

Packed bed reactor analysis by orthogonal collocation

BRUCE A. FINLAYSON

Department of Chemical Engineering, University of Washington, Seattle, Wash. 98105, U.S.A.

(First received 14 September 1970; accepted 25 November 1970)

Abstract—The equations governing a packed bed reactor with radial temperature and concentration gradients are solved using the orthogonal collocation method. The method is shown to be faster and more accurate than finite difference calculations. Using the orthogonal collocation method it is straightforward to extend one-dimensional (lumped parameter) models to the two-dimensional models needed when radial temperature and concentration gradients are important.

The two-dimensional model is necessary for large Biot numbers, $h_w R/k_e$, where h_w is the wall heat transfer coefficient, R is the tube radius, and k_e is the effective thermal conductivity. For Biot numbers less than one, seventy-five per cent of the resistance to heat transfer is at the wall, and a one-dimensional (lumped parameter) treatment gives good results.

Computations are illustrated for both plug flow and radially-varying velocity. In the latter case the velocity profile induces effective thermal conductivity and diffusivity profiles. Calculations made using the velocity profile predict a heat transfer coefficient which is used in the plug flow model. Good agreement is obtained between the models.

1. INTRODUCTION

CONSIDER flow through a cylindrical tube, packed with catalyst. At a given location along the length of the tube the velocity is a function of radius. This induces a radial variation in the effective thermal conductivity and diffusivity which model the dispersion in the radial direction. At the wall the void fraction approaches one, the velocity changes drastically and the resistance to heat transfer is altered. This increased resistance can be modeled by either a lower effective thermal conductivity at the wall or a heat transfer coefficient. In the simpler, plug flow model the velocity, effective thermal conductivity, and diffusivity are constant in the radial direction, and there is assumed a heat transfer coefficient at the wall. These two models are compared below. They lead to partial differential equations, in radius and length, and are called distributed parameter models. A simplification is often made when radial dispersion is very rapid. Then the temperature and concentration do not depend on radius and the equations simplify to ordinary differential equations to be integrated along the length of the reactor. The resistance to heat transfer is lumped at the wall, through a heat transfer coefficient, hence the

name lumped parameter model. An important consideration, treated below, concerns the question: when is the lumped parameter model adequate?

In the above models the governing differential equations are written in terms of a locally-averaged temperature and concentration, which are assumed to be the same in the fluid and catalyst. In heterogeneous models the temperature and concentration of the fluid may differ from those in the catalyst owing to heat and mass transfer resistances at the catalyst surface or diffusional resistance inside the catalyst. Such complications increase the computation time needed to solve the resulting equations and make particularly welcome efficient computational tools.

The orthogonal collocation method is presented here as a simple numerical method which is easy to program for the computer and converges rapidly. The basic method was developed by Villadsen and Stewart[44] and has been applied to nonlinear chemical reaction problems by Stewart and Villadsen[39] to predict the occurrence of multiple steady states in catalyst particles, Livbjerg *et al.*[29] and Villadsen[42] to study the catalytic oxidation of SO_2 , Mc-

Gowin and Perlmutter[30,31] to study asymptotic stability as well as the plug flow models of chemical reactors, and Ferguson and Finlayson [18] to study the transient heat and mass transfer in a catalyst pellet exhibiting multiple steady-state solutions. McGowin and Perlmutter[30] placed the collocation points arbitrarily and obtained slower convergence than in the study below.

We apply the orthogonal collocation method to the plug flow model and compare results to those from finite difference calculations. The orthogonal collocation method proves to be faster and more accurate than the finite difference method used, by factors ranging from two to ten. The validity of the plug flow model is verified by comparing results to those from a velocity profile model, and the possible prediction of the heat transfer coefficient is considered.

2. PLUG FLOW MODEL—COMPARISON OF COLLOCATION AND FINITE DIFFERENCE METHODS

Consider the equations governing a fixed-bed catalytic reactor under the assumptions of constant physical properties and plug flow and for a reaction governed by the conversion and temperature.

$$\begin{aligned}\frac{\partial c}{\partial z} &= \alpha' \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) + \beta R(c, T) \\ \frac{\partial T}{\partial z} &= \alpha' \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \beta R(c, T) \\ \partial c / \partial r = \partial T / \partial r &= 0 \quad \text{at } r = 0 \\ \frac{\partial c}{\partial r} = 0, -\frac{\partial T}{\partial r} &= Bi(T - T_w) \quad \text{at } r = 1 \\ c = 0, T = 1 &\quad \text{at } z = 0.\end{aligned}\tag{1}$$

The heat transfer resistance at the wall is characterized by the Biot number, as used by Beek[4], and is defined in terms of the effective thermal conductivity and tube radius, whereas the Nusselt number is defined in terms of the cata-

lyst particle diameter and fluid thermal conductivity. The effective thermal conductivity and diffusivity are constant and contained in the parameters α' and α . The prediction of these parameters for use in design calculations is discussed in review articles by Beek[4], Froment[23], Paris and Stevens[34], and Hlaváček[25] as well as references listed below.

If radial dispersion is very rapid there are no radial variations and the model reduces to the lumped parameter model.

$$\begin{aligned}\frac{dc}{dz} &= \beta R(c, T) \\ \frac{dT}{dz} &= -Nu'(T - T_w) + \beta' R.\end{aligned}\tag{2}$$

These ordinary differential equations can be integrated numerically using standard subroutines, and for this reason the lumped parameter model is widely used. The two-dimensional model (1), leading to partial differential equations, is more accurate, but requires additional computation. The method outlined below offers a rationale for deciding when the two-dimensional model is necessary and provides a means for reducing it to a set of ordinary differential equations, which are easily integrated using the same methods as applied to Eq. (2).

