AIChE Symposium Series
No. 323, 96, ~~176-191~~
176-191 (2000)
M.F. Malone & J. Trainham (ed)

REACTOR/TRANSPORT MODELS FOR DESIGN: HOW TO TEACH STUDENTS & PRACTITIONERS TO USE THE COMPUTER WISELY

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Abstract

As computer-aided design becomes more prevalent in the process industry, it is essential that graduating engineers have the breadth to know the capabilities of CAD as well as the skepticism to interpret computer results wisely. Current day students are caught between an educational system that focuses on analytical solutions to simplified problems and CAD programs that provide generality and power that can be overwhelming. Students are only too willing to accept computer results at face value, which could be disastrous in a commercial environment. An important aspect of current day education should be to instill in students and practitioners a critical examination of results from their CAD program. This paper presents experience with CAD tools in an educational environment as well as an industrial environment.

Keywords

Transport, Chemical Reactor, Bifurcations, MATLAB, FIDAP, CRDT, Industrial Radiant Furnace

Introduction

The question is broader than educational, however. There is a growing body of applied mathematicians, too, who are trying to quantify or analyze the risk of using models (Wheeler, 1999). They are mainly looking at the risk of models (like global warming) where there may be no way to test them, but the models are used for public policy decisions. There are several questions that must be asked of models:

1. What is the risk of leaving out some phenomena that needs to be included? Chemical engineers minimize this by comparing their predictions to experimental results.

2. Supposing the model includes the appropriate phenomena, there are four basic questions to answer:

a. Is the discretization (or method) correct, so that solutions converge to the right answer? There can be false bifurcations and the shocks can be in the wrong place, as shown below.

b. How sensitive are the results to the data used? (i.e. do a sensitivity analysis)

c. How accurate are the results? (error assessment)

d. Did you make any mistakes? This is a hard one to get students to worry about; some of them have a tendency to throw things together, say they are done, and move on to something else.

This paper gives examples of how these questions are answered primarily for applications to reactor and transport models. Examples will be taken from problems solved mostly by undergraduates using (i) MATLAB or Excel, as the 'numerical analysis engine'; (ii) a special reactor program, the Chemical Reactor Design Tool, CRDT; (iii) application of CRDT to an industrial design problem of a radiant furnace; and (iv) computational fluid dynamics (CFD). In order to keep the paper within reasonable bounds, all questions will not be answered for each example.

Undergraduate transport problems solved with EXCEL.

The first example is for heat transfer in a cylinder; the thermal conductivity depends on temperature, and there is internal heat generation. The problem statement is:

$$\frac{1}{r}\frac{d}{dr}\left[rk(T)\frac{dT}{dr} \right] = -2G(1-r^2)$$

$$k = k_0 + a(T - T_0)$$

$$\left.\frac{dT}{dr}\right|_{r=R} = 0, \quad T = T_0 \text{ at } r = R$$

We pose two questions: what is the heat flux at the boundary of the cylinder? What is the peak temperature? The first question is answered with a little thought: at steady state all the energy generated inside has to be coming out. In this case, the heat generation rate varies with position, so a simple integral must be evaluated. This questions illustrates an important lesson: think first! The second question can't be answered as easily. We solve it here with the finite difference method, but we do the programming in steps to make it easier to check our results.

The non-dimensional version of the problem is

$$\frac{1}{r'}\frac{d}{dr'}\left[r'(1+a'\theta)\frac{d\theta}{dr'} \right] = -2G'(1-r'^2)$$

$$\left.\frac{d\theta}{dr'}\right|_{r'=0} = 0, \quad \theta(1) = 1$$

Next the primes are dropped for convenience. There are various ways this equation can be solved; here we differentiate it and collect terms.

$$(1+a\theta)\left[\frac{d^2\theta}{dr^2} + \frac{1}{r}\frac{d\theta}{dr} \right] + a\left[\frac{d\theta}{dr} \right]^2 = -2G(1-r^2) \quad (1)$$

A special equation is needed at the origin, since the radial position goes to zero there. We use l'Hospital's Rule

$$\lim_{r\to 0}\frac{1}{r}\frac{d\theta}{dr} = \frac{d^2\theta}{dr^2}(0)$$

and get a different equation for the first node.

$$(1+a\theta)\,2\left.\frac{d^2\theta}{dr^2}\right|_{r=0} = -2G$$

If the finite difference method is applied to Eqn. (1) we get

$$(1+a\theta_i)\left[\frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{\Delta r^2} + \frac{1}{r_i}\frac{\theta_{i+1} - \theta_{i-1}}{2\Delta r} \right] + a\left[\frac{\theta_{i+1} - \theta_{i-1}}{2\Delta r} \right]^2 = -2G(1-r_i^2), \quad r_i = (i-1)\Delta r \quad (2)$$

Eqn. (2) (plus appropriate equations at the first and last node) provide a set of nonlinear equations to be solved. These are solved using the iteration feature in Excel spreadsheets. The equation is rearranged into a formula for the i-th node

$$\theta_i = \frac{1}{2}\left\{ \theta_{i+1} + \theta_{i-1} + \frac{\Delta r}{2r_i}(\theta_{i+1} - \theta_{i-1}) + \right.$$
$$\left. + [2G(1-r_i^2)\Delta r^2 + 0.25\,a(\theta_{i+1} - \theta_{i-1})^2]/(1+a\theta_i) \right\}$$

and this equation is placed into one cell.

```
B1:= 0.5*{A1 + C1 + 0.5*$B$4*(C1 – A1) / B2+
      + [2.*$B$5*B8 + 0.25*$B$7*(C1 – A1)^2 ] } / B3
```

where B2 is r_i (calculated for each node), B3 is $1 + a\theta_i$,

B4 is Δr, B5 is Δr^2, B6 is G, B7 is a, and B8 is $2*G*(1-r^2)$.

B1 is θ_i, A1 is θ_{i-1}, C1 is θ_{i+1}

The equation is copied into surrounding cells, and the iteration capability is turned on. After a few seconds the answer for θ at each node is shown in each cell. If a busy undergraduate with several classes, a part-time job, and a social life did that, would you accept the results as likely correct? I wouldn't, so let's see how to approach the problem in a way to improve the chances that the answers will be right. Solve a simpler, but related, problem first. Solve the problem with a = 0, G = 0, first. We know the answer is θ(r) = 1, and we make sure the program gives that answer. Then include the constant G, i.e. with the right-hand side = G. Now the exact answer is a quadratic function of r, and you can derive it and see that the computer gives the same result. (For this case, since the solution is a quadratic function of position, and the finite difference method is second order, the exact answer is obtained at the nodes; that won't be true in general; see the information on error assessment below.) Next put in the right-hand side = $-2G(1-r^2)$. Put this in one cell, and put specific values in the cells on either side. Do hand calculations to see that the value of θ_i is correct. Putting $\theta_{i+1} = \theta_{i-1} = 0.5$ makes the result

$$\theta_i = \frac{1}{2} \{ 1 + 2G(1 - r_i^2)\Delta r^2 \}$$

and it should give that answer to many (say 9) significant digits. However, even this isn't a good enough test. Since the values of the two adjacent nodes were the same, this check would not catch an error in which the formula used θ_{i+1} in place of θ_{i-1}. Thus, different values need to be used. In this step, one has to be sure that all terms are big enough to affect the result. Adding something that takes the value zero doesn't really check the formula, for example. Using $\Delta r = 10^{-6}$, G = 1 doesn't test the right-hand side.

