
3	0·237	0·005	·000133	·000000
6	4·097	0·0005	·000000	·000000

Boundary condition of the first kind

We consider next the diffusion of mass and energy in a spherical catalyst pellet with an exothermic firstorder irreversible reaction. The equations are given by McGuire and Lapidus.¹⁴

$$R_T \equiv \frac{N_1}{4} \frac{\partial T}{\partial t} - \frac{1}{x^2} \frac{\partial}{\partial x} \left(x^2 \frac{\partial T}{\partial x} \right) - \delta \beta c \exp \left\{ \gamma (1 - 1/T) \right\} = 0 \qquad (15)$$

$$R_{c} = \varepsilon \frac{N_{2}}{4} \frac{\partial c}{\partial t} - \frac{1}{x^{2}} \frac{\partial}{\partial x} \left(x^{2} \frac{\partial c}{\partial x} \right) + \delta c \exp \left\{ \gamma (1 - 1/T) \right\} = 0 \quad (16)$$

$$\frac{\partial T}{\partial x}(0,t) = \frac{\partial c}{\partial x}(0,t) = 0$$
(17)

$$T(x, 0) = 1.05, \quad c(x, 0) = 1.0$$
 (18)

$$T(1, t) = c(1, t) = 1.0$$
(19)

The collocation method is applied to eqn. (15) to obtain eqn. (5) and a similar equation results from eqn. (16). The boundary conditions (17) are satisfied automatically by the polynomials, (1). Values of the parameters are chosen to correspond to a case having multiple steady-state solutions and are listed in the nomenclature. The problem represents the response to a step change in temperature and the solution approaches the first steady-state solution. Calculations are made using orthogonal collocation and finite difference methods. For the reactor model the flux at the boundary is the most important quantity and is expected to be less accurate than the temperature and concentration values themselves. For the collocation solution the flux is given by

$$\left. \frac{\partial T}{\partial x} \right|_{x=1} = \sum_{j=1}^{n+1} A_{n+1,j} T_j \tag{20}$$

For the finite difference solutions the flux was initially evaluated by a two-point difference. This proved to be so inaccurate, however, that another means was devised. If eqn. (15) is integrated over x one obtains:

$$\frac{\partial T}{\partial x}\Big|_{x=1} = \int_0^1 \left[\frac{N_1}{4} \frac{\partial T}{\partial t} - \delta\beta c \exp\left[\gamma(1-1/T)\right] x^2 \,\mathrm{d}x \quad (21)$$

Simpson's rule was used to calculate the integral, and this gives a more accurate representation of the flux for coarse grid spacings. The collocation solution gave nearly identical results using either eqn. (20) or (21). Finite difference solutions are identified by the grid spacings (Δx , Δt) and collocation solutions by the number of collocation points and step size $(n, \Delta t)$.

The collocation solution was calculated using Jacobi polynomials and the equations were integrated to t = 5 using Hamming's method. The finite difference scheme used on this problem was Liu's method, which is an accurate, stable explicit scheme.⁹ Calculations for this problem were made on an IBM 7094 computer.

Exploratory calculations, Fig. 2, indicated that the development of the solution in time was relatively smooth except for small times. The large oscillations in the approximate initial condition arise because one is trying to approximate a step function with a low order polynomial. These oscillations die out rapidly (t < 1) and have little effect on the solution for $t \ge 1$. At the collocation points the temperature equals the initial condition value as would the temperature function in a finite difference solution. With a finite difference solution, one merely draws



Fig. 2. Temperature profiles for various times. (Using Jacob polynomials, N = 6; Hamming's method, $\Delta t = .05$) 1 to 9 correspond to t = 0.1, 5, 10, 25, 50, 75, 100, ∞ .

a curve through the solution; while with orthogonal collocation the 'curve' is already specified. To approximate temperature functions with steep gradients more terms are needed, as is shown below. Because of the smoothness of the solution for t > 5, and the fact that the steady state had a dimensionless time of the order of 100, it was decided to limit all further computations to $t \le 5$.

A comparison of the collocation solution (6, 0.05) to the best finite difference solution (0.01, 0.005) showed that they agree to within four or five digits.