Orthogonal collocation

The collocation method is one of a general class of approximate methods known as the Method of Weighted Residuals[14, 12, 1, 21, 19], which includes the better-known Galerkin, integral, and moments methods as special cases. The temperature and concentration are expanded in a series $\sum a_i(z)P_i(r)$ of known functions of radius, P_i , multiplied by unknown functions of z , a_i . The trial functions are substituted into the differential equations (1), which are satisfied at discrete radial collocation points, r_j . This gives a set of ordinary differential equations governing $a_i(z)$. In the orthogonal collocation method developed by Villadsen and Stewart [44] the known expansion functions are ortho-

gonal polynomials, e.g.

$$T(r, z) = T(1, z) + (1 - r^2) \sum_{i=1}^N a_i(z) P_{i-1}(r^2) \quad (3)$$

where the polynomials are defined by the relation (for cylindrical geometry)

$$\int_0^1 w(r^2) P_i(r^2) P_j(r^2) r dr = C_{ij} \delta_{ij} \quad j = 0, \dots, i-1 \quad (4)$$

where $P_i(r^2)$ is a polynomial in r^2 of degree i ; for example, with $w = 1$, $P_0 = 1$, $P_1 = 1 - 2r^2$, $P_2 = 1 - 6r^2 + 6r^4$. The weighting function $w(r^2) = 1 - r^2$ gives rise to one of the Jacobi polynomials [13] whereas $w(r^2) = 1$ gives a Legendre polynomial (which is also a Jacobi polynomial), generalized to the cylindrical geometry. Here we refer to the two sets of polynomials as simply Jacobi ($w = 1 - r^2$) and Legendre ($w = 1$) polynomials. The collocation points are denoted by r_j and are the roots to $P_n(r^2) = 0$.

Villadsen and Stewart [44] also point out that the equations can be solved in terms of the solution at the collocation points instead of the coefficients $a_i(z)$. This is more convenient and reduces Eq. (1) to

$$\frac{dc_j}{dz} = \alpha \sum_{i=1}^{N+1} B_{ji} c_i + \beta R_j \quad j = 1, \dots, N$$

$$\frac{dT_j}{dz} = \alpha' \sum_{i=1}^{N+1} B_{ji} T_i + \beta' R_j \quad (5)$$

$$-\sum_{i=1}^{N+1} A_{N+1,i} T_i = Bi(T_{N+1} - T_w)$$

$$\sum_{i=1}^{N+1} A_{N+1,i} c_i = 0$$

$$c_j(0) = 0, T_j(0) = 1$$

where T_j and c_j are the temperature and conversion at the collocation points, $T_j(z) = T(r_j, z)$, $r_{N+1} = 1$. The matrices B and A represent the Laplacian and first derivative and are easily

calculated with the algorithm described by Villadsen and Stewart [44]. One needs only the collocation points, which are readily available [40]. The set of Eqs. (5) is then integrated numerically. It has been proved [20, 18] that the solution to (5) converges to the solution to (1) as N is increased.

First approximation

It is instructive to examine the first approximation ($N = 1$) in detail. Eqs. (5) can be rearranged to give

$$\frac{dc_1}{dz} = \beta R_1 \quad (6)$$

$$\frac{dT_1}{dz} = -\left(\frac{6Bi\alpha'}{Bi+3}\right)(T_1 - T_w) + \beta' R_1$$

where c_1 and T_1 are the conversion and temperature at the collocation point, $r_1 = 0.577$. If Legendre polynomials are used $6Bi\alpha'/(Bi+3)$ is replaced by $8Bi\alpha'/(Bi+4)$ and $r_1 = 0.707$. Equation (6) is similar in form to the lumped parameter model, Eq. (2), with the equivalent heat transfer coefficient

$$\frac{1}{Nu'} = \frac{1}{2\alpha'} \left(\frac{1}{Bi} + \frac{1}{3} \right). \quad (7)$$

Equation (6), however, refers to the temperature at a particular radius, when it varies parabolically with r , whereas Eq. (2) refers to a temperature which is constant in r . In dimensional form Eq. (7) is

$$\frac{1}{U} = \frac{1}{h_w} + \frac{R}{3k_e} \quad (\text{Jacobi}) \quad (8)$$

$$\frac{1}{U} = \frac{1}{h_w} + \frac{R}{4k_e} \quad (\text{Legendre}). \quad (9)$$

For Legendre polynomials the T_1 is also the average temperature, and the equivalence (9) has been shown before for a parabolic temperature profile [5, 35, 26, 3, 22]. Equation (8) is close to that predicted by Crider and Foss [15].

In the first approximation the Jacobi polynomials give $T_1 > \langle T \rangle$, where $\langle \rangle$ denotes the radial average, and Legendre polynomials give $T_1 = \langle T \rangle$. Hence with the Jacobi polynomials the reaction rate expression is evaluated at a temperature above the average temperature, and this approximates more closely the average rate of reaction.

The relative importance of the wall resistance is evident in Eq. (7). The ratio of $1/Bi$ to $1/Bi + 1/3$ gives the fraction of the thermal resistance occurring at the wall: e.g., $Bi = 1$, 75 per cent; $Bi = 20$, 13 per cent. For small Biot numbers most of the resistance occurs at the wall and only a one-dimensional treatment is necessary. This can be obtained from the orthogonal collocation method using Eq. (5) with $N = 1$, or Eq. (6). As the Biot number increases, and radial dispersion becomes more important, the full two-dimensional treatment is necessary, Eq. (5), and N is increased as Bi increases.