Next, add in the variable thermal conductivity. Do this in one cell, put values in adjacent cells, and do the hand calculation to check. Once that check is satisfied, copy the formulas to all the cells, turn on the iteration feature, and wait for convergence. You can make one final check, using the results and putting them into the equation for one node, but if there is an error it will be hard to find at this stage; it is much better to have made all the prior steps correctly.

These are the steps you use to prevent mistakes in your work, which is one source of error. However, finite difference equations are approximate; the discretization step will introduce some error. How does one test that? **First test**: do the truncation error analysis. Substitute the Taylor series

$$\theta_{i+1} = \theta_i + \left.\frac{d\theta}{dr}\right|_i \Delta r + \left.\frac{d^2\theta}{dr^2}\frac{\Delta r^2}{2!}\right|_i + \left.\frac{d^3\theta}{dr^3}\right|_i \frac{\Delta r^3}{3!} + \left.\frac{d^4\theta}{dr^4}\frac{\Delta r^4}{4!}\right|_i + ..$$

$$\theta_{i-1} = \theta_i - \left.\frac{d\theta}{dr}\right|_i \Delta r + \left.\frac{d^2\theta}{dr^2}\frac{\Delta r^2}{2!}\right|_i - \left.\frac{d^3\theta}{dr^3}\frac{\Delta r^3}{3!}\right|_i + \left.\frac{d^4\theta}{dr^4}\frac{\Delta r^4}{4!}\right|_i + ..$$

into the finite difference form of the equation. What you find is

$$2\theta_i = 2\theta_i + \left.\frac{d^2\theta}{dr^2}\right|_i + O(\Delta r^2) + \left.\frac{1}{r}\frac{d\theta}{dr}\right|_i +$$

$$\frac{1}{(1+a\theta)} 2G(1-r^2) + \frac{1}{(1+a\theta)} a\left(\left.\frac{d\theta}{dr}\right|_i\right)^2 + O(\Delta r^2)$$

Thus, the error term is proportional to Δr^2. As $\Delta r \rightarrow 0$, the equation we solve is closer and closer to the exact equation. Second, is our application of the method correct? We think it is – due to the checks above, but if it is, we expect errors to go as Δr^2, too (Keller, 1972).

Second test: We know the exact heat flux, so we could check that and see that our values approach the exact value with an error Δr^2. Consider first the case with a = 0 (i.e. making the problem linear). We know the exact solution for the flux, and in this case we can derive an exact solution for the temperature at the center. The flux is calculated with a one-sided formula that is second order in Δr (Finlayson, 1980, p. 68). Table I shows the results, and the errors clearly are proportional to Δr^2.

Table I. Solution for Center Temperature and Heat Flux, Compared with the Analytical Solution; Generation Rate = 0.5 G (1 - r^2), G = 0.5, a = 0 (linear problem)

Δr	T(0)	Error in T(0)	q(1)	Error in q(1)
0.2	1.191161	0.00366	0.274476	0.0195
0.1	1.188431	0.00093	0.256498	0.0065
0.05	1.187734	0.00023	0.251672	0.0017
Exact	1.187500		0.250000	
Extrapol.	1.187502		0.250063	

Third test: We next solve the problem with a = 1 and G = 0.5. Now we have a problem for which we don't know the exact solution (at least we've not tried to find it). The problem is nonlinear with variable heat generation. However, we can still do the same tests as before. The truncation error analysis was done above. Next we solve the problem on one grid and do a hand calculation to insure that the correct equation is being solved. Then, we solve the problem on finer grids and make sure the results are proportional to Δr^2. Table II and Fig. 1 shows this clearly for both center temperature and heat flux at the boundary. Extrapolation of the last two points using a straight line

$$T_{est.}(0) = \frac{4\,T_{\Delta r/2}(0) - T_{\Delta r}(0)}{4-1}$$

gives the value $\theta_1 = 1.091651$. We use this as the answer and calculate the approximate error shown in Table II. Clearly the error decreases by about a factor of 4 as the Δr is halved, as required. The extrapolated heat flux is 0.250078, which is about 0.03% in error from the value of 0.25.

Now we have the answer. We claim the temperature is correct to ± 0.0001 (0.01%), and the heat flux is accurate within 0.0016 (0.64%). What does our claim depend upon?

(1) The finite difference equation is correct – the discretization error analysis showed that.

(2) The equations have been put into Excel correctly, based on a careful organization of our work and comparison with calculations.

(3) The discretization error has been estimated, and we can assign a number to it.

(4) In the case of heat flux, we can compare the result to an overall energy balance, which gives us the exact solution.

That is a good analysis, and it applies to problems without an analytical or 'exact' solutions, and to non-linear problems. For comparison, the extrapolated values are also given in Table I, for the case when we do know the exact solution. The extrapolated values are very close to the exact answer.

***Table II. Solution for Center Temperature and Heat Flux**; Generation Rate = 0.5 G (1 - r^2), G = 0.5, a = 1 (nonlinear problem)*

Δr	T(0)	Approx. Error in T(0)	q(1)	Approx. Error in q(1)
0.2	1.093282	0.00160	0.274123	0.0240
0.1	1.092066	0.00042	0.256499	0.0064
0.05	1.091754	0.00010	0.251683	0.00016
Extrapol.	1.091651		0.250078	

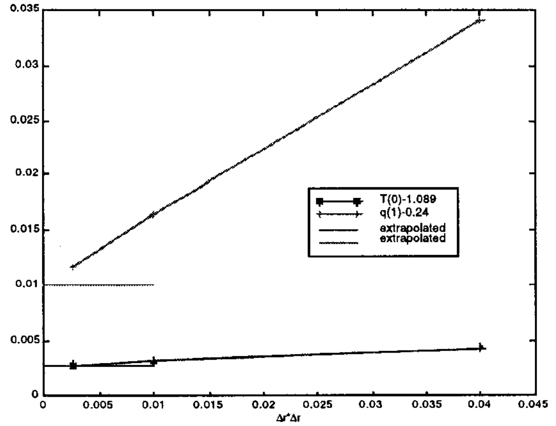

Figure 1. Center Temperature and Boundary Heat Flux as a Function of Mesh Size; Generation Rate = 0.5 G (1 - r^2), G = 0.5, a = 1 (nonlinear problem)

Undergraduate transport problems solved with MATLAB.