As *n* increases to eight and ten, the agreement increases to five or six digits. The behavior of the surface flux under different conditions is shown in Tables 2 and 3. The collocation method (n = 6) gives the surface flux within one-half per cent whereas the finite difference solution ($\Delta x = 0.05$) is in error by 3%. At t = 1, the collocation solution with n = 10

 Table 2

 COLLOCATION SURFACE DERIVATIVES

	Surfe	ace Heat F	Computation Time (Sec on IBM 7094)	
n	Δt	t = 1	t = 5	
6	·05	0.3419	0.1570	4.8
8	·01	0.3430	0.1570	27.7
10	· 0 1	0.3431	0.1570	39.2

gives better results than the finite difference solution with $1/\Delta x = 100$, demonstrating that the number of collocation points can be about ten times less than the number of finite difference grid points for equivalent accuracy. For the same Δt the collocation method with n = 8 uses about the same computation time as the finite difference method with $1/\Delta x = 20$. This provides a quantitative comparison of computation time when the matrix B in eqn. (7) is tri-diagonal or complete. In this case the collocation method would be preferred because it is more accurate.

 Table 3

 FINITE DIFFERENCE SURFACE DERIVATIVES

	Surface Heat Flux			Computation Time (Sec on IBM 7094)
Δx	Δt	t = 1	t = 5	
·05	·01	0.3537	0.1579	25.7
·025	·005	0.3465	0.1575	101-3
·01	·005	0.3449	0.1574	251.2

Figure 3 shows the error in the surface flux as a function of computation time. The values are compared to the average of the best finite difference and best collocation solutions (they differed by about $\frac{1}{2}$ %). The triangle symbols represent the values listed in Tables 2 and 3. For the collocation method the optimum Δt was just below the value of Δt for which the problem became numerically unstable. Further decreases in Δt , or increases in computation time, caused little if any change.

It is clear from Fig. 3 that the collocation solution is much faster than a finite difference solution of comparable accuracy. If the various solutions are compared to the best solution obtained using the *same* method, the collocation solution (6, 0.05) is about twenty times as fast as a finite difference solution (0.025, 0.005) of about the same accuracy. In this case the speed advantage is due to the ability to take larger time steps in the collocation method, and this is made possible due to the smaller number of terms necessary to obtain the solutions.



Fig. 3. Error in the temperature surface flux versus computation time (t = 1).

Boundary condition of third kind

For this case eqn. (19) is changed to

$$-\frac{\partial T}{\partial x} = \frac{\mathrm{Nu}}{2} \left(T - g(t)\right),$$
$$-\frac{\partial c}{\partial x} = \frac{\mathrm{Sh}}{2} \left(c - h(t)\right) \quad \text{at} \quad x = 1 \quad (22)$$
$$g(t) = 1.1, \quad h(t) = 1.0$$

The boundary conditions (22) are satisfied by eqn. (6) with a similar equation for concentration. The initial conditions are taken as the two-term approximation to the intermediate steady-state for the problem with infinite Nu and Sh. The 10% temperature perturbation on the boundary is sufficient to drive the solution to the third steady-state.

Collocation solutions were derived using Jacobi, Legendre, or Chebycheff polynomials and either the modified Euler or Hamming's method of integration. Calculations were made until t = 35. Finite difference solutions were obtained using Liu's method and the implicit method. In the implicit method the boundary conditions were handled using a false boundary to retain the second-order truncation error and the reaction rate term was evaluated at the previous time, as was done by McGuire and Lapidus.¹ Calculations were done on a CDC 6400 computer, which proved to be about twice as fast as the IBM 7094 for these problems.

Exploratory calculations, Fig. 4, indicated the solution had large spatial and time derivatives. Consequently, we expect that more terms are needed



Fig. 4. Temperature profiles for various times (Using Jacobi polynomials, N = 6, Hamming's method, $\Delta t = 0.05$) 1 to 6 correspond to t = 1, 10, 15, 20, 25, 30.

to approximate the solution. Experience showed, too, that even though the temperature was approximated within two to three digits using 6 to 10 terms and the Jacobi polynomials, the convergence with nwas rather slow(see Table 4). If Legendre polynomials are used instead the convergence is much faster. This is probably due to the fact that the Jacobi polynomials weight more heavily the region away from the boundary due to the factor $(1 - x^2)$, whereas the Legendre polynomials give equal weight to all regions (except for the skewness introduced by the spherical geometry). In boundary conditions of the