Numerical computations

Parameter values used were $Bi = 1$ or 20, $\alpha = \alpha' = 1$, $\beta = 0.3$, $\beta' = 0.2$, $T_w = 0.92$ or 1, $R = (1 - c) \exp[\gamma - \gamma/T]$, $\gamma = 20$. These values lead to severe hot spots and represent extreme cases. For more practical cases the computational difficulties are relaxed, and fewer terms (N) and larger $M = 1/\Delta z$ are possible. The reaction rate expression was programmed to be zero when $c > 1$, since such a case represents a mathematical instability of no interest physically. For $Bi = 1$, $T_w = 0.92$ the radially-averaged temperature is plotted as a function of reactor length in Fig. 1. For this Biot number 75 per cent of the heat transfer resistance is at the wall and we expect the first approximation ($N = 1$) to give good results. The one-term Legendre solution predicts the peak average temperature within 2 per cent, and the second and higher approximations are identical on the scale of the graph. As expected the Jacobi one-term solution is a better first approximation.

The Eqs. (5) were integrated using the Runge-Kutta method and the Euler method. The Euler method is less accurate for the same step

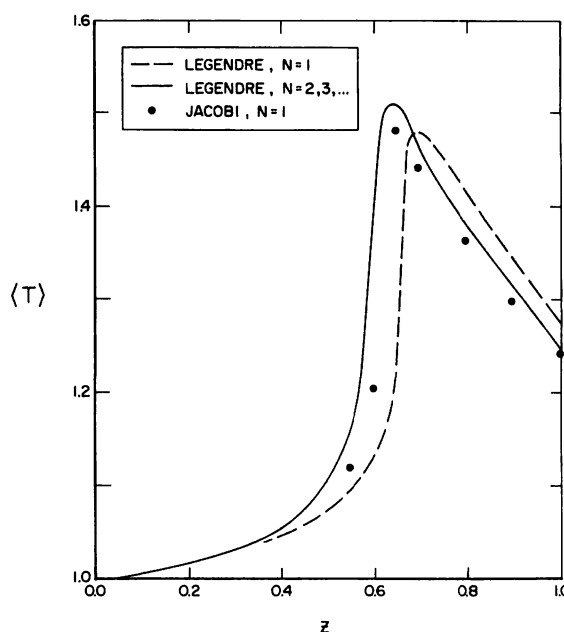


Fig. 1. Average temperature, $Bi = 1$, $T_w = 0.92$.

size but also faster since it evaluates the reaction rate expression only once per step rather than four times. The finite difference calculations were made using a Crank-Nicholson implicit method for the Laplacian operator and handled the reaction rate expression explicitly. False boundaries were used to insure the difference approximation was second order in Δr . The term N refers to the total number of radial grid points at which the rate expression was evaluated. For the finite difference solution this included the center point ($r = 0$) and the wall ($r = 1$). Computation time increases linearly with NM in both methods, since it is determined primarily by the number of times the exponential reaction rate is evaluated. The finite difference results were extrapolated to zero Δz keeping $\Delta z/\Delta r^2$ constant to establish the best finite difference estimate. Extrapolation to zero Δz keeping Δr^2 constant was less satisfactory since convergence had not yet been attained even for $N = 11$. For the collocation method, the results for a given N were extrapolated to zero Δz . For the Runge-Kutta method the largest stable Δz usually gave good results and little change

resulted as Δz was decreased. Since convergence in N was attained for the collocation method (to the accuracy reported here) no extrapolation in N was necessary.

The extrapolated collocation and finite difference solutions agree very well: the values of $T(1, 0.6)$ and $\langle c \rangle$ at $z = 0.4$ predicted by the two methods are within 0.2 and 0.001 per cent, respectively. Consider a set of finite difference calculations as all those having different Δr , Δz but the same $\Delta z/\Delta r^2$. The set is included in Table 1 if the values of $T(1, 0.6)$ and $\langle c \rangle$ at $z = 0.4$ for that set could be extrapolated as $\Delta z \rightarrow 0$ to give the exact answer within the tolerance specified.

Table 1. Comparison of collocation and finite difference methods for $Bi = 1$

Method	N	M	$\Delta z/\Delta r^2$	Computing time (sec)	Absolute error
Predict $T(1, 0.6)$ within 0.01†, exact value = 1.1564					
Legendre, Euler	3	200	—	0.45	0.01
Legendre, Euler	4	200	—	0.59	0.01
Legendre, Runge-Kutta	3	200	—	1.5	0.01
Finite difference‡	6	500	0.05	1.9	0.01
Legendre, Runge-Kutta	4	200	—	2.1	0.01
Legendre, Euler	5	1000	—	3.0	0.002
Legendre, Euler	6	1000	—	3.9	0.002
Finite difference	11	1000	0.10	6.4	0.008
Predict $\langle c \rangle$ at $z = 0.4$ within 1%; exact value = 0.17292					
Legendre, Euler‡	2	250	—	0.39	0.0017
Legendre, Runge-Kutta	2	100	—	0.64	0.0014
Legendre, Runge-Kutta	3	100	—	0.88	0.0011
Finite difference	6	400	0.063	1.5	0.0015
Finite difference‡	4	1000	0.009	2.5	0.0017

†When the inlet temperature is 300°C, an error in T of 0.01 represents an error of about 6°C.

‡Interpolated values.

Listed in Table 1 is the member of the set which has the smallest computation time, yet gives an answer within the tolerance specified. The collocation results are treated similarly, with the set defined as all calculations with the

same N . This procedure prevents undue bias against the finite difference results, which converge slowly with Δz , compared to the collocation method, so that if convergence in Δz is required (to some tolerance) large computation times are necessary for the finite difference results.

The results in Fig. 1 and Table 1 indicate that the collocation method with $N = 2$ is sufficiently accurate and that the collocation method is from two to four times faster than a finite difference method of equivalent accuracy. The computation times shown are for a CDC 6400 computer.