The next problem illustrates how one solves for sensitivity of the model to input data. Consider the two-dimensional heat transfer problem shown below. This is solved with the PDE toolbox in MATLAB (PDE Toolbox, 1997) which uses the finite element method. One must set the domain, identify boundary conditions, decide what terms need to be in the equation, let the computer generate a mesh, and solve the problem. The first mesh tried gave the following results.

$$\nabla^2 T = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0$$

$T = 1$ on $x = 0$, for all y; $y = 0$, for all x

$T = 0$ on $y = 1$ for all x

$\partial T / \partial n = 0$ on $x = 1$, for all y

$T = 0.5$ in the center block

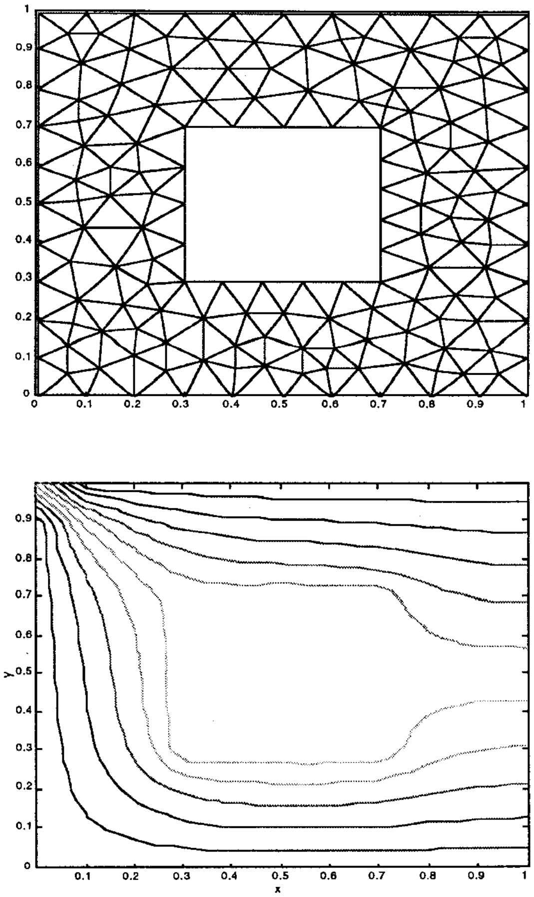

Figure 2. Heat Transfer Problem Solved with Finite Element Method; (a) Mesh, (b) Temperature Contours

The mesh needs to be refined (this is done by the click of a button in the PDE toolbox), and the new results are given below. These two cases indicate that the discretization errors are small enough and the finite element results are reliable. We could make this more precise, if desired, by looking at the solution at specific points obtained for the two solutions. It is harder to show the rate of convergence with mesh size, though, when using an automatic mesh generator. To check whether you have solved the right equation, the only real check you have is to look at the graphical user interface (gui) and see what are the coefficient values. In this case, one assumes that the program solves the equation it says it does, and even that can be checked by solving problems that others have solved reliably.

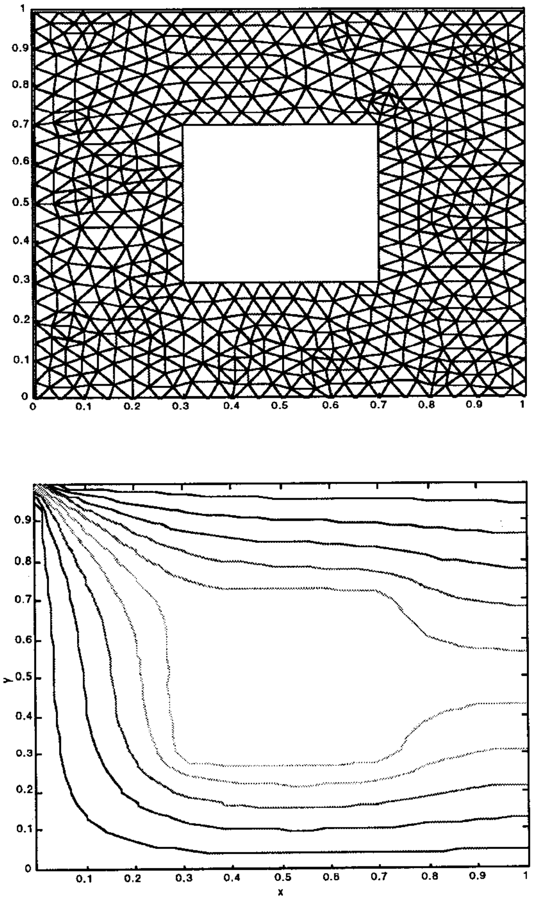

Figure 3. Heat Transfer Problem Solved with Finite Element Method; Refined Mesh; (a) Mesh, (b) Temperature Contours

Here, though, look at the sensitivity to the temperature in the center block, using a sensitivity equation since that approach can also be used for parameter estimation. Differentiate the equation and all boundary conditions with respect to T_0.

$$\frac{\partial}{\partial T_0}[\nabla^2 T = 0] => \nabla^2 \frac{\partial T}{\partial T_0} = 0$$

$$\frac{\partial}{\partial T_0}[T = 1] => \frac{\partial T}{\partial T_0} = 0 \text{ on } x = 0, \text{ for all } y$$

$$\text{and } y = 0, \text{ for all } x;$$

$$\frac{\partial}{\partial T_0}[T = 0] => \frac{\partial T}{\partial T_0} = 0 \text{ on } y = 1 \text{ for all } x$$

$$\frac{\partial}{\partial T_0}\left[\frac{\partial T}{\partial n} = 0\right] => \frac{\partial}{\partial n}\left[\frac{\partial T}{\partial T_0}\right] = 0 \text{ on } x = 1, \text{ for all } y$$

$$\frac{\partial}{\partial T_0}[T = 0.5] => \frac{\partial T}{\partial T_0} = 1 \text{ in the center block}$$

So, now solve for $z = \partial T / \partial T_{center}$.

$$\nabla^2 z = 0$$

$$z = 0 \text{ on } x = 0, \text{ for all } y;\ y = 0, \text{ for all } x;\ y = 1 \text{ for all } x$$

$$\frac{\partial z}{\partial n} = 0 \text{ on } x = 1, \text{ for all } y$$

$$z = 1 \text{ in the center block}$$

The result is in Fig. 4.

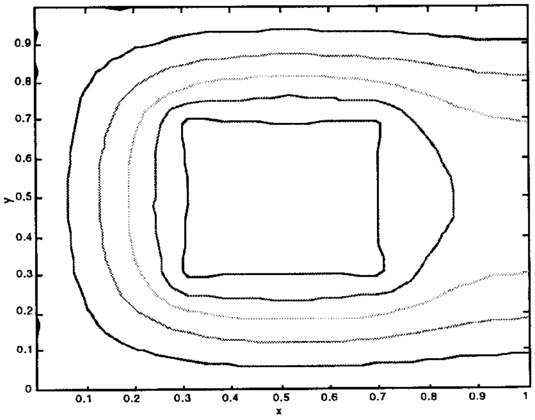

Figure 4. Contours of Sensitivity to Center-block Temperature

Now we know the temperature at every point, and how sensitive it is to the center temperature. The largest value of z along the line x = 1 is for y = 0.5. It is clear that the maximum sensitivity is at the middle of the right-hand side, so that is where we would place thermocouples. If we had heat transfer data we could determine the middle temperature by evaluating the model, comparing with data, forming an objective function (the absolute difference between calculational and experimental results), and use an optimization program to find the minimum. Since we have the derivative of the solution with respect to the optimization parameter, we can use an optimization routine that requires derivative evaluation. The same technique works with ordinary differential equations. So, now we have a technique for seeing how sensitive the result is to some part of our model.

