The Solution of a Boundary Value Problem in Reactor Design using Galerkin's Method

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Galerkin's technique for the approximate solution of ordinary and partial differential equations has been described by several authors (*1*). However, its application to chemical engineering problems has been rather limited (*2, 3, 4*). Since the method serves as a valuable alternate to conventional numerical techniques, it is worthy of further popularization and exploitation.

In the work presented here, the technique was applied to the problem of a tubular reactor in which axial diffusion is superimposed upon a one-dimensional flow. Several solutions to this problem have been published, providing a basis of comparison of the method with conventional analytical and numerical techniques.

The differential equation and associated boundary conditions were first investigated by Danckwerts (*5*) for the linear case of first-order kinetics. The boundary conditions have also been studied in detail (*6, 7*). For nonlinear kinetics, no analytical solutions have appeared and recourse has been made to numerical integrations. Bischoff and Levenspiel (*8*) have calculated results for a second-order reaction and these are summarized in Levenspiel's text (*9*). Fan and Bailie (*10*) have also calculated concentration profiles for kinetics of order *n*, for $n = \frac{1}{4}, \frac{1}{2}$, 2, and 3. Limited results for $n = 2$ have also appeared in the work of Lee (*11*).

For nonlinear kinetics it is difficult to account for the effects of the three physical parameters of the problem; the reaction rate group, the order of kinetics, and the axial Peclet number. For nonlinear kinetics one must either numerically integrate the differential equation or interpolate by using the limited curves of Levenspiel or Fan and Bailie.

The use of Galerkin's method yields approximate solutions which are both easier to utilize and more clearly show parameter behavior. Simple solutions were found for integral reaction orders. For general n^{th} order kinetics the problem is reduced to the solution of a single nonlinear algebraic equation. These approximate solutions are in excellent agreement with available results for wide ranges of the parameters of the problem. More complex Galerkin solutions in terms of additional parameters converge to published results, but here recourse must be made to digital computer solutions.

MATHEMATICAL STATEMENT OF THE PROBLEM

In dimensionless form, the differential equation and boundary conditions for a one-dimensional reactor are

$$\frac{1}{N_{Pe}} \cdot \frac{d^2y}{dz^2} - \frac{dy}{dz} - Ry^n = 0 \tag{1}$$

$$1 = y - \frac{1}{N_{Pe}} \cdot \frac{dy}{dz} \quad \text{at} \quad z = 0 \tag{2}$$

$$\frac{dy}{dz} = 0 \quad \text{at} \quad z = 1 \tag{3}$$

where *y* and *z* are the fraction of reactant remaining and the fractional distance into the reactor, respectively. Generally, the conversion of reactant at the outlet, $f = 1 - y(1)$, is desired and is a function of three parameters: (a) the axial Peclet Number, N_{Pe}; (b) a reaction rate group, *R*; and (c) the reaction order, *n*.

APPROXIMATE METHOD OF SOLUTION

In Galerkin's technique a solution, y_N, is assumed as a set of prespecified functions and associated parameters which must be determined. The set of functions $\phi_i(z)$ are chosen and the parameters are related so that all of the boundary conditions can be satisfied for all values of the parameters a_i. If the set ϕ_i are chosen as $(z-1)^{i-1}$ the Galerkin approximation in terms of *N* parameters is

$$y_N = \sum_{i=1}^{N} a_i\phi_i(z) = \sum_{i=1}^{N} a_i(z-1)^{i-1} \tag{4}$$

The second boundary condition (3) is satisfied if $a_2 = 0$ and the first condition (2) is satisfied if the a_i are related by

$$\sum_{i=1}^{N} (-1)^{i-1}\, a_i \left[1 + \frac{i-1}{N_{Pe}} \right] = 1 \tag{5}$$

The additional conditions needed to determine the remaining parameters are derived by requiring that the error in the fit of the assumed solution to the differential equation, $\epsilon(a_i, z)$, be orthogonal to each of the first $N - N_{BC}$ approximating functions, ϕ_i, over the domain of interest.

$$\int_v \epsilon(y_N)\, \phi_i dv = 0 \qquad i = 1, 2, \ldots, N - N_{BC} \tag{6}$$

For the problem under consideration, Galerkin's method requires the assumed solution to satisfy a material balance about the reactor, for if the differential equation is integrated and the boundary conditions are applied:

$$1 - y(1) = R \int_0^1 y^n dz \tag{7}$$

Equation (7) is a material balance, the left-hand side representing reactant input minus output, the right-hand side, conversion by reaction. If the first Galerkin function, ϕ_1, is chosen to be a constant, the first Galerkin integral condition reduces to (7) and the approximation satisfies a material balance.