For $Bi = 20$, $T_w = 1.0$ we expect more terms are needed since the radial dispersion in the bed is more important. Figure 2 shows the radially-averaged temperature as a function of reactor length. The solutions for $N = 1$ give poor results so that designs based on a lumped parameter model would be considerably in error. The reason is illustrated in Fig. 3 which shows temperature profiles in the bed. As the hot spot is approached ($z = 0.5$) the temperature rises sharply in the center of the bed ($r = 0$) and a "thermal wave" moves out towards the boundary. The profile at $z = 0.5$ is concave and is poorly represented by a parabolic profile.

Shown in Fig. 3 are the values obtained with

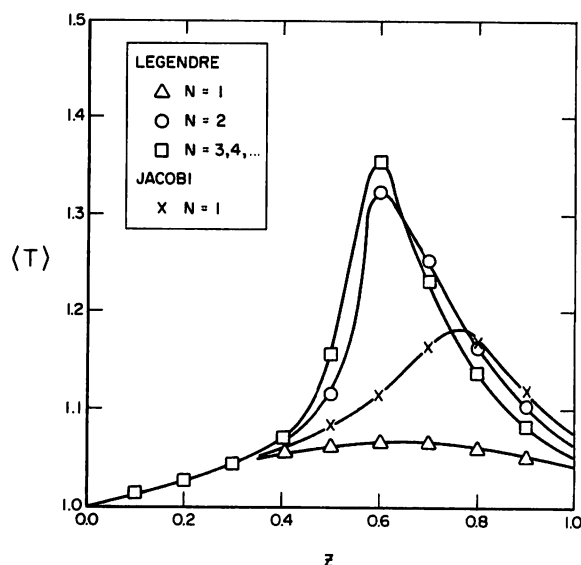


Fig. 2. Average temperature, $Bi = 20$, $T_w = 1.0$.

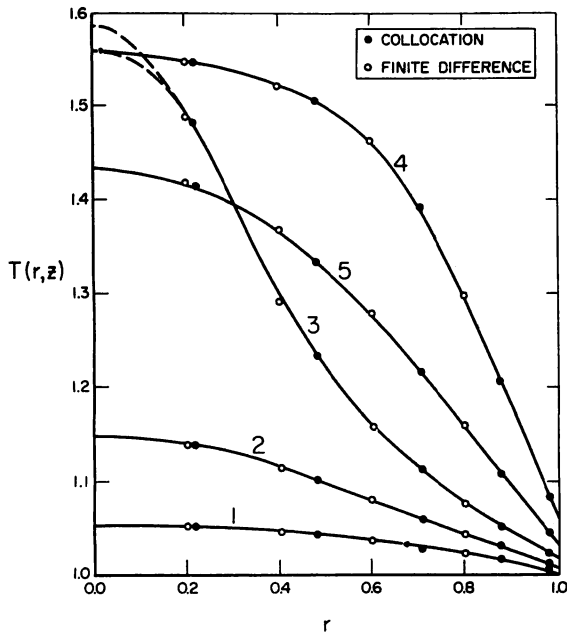


Fig. 3. Temperature profiles, $Bi = 20$, for $z = 0.2, 0.4, 0.5, 0.6, 0.7$ corresponding to 1-5.

the collocation ($N = 5$) and finite difference ($N = 11$) methods and there is good agreement. In the collocation method the solution is calculated at the collocation points, which are shown as black dots. The center ($r = 0$) is not a collocation point so that the center temperature is determined less accurately than the temperatures at collocation points. To find the center temperature we write Eq. (3) in an alternate form and evaluate it at the collocation points,

$$T_j = \sum_{i=1}^{N+1} d_i r_j^{2i-2}, j = 1, \dots, N+1. \quad (10)$$

The matrix $Q_{ji} = r_j^{2i-2}$ is inverted to find the coefficients d_i . The inverse is needed to calculate the matrixes A and B in Eq. (5) and is calculated only once for each N . The calculation of the center temperature then involves a matrix multiplication.

$$T(0, z) = d_1 = \sum_{j=1}^{N+1} [Q^{-1}]_{1j} T_j. \quad (11)$$

For $z = 0.5$ the center temperature is 2 per cent in error in the collocation method. The conver-

gence with N of the center temperature and average conversion at $z = 0.6$ is shown in Fig. 4. The phenomena illustrated there is true in general: in the collocation method a radially-averaged value converges with N very rapidly, whereas the convergence is slower for the solution at the collocation points and still slower for the center temperature. Results using Legendre polynomials converge faster than those using Jacobi polynomials. Keep in mind that the properties shown in Fig. 4 are very sensitive indicators of numerical error since the hot spot is at $z = 0.6$ and the average conversion rises rapidly from 0.4 at $z = 0.5$ to 0.9 at $z = 0.6$. Moving the hot spot very slightly in z would cause large changes in $T(0, 0.6)$ and $\langle c \rangle_{0.6}$ even though the change could not be discerned easily on a graph of these quantities versus z .