False Bifurcations Obtained with the Method of Lines

The next example illustrates the importance of understanding the method one uses when discretizing in space. Many computer programs for modeling transient phenomena provide an ODE solver. The user then writes a routine that is essentially the method of lines. The example chosen here shows how that user-supplied routine can give results which look like bifurcations and chaos, but in reality are the result of not using a small enough time-step for the type of discretization used. This is particularly troublesome because the program can be absolutely correct, yet the results can look like nonsense. Thus, the testing procedure described above would not uncover an error, because there isn't one; yet, the results can look extremely weird.

Consider the diffusion equation with reaction, called the Fisher equation.

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2} + \alpha u\ (1-u)$$

If a finite difference method is applied to this equation using an explicit, first-order method, the result is

$$\frac{u_i^{n+1} - u_i^n}{\Delta t} = D\frac{u_{i-1}^n - 2\,u_i^n + u_{i+1}^n}{\Delta x^2} + \alpha\, u_i^n\,(1-u_i^n)$$

Following Mitchell and Bruch (1985) we transform the equation using

$$v_i^n = \frac{\alpha\,\Delta t}{1+\alpha\,\Delta t}\,u_i^n$$

The result is

$$v_i^{n+1} = b\,(v_{i-1}^n - 2\,v_i^n + v_{i+1}^n) + a u_i^n\,(\,1 - v_i^n\,)$$

where

$$a = 1 + \alpha\,\Delta t,\ b = D\,\Delta t/\Delta x^2$$

First solve this problem without diffusion, i.e. b = 0; the equation is then called the logistic equation (Mitchell and Brunch, 1985). It is solved for a variety of a or time steps, and the solution as t approaches infinity is plotted in Fig. 5. These solutions are obtained by starting from different initial conditions. Clearly for high values of a, or $\alpha\Delta$ t, it is possible to get more than one solution. Next add diffusion; solutions for one value of a, and many values of b. The boundary conditions are no flux at x = 0, the value of v(1) = 0, and the initial condition is everywhere zero except at x = 0, where it is 0.6, 0.3, and 0.8 in successive runs to obtain all the solutions. Results are shown in Fig. 6 for a = 2.50 (thus $\alpha\ \Delta$ t = 1.50), Δ x = 0.5, and various b, i.e. various D. There is a clear bifurcation at b = 0.125. If one plotted the solution at infinite time versus both a and b, one can imagine Fig. 5 projecting out from the paper at the origin, b = 0, and a very complicated geometric pattern can be imagined. However, let us use a smaller Δ t by a factor of 4, corresponding to a = 1.375, and a smaller Δ x by half, corresponding to Δ x = 0.25; the results are in Fig. 7. The value of $\Delta t / \Delta x^2$ is the same in the Fig.s 6 and 7, so that situations with the same b are for the same physical situation. Fig. 7 shows that the bifurcation has disappeared! Thus, it was a result of the discretization. If one reduces Δ t without changing Δ x (a = 1.375), then the bifurcations also disappear. Thus, the bifurcations in this case were a result of using the method of lines and a discretization (in Δ x and Δ t) that was too big.

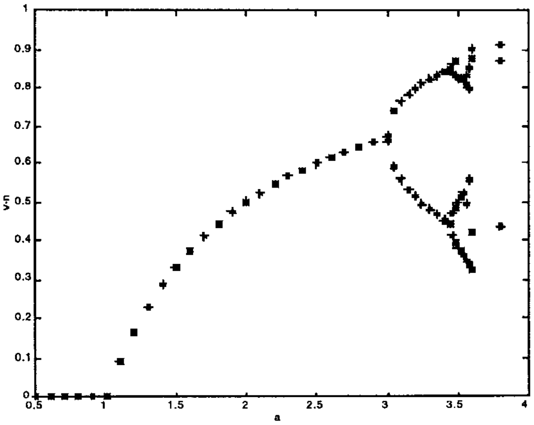

Figure 5. Solutions of Logistic Equation Obtained from Different Initial Conditions

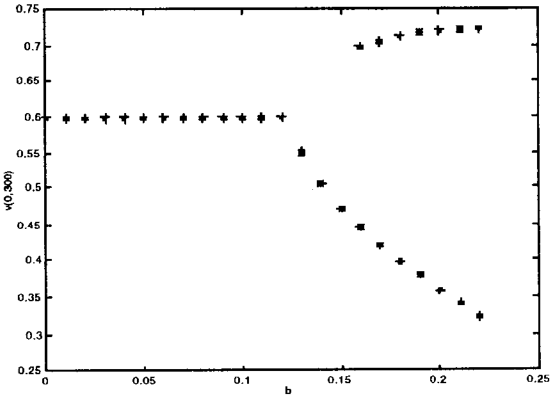

Figure 6. Solutions of the Fisher Equation Obtained from Different Initial Conditions; Finite Difference Method; a = 2.5, $\alpha\,\Delta\,t$ = 1.5, Δx = 0.5, $0 \le x \le 1$.

Now Mickens (1989) argues that such discretizations as used here can lead to false bifurcations (as demonstrated above), and that a better form of the equation is to evaluate the reaction term at different times, or at different spatial positions, e.g.

$$\frac{u_i^{n+1} - u_i^n}{\Delta t} = D\frac{u_{i-1}^n - 2u_i^n + u_{i+1}^n}{\Delta x^2} + \alpha\, u_i^n\,(1 - u_{i+1}^{n+1}\,)$$

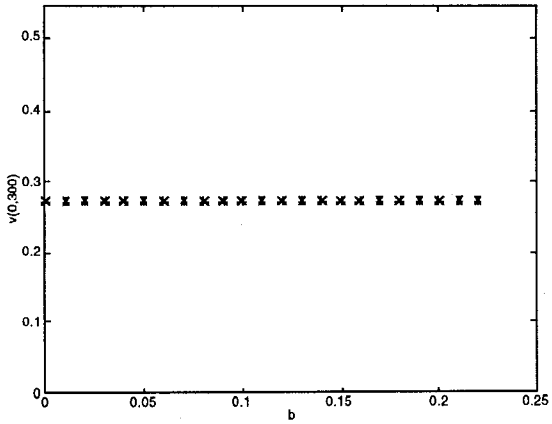

Figure 7. Solutions of the Fisher Equation Obtained from Different Initial Conditions; Finite Difference Method; a = 1.375, α Δ t = 0.375, Δ x = 0.25, 0 ≤ x ≤ 1