TABLE 4 HEAT FLUX FROM CATALYST

Polynomial		Δt	Flux		
roiynomiai	n		t = 22	<i>t</i> = 35	
Jacobi*	6	0.05	2.348	4.241	
Jacobi*	8	0.025	2.857	4.594	
Jacobi*	10	0.025	2.489	5.078	
Legendre [†]	6	0.10	2.477	5.159	
Legendre [†]	8	0.05	2.539	4.956	
Legendre [†]	10	0.04	2.572	5.042	
Legendre [†]	12	0.025	2.584	5.024	

* Jacobi results using Hamming's method.

† Legendre results using Euler's modified method.

third kind, the temperature at the boundary is not known, so that better results for the flux at the boundary are expected if the region near the boundary is emphasised, or at least not de-emphasised.

It was found that Euler's modified method of integration gave accuracy comparable to Hamming's method, took about the same computation time for the same Δt , but allowed time steps about twice as large. Consequently, Euler's modified method is preferred for these problems.

If one looks at the difference between the surface derivative for a collocation solution and the best finite difference solution as a function of time, one finds the type of behavior exhibited in Fig. 5. The spike at t = 5 should be ignored since it is in this region that the surface derivative passes through zero. Three characteristic values can be associated with Fig. 5:

- (i) let E_1 = typical error for 0 < t < 15
- (ii) let E_2 = maximum error for 15 < t < 25
- (iii) let E_3 = typical error for 25 < t (23)

Comparison of Figs. 4 and 5 shows that the error E_2 arises when the temperature increases rapidly in the



Fig. 5. Error in the surface heat flux as a function of time. (Using Legendre polynomials, N = 6, Hamming's method, $\Delta t = 0.5$).

Entry	n	Δt	Method of Integration	Expansion Functions	E_1	E_2	E_3	Computation Time (Seconds)
1	6	·05	Hamming	Jacobi	1.5%	19.6%	15.5%	11.9
2	8	·025	Hamming	Jacobi	1.0	15.6	8·6´	30-6
3	10	·025	Hamming	Jacobi	<1	12.0	1.0	41.1
4	10	·01	Hamming	Jacobi	<1	12.0	1.0	98.0
5	6	·05	Hamming	Chebycheff	<1	7.1	9.8	11.9
6	6	·05	Hamming	Legendre	< 1	$7 \cdot 2$	2.7	11.9
7	8	·025	Hamming	Legendre	<1	2.4	1.4	30.6
8	6	·10	Euler	Legendre	< 1	8.0	2.7	5.1
9	8	·05	Euler	Legendre	<1	2.4	1.4	13.3
10	10	·04	Euler	Legendre	<1	1.8	0.34	21.8
11	12	·025	Euler	Legendre	<1	1.4	0.02	45.6

TABLE 5

Entry	Δx	Δt	Method of Integration	E_1	E_2	E_3	Computation Time (Seconds)
1 2 3 4	0.05 0.05 0.025 0.01	0.05 0.05 0.0025 0.005	Implicit Liu's Liu's Liu's Liu's	6% 2 <1	15% 7·4 2·8	20 % 1·5 0·1	11 21 830 1050

particle. Using these values one can summarise the effects of the integration scheme, the expansion functions, and the step size as done in Tables 5 and 6.

Based on the results for the problem with boundary condition of the first kind, it was felt that the following choices of grid spacings should give representative results for the finite difference computations; (0.05,0.05), (0.025, 0.0025), and (0.01, 0.005). Additional values were not examined because of the excessive computation time necessary to use the finite difference methods.

The comparative errors for the classical implicit method (Table 6) are indicative of the unacceptable pointwise errors. Based on Liu's comparison of his own method to the implicit scheme,⁹ and the errors found in Table 6, it was decided not to use the implicit method further.