Comparison of collocation and finite difference calculations in Table 2 indicates that if one wants to calculate the average conversion at $z = 0.6$

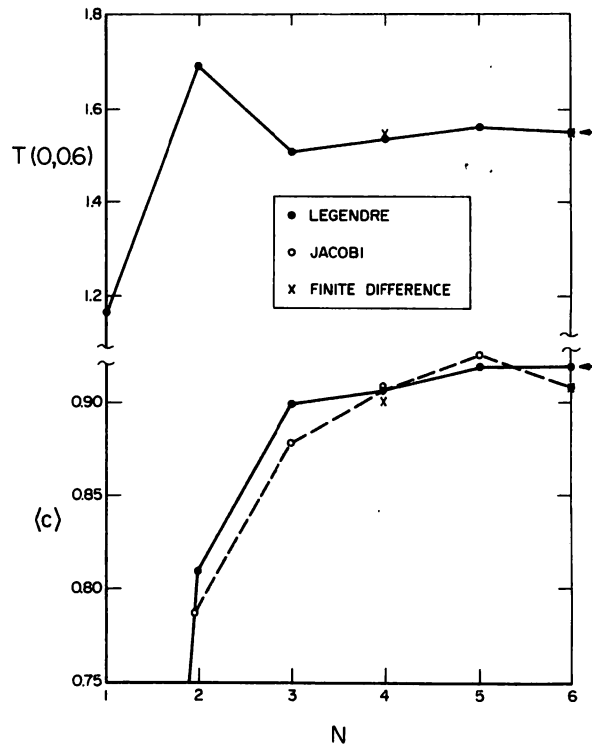


Fig. 4. Convergence of solutions with N . The arrow marks the finite difference result for $N = 11$.

Table 2. Comparison of collocation and finite difference methods for $Bi = 20$

Method	N	M	$\Delta z/\Delta r^2$	Computing time (sec)	Absolute error
Predict $\langle c \rangle$ at $z = 0.6$ within 1%, exact value = 0.919					
Legendre†	5	250	—	3.4	0.001
Finite difference	11	1000	0.10	6.5	0.010
Legendre†	6	500	—	8.3	0
Finite difference	11	2000	0.05	13.0	0.005
Predict $\langle c \rangle$ at $z = 0.6$ within 3%, exact value = 0.919					
Legendre†	3	200	—	1.6	0.020
Legendre†	4	200	—	2.1	0.015
Finite difference	4	1000	0.009	2.4	0.02
Finite difference	6	1000	0.025	3.4	0.02

†Runge-Kutta integration.

within 1 per cent, a collocation solution can be twice as fast and ten times as accurate or four times as fast and five times as accurate as a finite difference solution. If the tolerance is increased to 3 per cent the difference is not so marked: about $1\frac{1}{2}$ times as fast for the same accuracy. The integration in the z direction can be done using collocation as well[43], and this procedure is reported to be faster than the Runge-Kutta method used here[42].

Based on these comparisons it is clear that the orthogonal collocation method can give accurate answers to the mathematical model of a packed bed reactor, the method is an efficient numerical scheme, and converges rapidly. The number of terms needed in this application (which is a severe test) ranged from $N = 2$ for $Bi = 1$ to $N = 5$ for $Bi = 20$. It is clear from these calculations that McGreavy and Turner[32] obtained good agreement in their attempt to reduce the two-dimensional case (1) to a lumped parameter model primarily because they did calculations for a Biot number (their Nusselt number) of 2.

3. VELOCITY PROFILE MODEL

In a packed bed the velocity profile is flat near the center, rises to a peak near the wall and falls rapidly right at the wall[33, 38, 16, 9, 36].

This velocity profile introduces a radial variation in effective thermal conductivity and diffusivity [8, 11, 37, 10, 28, 36, 17, 16]. A model including these complications was used to assess their influence on the heat transfer and conversion predictions. Valstar[41] made computations using a velocity profile for a vinyl acetate reactor and found the radial variation important.

Several sources[37, 28, 36] suggest that the effective thermal conductivity at any radial position varies linearly with the local Reynolds number. The local Reynolds number, or velocity profile, is difficult to predict, however, especially in nonisothermal situations. Schertz and Bischoff [36] suggest a correlation based on the void fraction and viscosity, but their data were taken under conditions where the flow was probably laminar in the center of the tube and turbulent near the wall. Instead we use here the experimental data of Schwartz and Smith[38] taken under isothermal conditions, and assume the velocity profile would remain similar in the nonisothermal case. The velocity profiles, tabulated in Table 3, are for a 4-in. dia. tube packed with $\frac{5}{32}$ -in. dia. spheres ($d_p/d_t = 0.039$). Somewhat similar profiles were obtained experimentally for Reynolds numbers between 130 and 290[38].

Table 3. Velocity and effective thermal conductivity profiles

r	$G(r)/\langle G \rangle$	$k_e(r)/\langle k_e \rangle$
0.184	0.942	0.957
0.412	0.942	0.957
0.617	0.980	0.985
0.787	1.112	1.083
0.911	1.076	1.056
0.983	0.768	0.291
1.000	0.000	0.230

The profile is used here for $Re = 190$ in a reactor 80 in. long. The radial Peclet number for mass transfer is between 8 and 10[7, 17, 16, 36], and we use 10 here. The data of Schertz and Bischoff [36] suggest that the Peclet number for mass is constant even though the velocity is a function of radius. We use this relation, so that the diffusivity varies linearly with velocity.

$$Pe_m \equiv \frac{G(r)d_p}{\rho D_e(r)} = 10. \quad (12)$$

The effective thermal conductivity follows a relation of the form $k_e = k_e^0 + b Re$. The constant k_e^0 represents the static bed effective thermal conductivity and can be calculated using the methods of Yagi and Kunii[45], Kunii and Smith [27], or Baddour and Yoon[2]. The latter authors use a different method to calculate k_e within one-half particle diameter of the wall and they give experimental verification as well. The k_e at this position is smaller and accounts for added resistance to heat transfer at the wall. Thus it is not necessary to use a heat transfer coefficient to account for the same resistance. Baddour and Yoon's methods were used to obtain the following relations

$$k_e/k_f = 8.1 + 0.09 Re Pr \quad (13)$$

$$k_e/k_f = 6.9 + 0.01 Re Pr, \text{ within } \frac{1}{2}dp \text{ of wall} \quad (14)$$

and these were used with the local Reynolds number, $G(r)d_p/\mu$. The resulting thermal conductivity distribution is shown in Table 3. Physical properties were used for air at 300°C and assumed constant, although their variation with temperature could be easily included. The governing equations are a generalization of Eq. (1).