This is similar to what the Galerkin finite element method does. The Galerkin method gives (Finlayson, 1980)

$$\frac{1}{6}\frac{u_{i-1}^{n+1}-u_{i-1}^{n}}{\Delta t}+\frac{4}{6}\frac{u_{i}^{n+1}-u_{i}^{n}}{\Delta t}+\frac{1}{6}\frac{u_{i+1}^{n+1}-u_{i+1}^{n}}{\Delta t}=$$

$$D\,\frac{u_{i-1}^{n}-2\,u_{i}^{n}+u_{i+1}^{n}}{\Delta x^{2}}+\frac{\alpha}{6}\,(u_{i-1}^{n}+4\,u_{i}^{n}+u_{i+1}^{n})$$

$$-\frac{\alpha}{12}\,[(u_{i-1}^{n})^{2}+2\,u_{i-1}^{n}u_{i}^{n}+6\,(u_{i}^{n})^{2}+2\,u_{i}^{n}\,u_{i+1}^{n}+(u_{i+1}^{n})^{2}]$$

There is a variant of the Galerkin method which makes the term multiplying the time derivative diagonal, too. It is called a lumped, Galerkin method. (The term lumped means that the left-hand side has been made diagonal by adding all coefficients and putting them on the diagonal). This form of the problem, plus the transformation to v, gives

$$v_{i}^{n+1}=b\,(v_{i-1}^{n}-2\,v_{i}^{n}+v_{i+1}^{n})+\frac{a}{6}\,(\,v_{i-1}^{n}+4\,v_{i}^{n}+v_{i+1}^{n})+$$

$$-\frac{a}{12}\,[(v_{i-1}^{n})^{2}+2\,v_{i-1}^{n}\,v_{i}^{n}+6\,(v_{i}^{n})^{2}+2\,v_{i}^{n}\,v_{i+1}^{n}+(v_{i+1}^{n})^{2}]$$

Calculations with the lumped Galerkin method are shown in Fig. 8 for the same parameters used in Fig. 6. The bifurcations now occur at a much larger value of b, b = 0.2.

Lest one think this is a trivial matter, the solutions for one of these cases with bifurcations is shown in Fig. 9. The first response to seeing such a result is to seek to find an error in the computer code. Yet there isn't one. Thus, one must be very careful when using the method of lines; it is possible that more advanced integration methods will eliminate these false bifurcations, too. Of course, there are many situations for which bifurcations are real (Varma, *et al.*, 1998). One must do careful analysis to distinguish the difference.

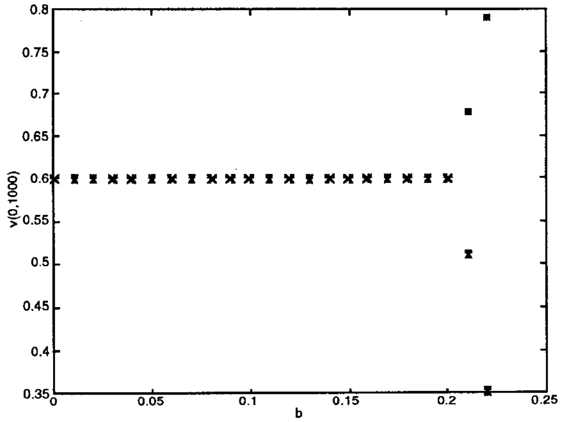

Figure 8. Solutions of the Fisher Equation Obtained from Different Initial Conditions; Galerkin Method, Lumped; a = 2.5, α Δ t = 1.5, Δ x = 0.5, 0 ≤ x ≤ 1.

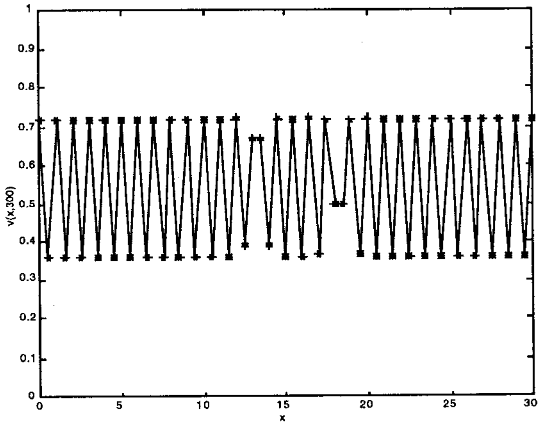

Figure 9. Spatial Variation of the Solution of the Fisher Equation Obtained from the Finite Difference Method; a = 2.5, α Δ t = 1.5, b = 0.20, Δ x = 0.5, 0 ≤ x ≤ 1

Incorrect Shock Movement with Method of Lines

Another area where careful numerical analysis is needed is a problem whose solution exhibits shocks. Consider adsorption in a packed bed with rapid mass transfer so that the fluid and solid adsorbate are in equilibrium. The equations are

$$\phi\,\frac{\partial c}{\partial t}+\phi\,V\,\frac{\partial c}{\partial x}+(1-\phi)\,\frac{\partial n}{\partial t}=0,$$

$$n=f(c)=\frac{\alpha\,c}{1+K\,c}$$

Let

$$\sigma(c) = \frac{d}{dc}\left(c + \frac{1-\phi}{\phi} n \right) = 1 + \frac{1-\phi}{\phi}\frac{df}{dc} =$$

$$= 1 + \frac{1-\phi}{\phi}\frac{\alpha}{(1+Kc)^2}$$

and transform the equations to

$$\sigma(c)\,\frac{\partial c}{\partial t} + V\,\frac{\partial c}{\partial x} = 0$$

This equation underlies models like those used by Strube and Schmidt-Traub (1998) after the equilibrium assumption has been made. Usually, special techniques are used to solve this equation (Finlayson, 1992; Poulain and Finlayson, 1993; Anklam, *et al.* , 1997) in order to maintain a shock if one occurs. However, even those methods can be led astray if the equation is not solved in the correct form (Poulain and Finlayson, 1993).

If one solves the equations in the form

$$\frac{\partial c}{\partial t} + \frac{V}{\sigma(c)}\frac{\partial c}{\partial x} = 0$$

or

$$\frac{\partial c}{\partial t} + \frac{\partial M\,(c)}{\partial x} = 0, \quad M\,(c) = \int_0^c \frac{du}{\sigma(u)}$$

then an explicit, upwind method is

$$c_i^{n+1} = c_i^n - \frac{V\,\Delta t}{\Delta x}\,[\,M(c_i^n) - M(c_{i-1}^n)]$$

No matter how this equation is solved, the wave speed of a shock is (Poulain and Finlayson, 1993)

$$\frac{\text{shock speed}}{V} = \frac{M\,(c^l) - M\,(c^r)}{c^l - c^r}$$

If one solves the equation in the form

$$\frac{\partial g}{\partial t} + V\,\frac{\partial c}{\partial x} = 0, \quad g\,(c) = c\left[\,1 + \frac{1-\phi}{\phi}\,\frac{\alpha\,c}{1+K\,c}\right]$$

then the solution method is more complicated (given g(c), one must find c), and the wave speed is

$$\frac{\text{shock speed}}{V} = \frac{c^l - c^r}{g\,(c^l) - g\,(c^r)}$$

These differ by 9 % (0.547 vs. 0.500). One can show (Poulain and Finlayson, 1993) that as one reduces Δ t and Δ x, the solution based on method 1 converges to its wave speed, and those based on method 2 converge to its wave speed, but the two wave speeds are different. As shown by Leveque (Leveque, 1992) it is necessary that the Rankine-Hugoniot shock speed be consistent with a conservation law. This is satisfied for method 2 but not for method 1. The conservation law for method 2 is just an overall mass balance including the fluid and adsorbed fluid. However, the more likely method of solution, method 1, leads to the incorrect solution, even when Δ t and Δ x approach zero. Thus, even when one has an ODE solver available, one must be careful how the partial differential equations are treated.