Based on the data in Tables 4 and 5 the modified Euler method is recommended over Hamming's method for integration of the ODE. For boundary conditions of the third kind Legendre polynomials are recommended over Jacobi polynomials. Comparison of the collocation solution, entries 10 and 11 in Table 5, with a finite difference solution of comparable accuracy, entry 3 in Table 6 reveals that the collocation solution is from twenty to forty times faster. This advantage is due to the larger time step and the smaller number of terms in the collocation method (10–12 rather than 40–100). It is also clear from this problem and the previous one that large computation times are necessary to model nonisothermal diffusion with reactions of this type, and the time savings made possible by the collocation method is especially welcome when several of these problems must be solved as is the case in the reactor model.

CONCLUSIONS

The orthogonal collocation method is shown to give an accurate solution to the problem of nonisothermal reaction and diffusion in a catalyst pellet. The method is shown to converge and a stability criterion is suggested which gives the maximum step size to use in the numerical calculations. Comparisons with finite difference calculations show that orthogonal collocation was from four to forty times faster for comparable accuracy. This speed advantage is due to a larger possible step size and many fewer number of terms.

The following procedure is recommended for orthogonal collocation. Write computer codes in terms of the pointwise values of the functions instead of the expansion coefficients. The matrices giving expressions for the Laplacian operator and first derivatives can be calculated directly from the roots to the polynomials, which are well tabulated. The criterion for a stable step size is given by eqn. (13), and this Δt gives good accuracy as well. Euler's modified method is a possible choice for integration of the ODE. Legendre polynomials should be used as expansion functions for boundary conditions of the third kind and Jacobi polynomials should be used for boundary conditions of the first kind. From six to twelve collocation points are needed for accurate solutions to the problems treated here.

ACKNOWLEDGEMENT

This research was supported by NSF Grant GK-3083.

This paper was presented at the Third Joint AIChE-IMIQ meeting, Denver, Colorado, Aug. 30-Sept. 2, 1970.

r	radius of catalyst
R_1	gas constant
Sh	$k_g d_p / D_p$, Sherwood number, 66.5
t	dimensionless time
To	reference temperature
$u_j = u(x_j, t)$	approximate solution at <i>j</i> th collocation point
v	interstitial velocity of fluid
x	dimensionless spatial variable
x_j	jth collocation point
Δx	spatial step size

NOMENCLATURE

a	frequency factor in Arrhenius expres- sion
$a_i(t)$	time dependent expansion coefficient
A_{ij}, B_{ij}	Lagrange interpolation coefficients for
	$\frac{\partial}{\partial x}$ and ∇^2 , defined by eqn. (4)
Co	reference concentration
Cs	heat capacity of catalyst particle
D _{ij}	elements of linearised stability analysis, defined by eqn. (10)
d_p	diameter of catalyst particle
D_p	diffusivity of particle fluid
e _j	error (in numerical integration) of <i>j</i> th dependent variable
ΔE	activation energy
g(t), h(t)	functions, defined in eqn. (22)
$h, \Delta t$	time step size
h_f	heat transfer coefficient in fluid
ΔH	heat of reaction
k _o	$a \exp(-\Delta E/R_1T_o)$, reaction rate co- efficient evaluated at T_o
k	thermal conductivity of porous solid
k_g	mass transfer coefficient
т	number of quadrature points
n	number of expansion functions
N ₁	$d_p v \rho_s c_s / k$, inverse of dimensionless thermal diffusivity, 705
N ₂	$d_p v/D_p$, inverse of dimensionless mass diffusivity, 1225
N_{ij}	elements of matrix, defined by eqn. (9)
Nu	$h_f d_p/k$, Nusselt number, 55·3
• <i>«</i>	norm, defined by eqn. (11)
$P_i(x^2)$	expansion function

Greek symbols

β	$-c_o \Delta HD_p/kT_o$, dimensionless heat of reaction, 0.6
δ	$r^2 k_o/D_p$, Thiele modulus squared, 0.25
3	void fraction of catalyst, 0.65
γ	$\Delta E/R_1T_o$, dimensionless activation energy, 20
$ ho_s$	density of catalyst