$$G(r) \frac{\partial c}{\partial z} = \alpha G \nabla^2 c + \alpha \nabla G \cdot \nabla c + \beta R$$

$$G(r) \frac{\partial T}{\partial r} = \alpha' k \nabla^2 T + \alpha' \nabla k \cdot \nabla T + \beta' R \quad (15)$$

$$T = T_w, \partial c / \partial r = 0 \quad \text{at } r = 1.$$

The collocation version of the same equations is

$$\begin{aligned} \frac{dc_j}{dz} = & \alpha \sum_{i=1}^{N+1} B_{ji} c_i + \frac{\alpha}{G_j} \left(\sum_{i=1}^{N+1} A_{ji} G_i \right) \\ & \times \left(\sum_{i=1}^{N+1} A_{ji} c_i \right) + \beta \frac{R_j}{G_j} \end{aligned}$$

$$\begin{aligned} \frac{dT_j}{dz} = & \alpha' \frac{k_j}{G_j} \sum_{i=1}^{N+1} B_{ji} T_i + \frac{\alpha'}{G_j} \left(\sum_{i=1}^{N+1} A_{ji} k_i \right) \\ & \times \left(\sum_{i=1}^{N+1} A_{ji} T_i \right) + \beta' \frac{R_j}{G_j} \end{aligned} \quad (16)$$

$$j = 1, \dots, N$$

$$T_{N+1} = T_w, \sum_{i=1}^{N+1} A_{N+1,i} c_i = 0$$

$$T_j(0) = 1.0, c_j(0) = 0.$$

Typical temperature and concentration profiles are shown for this model by the solid lines in Figs. 5 and 6. In the velocity profile model no heat transfer coefficient is needed at the wall since the increased resistance is accounted for

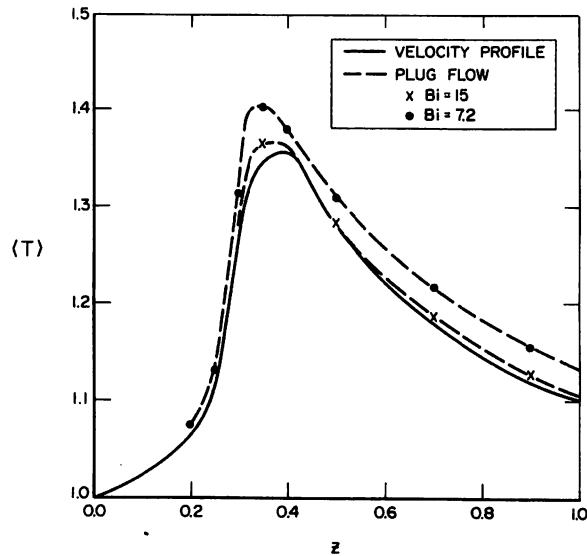


Fig. 5. Comparison of average temperature for velocity profile and plug flow models.

by the lower effective thermal conductivity given by Eq. (14). During the computations a Biot number was calculated.

$$Bi = \frac{k(1) \partial T / \partial r|_{r=1}}{T^* - T_w} \quad (17)$$

where T^* is the average temperature within

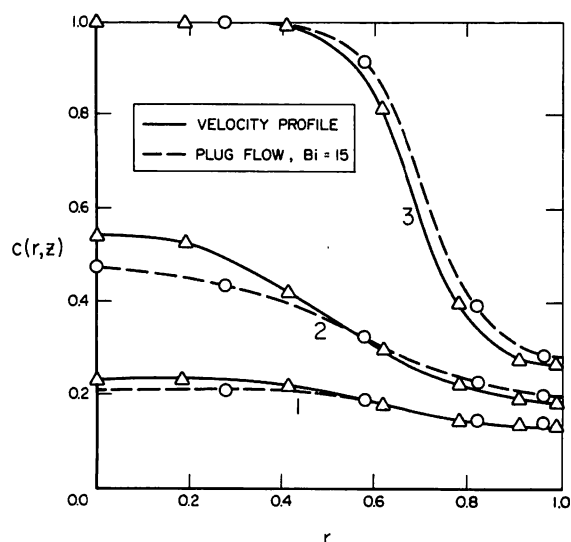


Fig. 6. Comparison of conversion profiles for velocity profile and plug flow models. $z = 0.20, 0.25, 0.30$ corresponds to 1-3.

one-half particle diameter of the wall. This is the distance over which the void fraction varies from 0.4 to 1.0 at the wall[6]. The predicted Biot number was 15 and varied only a few per cent down the bed. $Bi = 15$ was then used in the plug flow model, and the results are compared in Figs. 5 and 6. Pointwise comparisons are not to be expected since the two models are obviously different. Even so the comparisons are quite good. To test the sensitivity an additional calculation was made using $Bi = 7.2$ in the plug flow model, and the results do not compare nearly as well. The three correlations available [24, 47, 46] for Nusselt number of beds packed with spheres with small d_p/d_t give Biot numbers of 9.4, 8.2 and 6.6 respectively. Agreement with these correlations, based on experimental results, is not necessarily expected since the experiments are for a velocity profile in a nonisothermal situation whereas the calculations use a velocity profile from an isothermal case. The results do indicate that the velocity profile model can be used to predict the heat transfer coefficient needed in the plug flow model. Further work is needed to predict the velocity profile and compare to experimental correlations. These results

can be contrasted to those of Valstar[41], who used a relation of the form (13) *plus* a heat transfer coefficient. Thus the resistance at the wall was accounted for in two ways, and the plug flow and velocity profile model did not agree as well as in the case studied here.