Reactor problems solved with the Chemical Reactor Design Tool (CRDT).

The next examples are for modeling chemical reactors with a computer code that the user accesses only through a graphical user interface (gui). Thus, it relates most closely to the present day use of computers by engineers who have not programmed the computer themselves. The CRDT has been described in detail (Rosendall and Finlayson, 1994) and applied to three industrial chemical reactors (Rosendall and Finlayson, 1994, 1995) Briefly, it permits a user to design chemical reactors including the realistic transport effects that are frequently present. When attempting to solve real problems, students are faced with difficulties which are primarily bookkeeping and manipulation rather than conceptual. Phenomena that might be important, and might be hard to include in a student-written program are:

- multiple reactions (leads to lots of bookkeeping, OK if reactor is not too complicated)
- the temperatures of the catalyst and the fluid may be different (requires solving sets of nonlinear algebraic equations along with the reactor model)
- internal mass transfer (requires solving two-point boundary value problems at every node)
- there may be cooling at the wall (leading to radial dispersion and partial differential equations).

Textbooks usually treat only simple systems such as batch, CSTR, or plug flow reactors, usually for only a few components. The inclusion of the above effects are time-consuming to include, and hence are seldom included even though the phenomena are sometimes important. This leads students to think that it is acceptable to leave out important phenomena just because they can't easily do the computation when it is included.

The CRDT can solve reactor equations with up to 20 components plus temperature when the reactors are CSTR, batch, plug flow, axial dispersion, or radial dispersion reactors. Phenomena included are:

- intraparticle heat and mass transfer is important
- significant mole changes occur
- significant pressure changes occur

These effects are especially important for selectivity, especially in non-isothermal cases, and this makes the models useful for pollution prevention by not making unwanted products. The user supplies a FORTRAN routine that evaluates the reaction rate, chooses the type of reactor and phenomena to include, and provides the parameters needed for that application. CRDT solves the problem and provides output files for plotting. Batch and plug flow reactors involves solving ordinary differential equations as initial value problems, and the capability to do that is in most numerical analysis packages today. One feature added by CRDT is the addition of intraparticle heat and mass transfer resistance: the user includes this by pressing a button, and coupled nonlinear differential-algebraic equations are solved. A sophisticated program will be invoked to identify if there are multiple solutions to any of the intraparticle problems. It uses linear programming techniques to get a good initial guess for the iterations, and to test for multiple solutions. This same capability is in all the reactor modules. Axial dispersion reactors can, of course, have multiple steady state solutions without any intraparticle resistance, and these are predicted as well. Finally, radial dispersion reactors require solving multiple partial differential equations. This is clearly beyond the capabilities of most undergraduates, at least for complicated problems. So, the program is very powerful. How do you know you've solved the problem correctly?

The first test is the reaction rate. The interface with the main CRDT must be correct. Because of the generality of the program (especially due to intraparticle resistance), the reaction rate subroutine has to be correct for every possible set of concentrations and temperature, even those unexpected in the eventual solution (they arise occasionally in iterative methods). So what did we do? We designed a program, test_rate, that uses the user's rate subroutine but interacts in the same way the program does. The user can run interactively with various inputs and obtain values of the rates of reaction. These can be checked with hand calculations to insure that the subroutine is correct under all conditions. The second test is to run sample cases (with a simpler reaction rate expression) to compare with analytical results. This is a most important step, since it assures the student that they are using the code as intended.

The third test is empirical. Run the CRDT with different sets of numerical parameters and make sure that the results do not depend on arbitrary choices of the numerical parameters. For example, when solving ordinary differential equations using either RKF45 or LSODE, the user sets an error criterion. Thus, the user needs to run the CRDT with at least two different error criteria to make sure that the results do not depend on the numerical analysis parameters. For partial differential equations, since the program uses the method of lines, either finite difference or orthogonal collocation is used to reduce the partial differential equations to sets of ordinary differential equations. We have the same tests for the error criterion for the ODE solver. However, we also have discretization error associated with the spatial discretization. For example, you can fix the number of finite difference grid points, solve with an ODE solver, reduce the error criterion, and solve again. The answer will be a more accurate solution of the ordinary differential equations, but not necessarily a more accurate solution of the partial differential equations. There may still be discretization error in space. So, one then finds solutions with N = 4, 8, 16, etc., and for each of these uses several error criteria in the ODE solver. One finds that as the number of finite difference points increases, the error criteria must become smaller to get any solution at all. Sometimes the discretization analysis is such that the error term has a positive term times Δ t plus a negative term times Δx^2. Thus, by choosing a 'magic' mesh and step size, one can even make the error zero; just don't change anything or look at any other value! Thus, figuring out the solution to partial differential equations and the errors in the numerical method when both Δ t and Δ r are decreasing can be difficult.

As an example of the kind of things CRDT can do, consider a reactor to oxidize SO_2. The reaction is

$$SO_2 + \frac{1}{2} O_2 <=> SO_3$$

and the reaction rate is written in terms of partial pressures.

$$\text{Rate of oxidation} = \frac{k_1 p_1 p_2 - k_2 p_3 p_2^{1/2}}{p_1^{1/2}}$$

$$\ln k_1 = 12.07 - \frac{31000}{R\,T}, \ \ln k_2 = 22.757 - \frac{53600}{R\,T}$$

The first index is for SO_2, then O_2, SO_3, and N_2. After writing a 10-line FORTRAN program and testing it with test_rate, the user is ready to use CRDT. In this paper the focus is on whether radial dispersion is important and how that is determined. Once the 10-line reaction rate program is written, the only thing the student has to do to handle radial dispersion is click a button, provide radial dispersion parameters, and choose either the finite difference or orthogonal collocation method. For a typical case (Hill, 1977; Rosendall and Finlayson, 1994) the radially-averaged concentration versus length is shown in Fig. 10.