REFERENCES

- 1. MCGUIRE, M. L., AND LAPIDUS, L., A.I.Ch.E.J., 1965 11 85.
- FINLAYSON, B. A., AND SCRIVEN, L. E., Chem. Eng. Sci. 1965 20 395.
- 3. FINLAYSON, B. A., AND SCRIVEN, L. E., *Appl. Mech. Rev.* 1966 **19** 735.
- 4. FINLAYSON, B. A., Brit. Chem. Eng., 1969 14 53 179.
- VILLADSEN, J. V., AND STEWART, W. E., Chem. Eng. Sci., 1967 22 1483.
- STEWART, W. E., AND VILLADSEN, J. V., A.I.Ch.E. J., 1969 15 28.
- 7. LIVBJERG, H., ANTONSEN, P., AND VILLADSEN, J., 3rd CHISA Congress, Marianske Lazne 1969, paper A4.7.
- 8. McGowin, C. R., and Perlmutter, D. D., to be published.
- 9. LIU, S. L., A.I.Ch.E. J., 1969 15 334.
- 10. STROUD, A. H., AND SECREST, D., Gaussian Quadrature Formulas, Prentice-Hall, 1966.
- 11. VILLADSEN, J., AND SORENSEN, J. P., Chem. Eng. Sci., 1969 24 1337.
- 12. RALSTON, A., in *Mathematical Methods for Digital Computers*, Vol. 1 (Edited by A. RALSTON and H. S. WILF) Wiley 1966.
- 13. FINLAYSON, B. A., to be published, SIAM J. Num. Analysis.

RÉSUMÉ

ZUSAMMENFASSUNG

Les modèles de réacteurs chimiques à lit fixe doivent fréquemment tenir compte de la diffusion de matière et d'énergie à l'intérieur des particules de catalyseur. La méthode de l'arrangement orthogonal est développée pour des problèmes transitoires non linéaires de ce type. On démontre qu'une suite de solutions approchées converge vers la solution exacte. On donne un critère de stabilité permettant d'estimer le pas maximum à choisir dans l'intégration.

On applique la méthode de l'arrangement orthogonal au cas de la diffusion linéaire transitoire; en utilisant six développements en série, elle permet d'obtenir avec précision six chiffres significatifs pour des temps adimensionnels supérieurs à 0,1. La méthode est alors appliquée aux problèmes de diffusion non linéaire et de réaction qui possédent des solutions multiples. Huit à douze développements en série sont nécessaires pour obtenir les températures avec une précision de 0,03 à 0,1 pour cent ainsi que le flux de chaleur à la surface de la pastille de catalyseur avec une précision de 1 %. Pour des conditions aux limites de première espèce, il est préférable d'utiliser les polynômes de JACOBI tandis qu'on recommande les polynômes de LEGENDRE pour des conditions aux limites de troisième espèce. En comparant la méthode de l'arrangement à deux méthodes des différences finies on montre que pour une précision comparable, elle est de quartre à quarante fois plus rapide que ces dernières.

Häufig werden Modelle für Katalysatorschichte für die Diffusion von Masse und Energie in Katalysatorteilchen herangezogen. Die orthogonale Kollokationsmethode wird für vorüber gehende nichtlinearer Probleme dieses Typs herangezogen. Es wird bewiesen, daß eine Folge von Näherungslösungen in die exakte Lösung konvergiert. Es wird ein Stabilitätskriterium vorgestellt, das zur Abschätzung der maximalen Größe der Stufen, die bei der Integration verwendet werden können, benutzt werden kann.

Die orthogonale Kollokationsmethode wird angewendet auf die lineare Transient-Diffusion und gibt eine Genauigkeit von sechs Stellen für die dimensionslosen Zeiten, die größer sind als 0,1, wenn 6 Erweiterungsfunktionen benutzt werden. Die Methode wird dann auf nichtlineare Diffusionsund Reaktionsprobleme angewandt, die Mehrfachlösungen aufweisen. Acht bis zwölf Erweiterungsfunktionen werden benötigt, um die Temperaturen mit einer Genauigkeit von 0.03% bis 0,1% und den Wärmefluß an der Oberfläche des Katalysator-Pellets innerhalb 1% zu erhalten. Jacobi Polynome sind die bevorzugten Erweiterungsfunktionen für die Randbedingungen erster Art und Legendre Polynome werden vorgeschlagen für Randbedingungen der dritten Art. Der Vergleich mit zwei Methoden endlicher Differenzen zeigt, daß die Kollokationsmethode vier bis 4 omal schneller ist bei vergleichbarer Genauigkeit.