An approximation of the form of Equation (4) is first assumed in terms of three arbitrary parameters. Satisfying boundary conditions (2) and (3) yields:

$$a_2 = 0 \tag{8}$$

$$a_3 = (1 - a_1)/\lambda \qquad \lambda = 1 + 2/N_{Pe} \tag{9}$$

The assumed approximation $y_3(z)$, is a quadratic in *z* in terms of a single parameter a_1 and is equivalent to a Taylor series expansion of the solution about the reactor outlet ($z = 1$). The free parameter a_1 is determined using the first Galerkin condition (6):

$$1 - a_1 = R \int_0^1 [a_1 + a_3\Psi^2]^n \, d\Psi \tag{10}$$

Unfortunately, Equation (10) does not appear to be integrable in closed form for general *n*. Simple solutions can be found, however, for both integer and half-integer values of *n* and these are considered later in more detail.

For general kinetics, in the limiting case of a well-mixed reactor ($N_{Pe} \to 0$), Equation (10) reduces to the exact result and the quadratic approximation is a flat profile, namely $y_3 = a_1 =$ constant. The assumed approximation

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thus approaches the exact solution as $N_{Pe} \rightarrow 0$, for all values of the reaction order n.

COMPARISON OF APPROXIMATIONS WITH PREVIOUS RESULTS

The results using the three parameter Galerkin approximations for various reaction orders will now be compared with available results to establish the accuracy of the approximation. For $n = 0$ and $n = 1$ the solutions for outlet conversion can be expressed explicitly:

$$n = 0: \qquad f = R \tag{11}$$

$$n = 1: \qquad f = R/(R + W) \tag{12}$$

where

$$W = \frac{1 + \frac{N_{Pe}}{2}\left(1 - \frac{R}{3}\right)}{1 + \frac{N_{Pe}}{2}} \tag{13}$$

For $n = 2$ or $n = 3$ the results are obtained as the roots of a quadratic or cubic equation, respectively:

$$n = 2: \quad \left(\lambda^2 - \frac{2}{3}\lambda + \frac{1}{5}\right) a_1^2 + \left(\frac{1}{R}\lambda^2 + \frac{2}{3}\lambda - \frac{2}{5}\right) a_1 + \left(-\frac{1}{R}\lambda^2 + \frac{1}{5}\right) = 0 \tag{14}$$

$$n = 3: \quad \left(\lambda^3 - \lambda^2 + \frac{3}{5}\lambda - \frac{1}{7}\right) a_1^3 + \left(\lambda^2 - \frac{6}{5}\lambda + \frac{3}{7}\right) a_1^2 + \left(\frac{1}{R}\lambda^3 + \frac{3}{5}\lambda - \frac{3}{7}\right) a_1 + \left(-\frac{1}{R}\lambda^3 + \frac{1}{7}\right) = 0 \tag{15}$$

$n = 0$

For zero-order kinetics, conversion is independent of mixing, and the Peclet number does not appear in the solution. In this case the quadratic approximation yields the exact solution for all parameter values.

$n = 1$

When compared with the analytical solution for first-order kinetics (5), the approximate solution predicts conversion accurately for cases approaching complete mixing ($N_{Pe} \rightarrow 0$) and as the Peclet number increases ($N_{Pe} \rightarrow \infty$) the approximation gives good agreement for R small ($< \sim 1$), or for conversions less than about 60%.

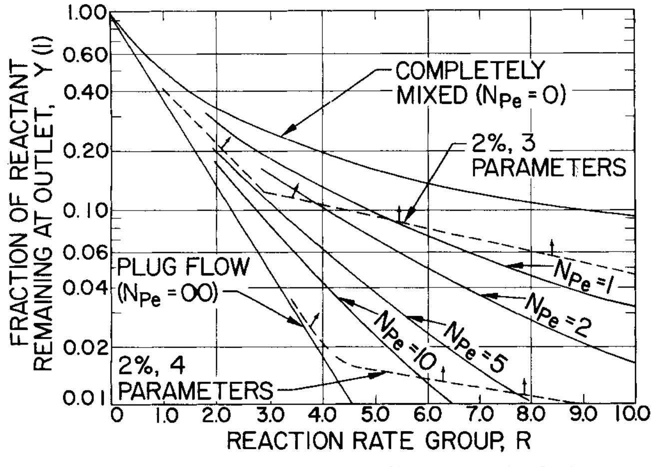

Fig. 1. First-order reaction, regions of 2% accuracy for 3, 4 parameter Galerkin approximations.