The 2D profiles of SO_3 and temperature are shown in Fig. 11. One feature of the CRDT, since it is an educational program, is to let the user see the magnitude of various terms in the equations. Fig. 12 shows the radially-averaged diffusion and convection terms. The convection term is naturally negative for the reactants and positive for the products. Note particularly that the diffusion term is small compared with the convection term (thus suggesting a 1D model is OK) except for the last part of the reactor where the reaction is stronger. Other results (Rosendall and Finlayson, 1994) show that the reactor model including radial dispersion can be 15% shorter than the 1D model, to achieve the same conversion. Thus, the CRDT allows one to quantify the results of the assumptions made. With students it is important to keep asking for numerical values, rather than just vague generalities, so that they learn to figure out what phenomena is really important based on quantitative criteria.

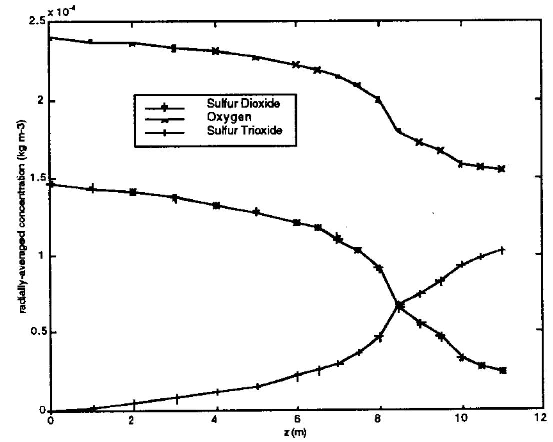

Figure 10. Reactor to Oxidize Sulfur Dioxide, Finite Difference Method Radially, N = 5, 4th-5th Order Runge-Kutta Method Axially.

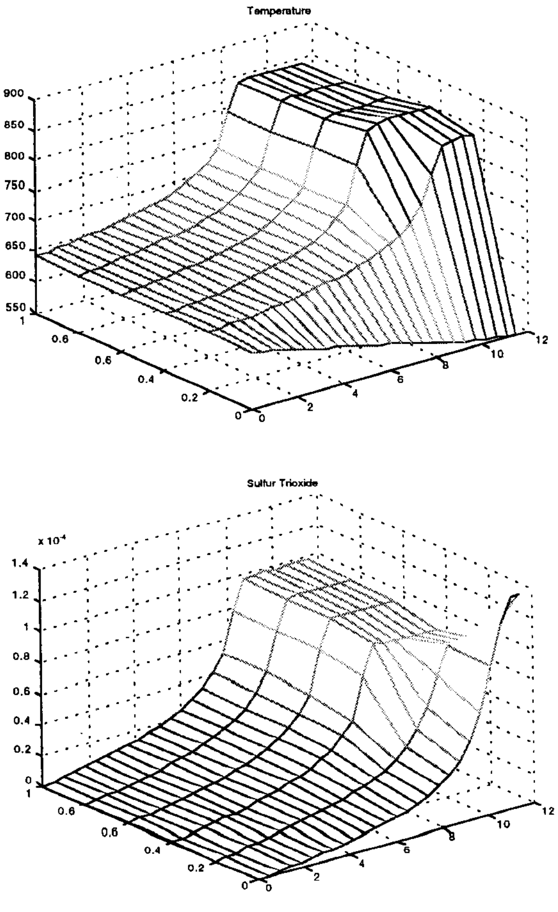

Figure 11. Reactor to Oxidize Sulfur Dioxide; (a) Temperature; (b) Sulfur Trioxide

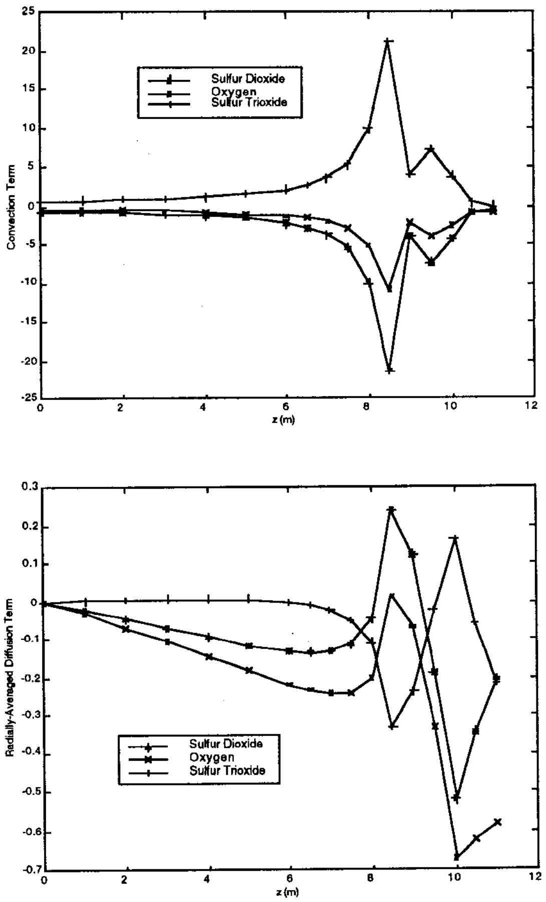

Figure 12. Reactor to Oxidize Sulfur Dioxide; Radially Averaged Convection and Diffusion Terms; (a) Convection; (b) Radial Dispersion

The effects of radial gradients, heat and mass transfer limitations, and total molar and pressure changes would be most important in cases involving multiple reactions where selectivity is important, either for economic reasons or because one of the products is a pollutant. Thus, it is of interest to examine the effect of radial heat transfer for a case involving several reactions. The problem selected is the reaction of propylene and chlorine to form allyl chloride (Smith, 1970; Carberry, 1976).

The reactions are simplified here to include the three main ones, involving the formation of allyl chloride, 1,3-dichloropropene, and 1,2-dichloropropane.

$$Cl_2 + C_3H_6 \rightarrow CH_2{=}CHCH_2Cl + HCl$$

allyl chloride

$$Cl_2 + CH_2{=}CHCH_2Cl \rightarrow CHCl{=}CHCH_2Cl + HCl$$

allyl chloride 1,3–dichloropropene

$$Cl_2 + C_3H_6 \rightarrow CH_2ClCHClCH_3$$

1,2–dichloropropane

The total molar change will be small. However, the reaction rates depend on temperature and concentration as follows.

$$r_1 = A_1 \exp\left(-\frac{15{,}840}{R\,T}\right) C_{Cl_2} C_{C_3H_6}$$

$$r_2 = A_2 \exp\left(-\frac{23{,}760}{R\,T}\right) C_{Cl_2} C_{allyl\ chloride}$$

$$r_3 = A_3 \exp\left(-\frac{7920}{R\,T}\right) C_{Cl_2} C_{C_3H_6}$$

Thus, temperature will have a big effect on selectivity. At high temperatures, allyl chloride is favored, but at lower temperatures more 1,2-dichloropropane is formed. Typical operating conditions are 500 °C and 40 psia (Fairbairn, *et al.* 1947), and the reaction is carried out in the gas phase which is flowing in an empty tube. Most published models are one-dimensional; they ignore radial gradients of concentration and temperature on the grounds that they will be small in turbulent flow in a pipe because the velocity is flat. Using the Colburn analogy, it is assumed that the radial gradients of temperature are also small. Of course, the turbulent velocity profile is not exactly flat, and a small temperature difference radially can cause a reaction rate difference, which causes a concentration difference, which in turn affects the temperature. Thus, it is of interest to find out how strong those effects are.