4. CONCLUSIONS

The orthogonal collocation method is an efficient numerical method for solving the equations governing packed bed reactors with radial gradients. The number of terms needed in the expansion increases with increasing Biot number. The velocity profile model predicts a Biot number which can be used in the plug flow model to give similar temperature and conversion predictions.

Acknowledgments—This work was supported in part by NSF Grant GK-3083. The author thanks Professor L. N. Johanson for several stimulating discussions related to this work.

NOTATION

a_i	coefficient in Eq. (3)
A_{ji}	matrix representing d/dr
Bi	Biot number, $h_w R/k_e$
B_{ji}	matrix representing ∇^2
c	conversion
c_p	heat capacity per unit mass
$C_{(i)}$	normalization constant in Eq. (4)
d_p	particle diameter
d_i	coefficient in Eq. (10)
d_t	tube diameter
D_e	effective diffusivity
E	activation energy
G	mass flow rate based on area of empty reactor
h_w	heat transfer coefficient
$-\Delta H$	heat of reaction
k	effective thermal conductivity, normalized with respect to $\langle k_e \rangle$
k_e	effective thermal conductivity
k_e^0	static bed effective thermal conductivity
k_f	fluid thermal conductivity
k_0	reaction rate
L	length of reactor
M	$1/\Delta z$

N	number of interior collocation points; for finite difference results $1 + 1/\Delta r$	U	heat transfer coefficient, lumped parameter model
Nu	Nusselt number, $h_w d_p/k_f$	w	weighting function in Eq. (4)
Nu'	$2UL/Gc_p R = St2L/R$	z	length
P_i	polynomial of degree i in r^2	Greek symbols	
Pe_h	Peclet number for heat transfer, $c_p G d_p/k_e$	α	$Ld_p/R^2 Pe_m$
Pe_m	Peclet number for mass transfer, $G d_p/\rho D_e$	α'	$Ld_p/R^2 Pe_h$
Pr	Prandtl number, $C_{p\mu}/k_f$	β	Damköhler Group I, $k_0 L/G$
Q_{ji}	r_j^{2i-2}	β'	Damköhler Group III, $-\Delta H k_0 c_0 L / (c_p G T_0)$
r	radius	γ	$E/\bar{R}T_0$
R	radius of reactor	δ	Kronecker delta
Re	Reynolds number, $G d_p/\mu$	ρ	density
\hat{R}	gas constant	μ	viscosity
St	Stanton number, U/Gc_p	Subscripts	
T	temperature (dimensionless)	j	value at collocation point
T_0	reference temperature, taken as inlet temperature	o	reference value
T_w	external wall temperature	$\langle \rangle$	radial average, $2 \int_0^1 () r dr$
T^*	average temperature with $\frac{1}{2}d_p$ of wall		

REFERENCES

- [1] AMES W. F., *Nonlinear Partial Differential Equations in Engineering*. Academic Press 1965.
- [2] BADDOUR R. F. and YOON C. Y., *Chem. Engng Prog. Symp. Ser.* No. 32, 1961 57 35.
- [3] BARKELEW C. H., *Chem. Engng Prog. Symp. Ser.* No. 25, 1959 55 37.
- [4] BEEK J., *Adv. Chem. Engng* 1962 3 223.
- [5] BEEK J., Jr. and SINGER E., *Chem. Engng Prog. Symp. Ser.* No. 47, 1951 5 534.
- [6] BENENATI R. F. and BROSILOW C. B., *A.I.Ch.E.Jl* 1962 8 359.
- [7] BERNARD R. A. and WILHELM R. H., *Chem. Engng Prog.* 1950 46 233.
- [8] BUNNELL D. G. *et al.*, *Ind. Engng Chem.* 1949 41 1977.
- [9] CAIRNS E. J. and PRAUSNITZ J. M., *Ind. Engng Chem.* 1959 51 1441.
- [10] CALDERBANK P. H. and POGORSKI L. A., *Trans. Instn chem. Engng* 1957 35 195.
- [11] COBERLY C. A. and MARSHALL W. R., *Chem. Engng Prog.* 1951 47 141.
- [12] COLLATZ L., *The Numerical Treatment of Differential Equations*. Springer-Verlag, Berlin 1960.
- [13] COURANT R. and HILBERT D., *Methods of Mathematical Physics*, Vol. 1. Interscience 1953.
- [14] CRANDALL S. H., *Engineering Analysis*. McGraw-Hill 1956.
- [15] CRIDER J. E. and FOSS A. S., *A.I.Ch.E.Jl* 1965 11 1012.
- [16] DORWEILER V. P. and FAHIEN R. W., *A.I.Ch.E.Jl* 1959 5 139.
- [17] FAHIEN R. W. and SMITH J. M., *A.I.Ch.E.Jl* 1955 1 28.
- [18] FERGUSON N. B. and FINLAYSON B. A., *Chem. Engng J.* 1970 327.
- [19] FINLAYSON B. A., *Br. Chem. Engng* 1969 14 53, 179.
- [20] FINLAYSON B. A., *SIAM J. Num. Anal.* No. 2, 1971 8.
- [21] FINLAYSON B. A. and SCRIVEN L. E., *Appl. Mech. Rev.* 1966 19 735.
- [22] FROMENT G. F., *Chem. Engng Sci.* 1962 17 849.
- [23] FROMENT G. F., *Ind. Engng Chem.* No. 2, 1967 59 18.
- [24] HANRATTY T. S., *Chem. Engng Sci.* 1954 3 209.
- [25] HLAVACEK V., *Ind. Engng Chem.* No. 7, 1970 62 8.
- [26] HOELSCHER H. E., *Chem. Engng Sci.* 1957 6 183.
- [27] KUNII D. and SMITH J. M., *A.I.Ch.E.Jl* 1960 6 71.
- [28] KWONG S. S. and SMITH J. M., *Ind. Engng Chem.* 1957 49 894.
- [29] LIVBJERG H., ANTONSEN P. and VILLADSEN J., *Third CHISA Congr.*, Marianske Lazne 1969, paper A4.7.
- [30] MCGOWIN C. R. and PERLMUTTER D. D., *Chem. Engng Sci.* 1971 3 275.
- [31] MCGOWIN C. R. and PERLMUTTER D. D., To be published in *A.I.Ch.E.Jl* 1971.
- [32] MCGREAVY C. and TURNER K., *Can. J. Chem. Engng* 1970 48 200.
- [33] MORALES M., SPINN C. W. and SMITH J. M., *Ind. Engng Chem.* 1951 43 225.