Calculations comparing the approximation with the analytical solution are summarized in Figure 1 which is a plot of $1 - f$ vs. R for various degrees of mixing, N_{Pe}. Shown is the limiting curve above which the three-parameter solution predicts the absolute level of conversion to better than 2% ($N_{Pe} < \sim 2$, for conversions up to about 90%). For $N_{Pe} \sim 10$, the accuracy falls to about 5% at the 90% conversion level. The approximation predicts f to about 2% when the product $N_{Pe}R < \sim 4$.

The above approximation contains only three free parameters and utilizes only one Galerkin condition. For a four-parameter approximation an additional Galerkin condition is required and results in three linear algebraic equations for the parameters. The outlet conversion can be expressed in the form of Equation (12) with a modified expression for W.

$$W = \frac{1 + \frac{1}{2}N_{Pe}\left(1 - \frac{2}{15}R\right) + N_{Pe}^2\left(1 - \frac{2}{5}R + \frac{1}{20}R^2\right)}{1 + \frac{1}{2}N_{Pe}\left(1 + \frac{1}{5}R\right) + N_{Pe}^2\left(1 + \frac{1}{10}R\right)} \tag{16}$$

Shown in Figure 1 is the greatly expanded region for which the four-parameter solution is accurate to 2% for predicting the absolute level of conversion. In the limit of plug flow, for small R, the four-parameter approximation is accurate to order R^2 in the prediction of f, whereas the three-parameter solution is accurate only to order R.

The addition of a fifth free parameter again greatly expands the range over which the approximation is accurate. In this case, all points within the 2% accuracy region of the four-parameter solution are now accurate to $< 0.2\%$, and the region of 2% accuracy is greatly expanded.

$n = 2$

For second-order kinetics, no analytical solution to the differential equation has been found in the literature. Although limited results have been given by Fan and Bailie (*10*), Levenspiel and Bischoff (*8*), Lee (*11*), and Lapidus (*12*), it is useful to have an equation for rapid calculation or interpolation. Using the quadratic Galerkin approximation, the solution is obtained from the roots of a quadratic Equation (14). This solution is exact in the limit of complete mixing and is accurate to order R in the prediction of f in the limit of plug flow.

By comparing Equation (14) with the results of Fan and Bailie for $R = 0.10$, the maximum error in the reactant concentration profile is only 2% for any value of N_{Pe}. The detailed concentration profile is accurately predicted (2%) when the product $N_{Pe}R < \sim 5$. Approximation (14) not only accurately predicts the outlet conversion, but the details of the concentration profile as well, for most of the values given by Fan and Bailie.

The results of Fan and Bailie were presented graphically and hence a detailed quantitative comparison is not possible. Recently, however, Lee (*11*) published a limited set of values in which five significant figures were given. For the case presented by Lee, the outlet conversion is predicted to about two significant figures by the three parameter Galerkin approximation, and to at least five significant figures by a six parameter approximation.

$n = 3$

For third-order kinetics in the limit of plug flow, approximation (15) is correct to order R in the prediction of outlet conversion. A comparison with the results of Fan and Bailie shows that the approximation predicts the detailed concentration profiles well when $N_{Pe}R < 5$.

APPROXIMATIONS FOR GENERAL REACTION ORDER, *n*

The integral appearing in the three-parameter approximation, Equation (10), can be analytically evaluated when $n = M/2$ or $n = M$, where M is an integer. For integer n, the resultant equation is an n^{th} order polynomial in a_1 which can be solved using the techniques for finding the roots of a polynomial.

For values of n for which the integral in (10) cannot be expressed analytically, additional approximations can be made. If the concentration through the reactor is nearly uniform (as in a well-mixed reactor or in one with low conversion) the integral can be expanded using the binomial theorem and neglecting higher order terms in the integral.

$$1 - a_1 = R\, a_1^n \left[1 + \frac{n}{3\lambda} \frac{1-a_1}{a_1} \right] \qquad (17)$$

Note that Equation (17) is the solution for a well-mixed reactor with the addition of the term in brackets on the right-hand side.

Another expansion of Equation (10) is obtained by applying the trapezoidal rule to the integral.

$$a_1^n + \left[a_1 + \frac{1-a_1}{\lambda} \right]^n = \frac{2}{R} (1 - a_1) \qquad (18)$$

Solutions to this equation can be readily obtained using iterative techniques such as the Newton-Raphson procedure. For $n = \frac{1}{2}$, a comparison with Fan and Bailie's results show that although the details of the concentration profile are slightly in error, the final level of concentration is predicted to better than 1% for all values given by Fan and Bailie.

APPROXIMATIONS WITH MORE PARAMETERS

The three parameter approximations derived above require the solution of a single algebraic equation of n^{th} order. This provides a good first approximation to the exact solution in a simple format. In those cases where increased accuracy is required, additional parameters and conditions must be imposed.

For N parameters, the Galerkin approach requires the solution of a set of $N - 2$, n^{th} order algebraic equations. This is accomplished on a digital computer using a bootstrap technique. That is, for given values of n, N_{Pe}, and R, a starting solution is first calculated using a three-parameter approximation. This solution is then used as the starting point for an iterative Newton-Raphson procedure to find the additional parameter in a four-parameter approximation. The resulting solution is then used to start the five-parameter iterations, etc. As is well-known, the Newton-Raphson procedure converges rapidly when the assumed solution is close to the exact result. Calculations generally converged to five significant figures in less than ten iterations using this technique.

CONCLUSIONS

What advantages are there in using the Galerkin technique for the solution of partial or ordinary differential equations when many numerical integration schemes exist? Firstly, there is the advantage of having an alternate method of solution available since conventional numerical methods often experience difficulties particularly for partial differential equations. The Galerkin method does possess a significant advantage since the results are expressed in an analytical format in terms of only a few parameters. This often provides greater physical insight into a problem than a tabulation of numerical results. Interpolation or extrapolation is also generally simpler and more accurate. In simulation work an analytical format can also permit a significant reduction in computer storage requirements.

Two areas of research will have increasingly significant effects on future applications of the Galerkin technique.

Setting up the Galerkin equations can entail an excessive amount of algebraic manipulation, particularly if a large number of parameters are employed. Developments in the area of symbolic manipulative compilers (*13*) will permit these operations to be done conveniently by computer.

After the Galerkin equations are formed, it is necessary in general to obtain solutions to a set of nonlinear equations. Developments in the area of mathematical programming (nonlinear optimization) will also exert an important influence on the utility of Galerkin's method. As mentioned previously, a boot-strap approach using the Newton-Raphson procedure worked well in the problem discussed here but, more sophisticated methods may be required in other applications.

NOTATION

a_i = arbitrary parameter
C = reactant concentration
D = axial diffusion coefficient
f = fractional conversion of reactant at reactor outlet
k = reaction rate constant
L = length of reactor
N = number of arbitrary parameters
N_{BC} = number of boundary conditions
N_{Pe} = axial Peclet number = UL/D
n = order of reaction
R = reaction rate group = $kLCo^{n-1}/U$
U = axial velocity
V = domain of interest for differential equation
W = parameter in Equation (12)
x = dimensional distance into reactor
y = dimensionless concentration = C/C_o
y_N = Galerkin approximation to y in terms of N parameters
z = dimensionless distance into reactor = x/L

Greek Leters

ϵ = error in the fit of approximation to the differential equation
λ = parameter defined by Equation (9)
ϕ_i = arbitrary function in Galerkin approximation

LITERATURE CITED

1. Kantorovich, L. V., and V. I. Krylow, "Approximate Methods of Higher Analysis, p. 258, Interscience, New York (1958).
2. Finlayson, B. A., and L. E. Scriven, *Appl. Mech. Rev.*, **19**, 735 (1966).
3. Snyder, L. J., T. W. Spriggs, and W. E. Stewart, *AIChE J.*, **10**, 535 (1964).
4. Hamielec, A. E., T. W. Hoffman and L. L. Ross, *ibid.*, **13**, 212, (1967).
5. Danckwerts, P. V., *Chem. Eng. Sci.*, **2**, 1 (1953).
6. Wehner, J. F., and R. H. Wilhelm, *ibid.*, **6**, 89 (1956).
7. Pearson, J. R. A., *ibid.*, **10**, 281 (1959).
8. Levenspiel, O., and K. B. Bischoff, *Ind. Eng. Chem.*, **51**, 1431 (1959).
9. ———, "Chemical Reaction Engineering," p. 280, John Wiley, New York, (1962).
10. Fan, L. T., and R. C. Bailie, *Chem. Eng. Sci.*, **13**, 63 (1960).
11. Lee, E. S., *ibid.*, **21**, 183 (1966).
12. Lapidus, L., "Digital Computation for Chemical Engineers," McGraw Hill, New York (1962).
13. Sammet, J. E., "Advances in Computers," Vol. 8, Academic Press, New York (1967).