- [34] PARIS J. R. and STEVENS W. F., *Can. J. Chem. Engng* 1970 **48** 100.
- [35] QUINTON J. H. and STORROW J. A., *Chem. Engng Sci.* 1956 **5** 245.
- [36] SCHERTZ W. W. and BISCHOFF K. B., *A.I.Ch.E.Jl* 1969 **15** 597.
- [37] SCHULER R. W., STALLINGS V. P. and SMITH J. M., *Chem. Engng Prog. Symp. Ser. No. 4*, 1952 **48** 19.
- [38] SCHWARTZ G. S. and SMITH J. M., *Ind. Engng Chem.* 1953 **45** 1209.
- [39] STEWART W. E. and VILLADSEN J. V., *A.I.Ch.E.Jl* 1969 **15** 28.
- [40] STROUD A. H. and SECREST D., *Gaussian Quadrature Formulas*. Prentice Hall 1966.
- [41] VALSTAR J. M., Ph.D. Thesis, Technische Hogeschool, Delft 1969.
- [42] VILLADSEN J., *Selected Approximation Methods for Chemical Engineering Problems*, Institutet for Kemiteknik Numerisk Institut, Danmarks Tekniske Højskole 1970.
- [43] VILLADSEN J. and SØRENSEN J. P., *Chem. Engng Sci.* 1969 **24** 1337.
- [44] VILLADSEN J. V. and STEWART W. E., *Chem. Engng Sci.* 1967 **22** 1483.
- [45] YAGI S. and KUNII D., *A.I.Ch.E.Jl* 1957 **3** 373.
- [46] YAGI S. and KUNII D., *A.I.Ch.E.Jl* 1960 **6** 97.
- [47] YAGI S. and WAKAO N., *A.I.Ch.E.Jl* 1959 **5** 79.

Résumé—Les équations gouvernant un réacteur à couche garnie, avec des degrés de température et de concentration radiaux, sont résolues par la méthode de collocation orthogonale. Il est démontré que cette méthode est plus rapide et plus précise que des calculs de différence limitée. Avec la méthode de collocation orthogonale, il est aisé d'étendre les modèles unidimensionnels (paramètre groupé) aux modèles bidimensionnels nécessaires quand les degrés de concentration et de la température sont importants.

Le modèle bidimensionnel est nécessaire pour des nombres de Biot élevés, $h_w R/k_e$, dans lequel h_w est le coefficient de transfert de chaleur à la paroi, R le rayon du tube et k_e la conductivité thermique effective. Pour des nombres de Biot inférieurs à 1, 75 pour cent de la résistance au transfert de chaleur se situe à la paroi et le procédé unidimensionnel (paramètre groupé) donne de bons résultats.

Les calculs sont illustrés à la fois pour la vitesse d'un courant tampon et à variation radiale. Dans ce dernier cas, les courbes de diffusivité et de conductivité thermique effectives sont induits par la courbe de vitesse. Les calculs utilisant la courbe de vitesse prédisent un coefficient de transfert de chaleur qui sert aux modèles à écoulement tampon. Un accord satisfaisant est obtenu entre ces modèles.

Zusammenfassung—Die Gleichungen, die einen Füllkörperreaktor mit radialen Temperatur- und Konzentrationsgradienten regeln werden unter Verwendung der orthogonalen Zusammenstellungsmethode gelöst. Es wird gezeigt, dass diese Methode schneller und genauer ist als die endlichen Differenzberechnungen. Bei Verwendung der orthogonalen Zusammenstellungsmethode ist es ohne weiteres möglich eindimensionale (zusammengefasste Parameter) Modelle auf die zweidimensionalen Modelle zu erweitern, die erforderlich sind wenn radiale Temperatur und Konzentrationsgradienten eine Rolle spielen.

Das zweidimensionale Modell ist notwendig für grosse Biot Zahlen, $h_w R/k_e$, worin h_w der Wärmeübertragungskoeffizient der Wand ist, R der Rohrradius, und k_e effektive Wärmeleitfähigkeit. Für Biot Zahlen von unterhalb eins, befinden sich fünfundsechzig Prozent des Widerstands gegen Wärmeübertragung an der Wand, und eine eindimensionale (zusammengefasster Parameter) Behandlung gibt gute Resultate.

Es werden Berechnungen für Pfropfströmung sowie für radial variierende Geschwindigkeit angeführt. Im letzteren Falle verursacht das Geschwindigkeitsprofil effektive Wärmeleitfähigkeits- und Diffusionsvermögensprofile. Die unter Verwendung des Geschwindigkeitsprofils ausgeführten Berechnungen sagen einen Wärmeübertragungskoeffizienten voraus, der in dem Pfropfströmungsmodell verwendet wird. Es wird gute Übereinstimmung unter den Modellen erhalten.