The problem is solved in CRDT. The feed rate of propylene to chlorine is taken as 2.5 (industrial ranges are 1.7 to 3.8), and the parameters are chosen to agree with those in Carberry (1977). The equations for a 1D model are

$$\frac{dF_i}{dV} = Da_I R A_i,\ F_i = F_{j0}\ at\ V = 0$$

$$\sum_{j=1}^{NC} F_j C_{pj} \frac{dT}{dV} = Da_{III} R T - St\ (T - T_c)$$

$$T = T_{in}\ \text{at}\ V = 0$$

$$St = \frac{UA}{F_s C_{ps}},\ \text{where } F_s \text{ and } C_{ps} \text{ are standard}$$

molar flow rates and heat capacities

while those for a 2D model are

$$\frac{\partial F_i}{\partial V} = \alpha_i \nabla^2 C_i + Da_I R A_i$$

$$\sum_{j=1}^{NC} F_j C_{pj} \frac{\partial T}{\partial V} = \alpha_T \nabla^2 T + Da_{III} R T$$

$$-\frac{\partial T}{\partial r} = Bi_w\ (T - T_c)\ \text{at}\ r = 1$$

The additional parameters needed for the 2D model are taken as

$$\alpha_i = \frac{V D C_s}{R^2 F_s},\quad \alpha_T = \frac{V k}{R^2 F_s C_{ps}},\quad Bi_w = \frac{h_w R}{k}$$

and here $\alpha = 0.022$ and $\alpha_T = 1$. The Biot number at the wall is chosen so that the heat losses at the wall are equivalent in the 1D and 2D models, by taking (Finlayson, 1980)

$$\frac{1}{St} = \frac{1}{2\,\alpha_T}\left(\frac{1}{Bi_w} + \frac{1}{3}\right)$$

Here, $B_w = 0.27$. For the 2D model, the velocity is taken as the same average value as in the 1D model, but with a one-seventh power with respect to radius, which is a reasonable representation for turbulent flow in a pipe.

The results are shown in Figures 13-15. Figure 13 shows the radially-averaged concentration of chlorine versus the length of the reactor (chlorine is the limiting reagent). The adiabatic result shows almost complete conversion of the chlorine, but the 1D and 2D models have about 5% of the initial chlorine unreacted. There is little difference between the 1D and 2D models when comparing the radially-averaged values. Thus, the radial effects are not large for this case. The radially-averaged temperature is shown in Figure 14. The adiabatic case approaches the adiabatic temperature rise (which in itself depends on selectivity, hence the transport conditions in the reactor). The 1D and 2D models give about the same radially-averaged temperature profile versus length.

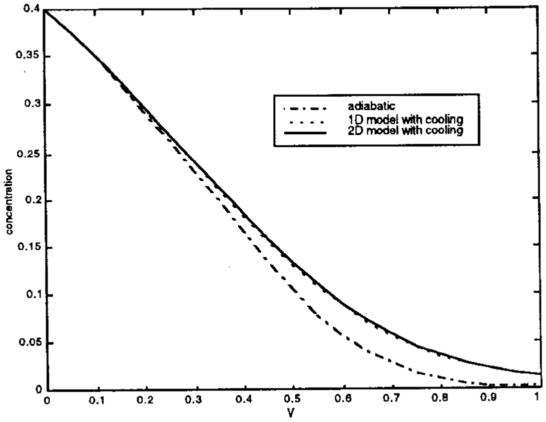

Figure 13. Average Concentration of Chlorine

Despite this agreement of the radially-averaged values, there do exist profiles of the components in the radial direction. The outlet profile of chlorine is shown in Figure 15 for the 1D and 2D models. (The small dip near the centerline is due to the interpolation process.) While there is a about a 40% change in

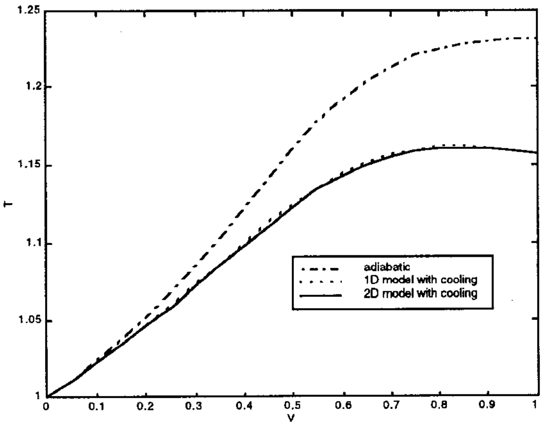

Figure 14.Radially-Averaged Temperature

the concentration of chlorine from the center to the wall, the average values are close (within 6%). In some cases that may be significant enough difference when trying to react the chemical completely.

This example shows how a 2D model can be done relatively easily once a 1D model has been constructed, and the effects of temperature and velocity profile are easily included. The CRDT is constructed to make this easy to do; the hard part is getting the numbers for the first model – the other models are within a click of a button.

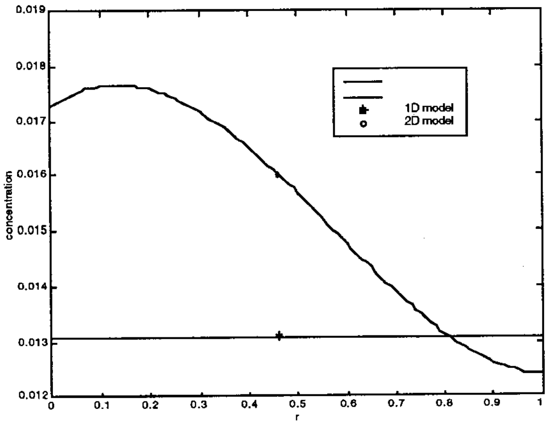

Figure 15. Chlorine Concentration at Exit

Using the Chemical Reactor Design Tool (CRDT) with CFD programs.

The next example illustrates how one can use the CRDT in conjunction with CFD programs. The CFD model is of a industrial radiant furnace (Berkoe, *et al.*, 1998). The commercial CFD code, CFX version 4, was coupled to a one-dimensional model for the cracking reactions occurring inside the process tube passing through the firebox. This model allows for the prediction and evaluation of detailed heat flux, temperature profiles, and flow distribution within the furnace. The CFX model accounts for

- 3D heat transfer due to radiation, convection, and conduction
- Combustion
- 3D fluid flow, including the effects of compressibility.

The one-dimensional, tube-side model includes

- Momentum balance for the process fluid
- Cracking reaction kinetics leading to vaporization
- Temperature dependent physical properties
- Heat transfer from the furnace side.

A typical situation is shown in Fig. 16.

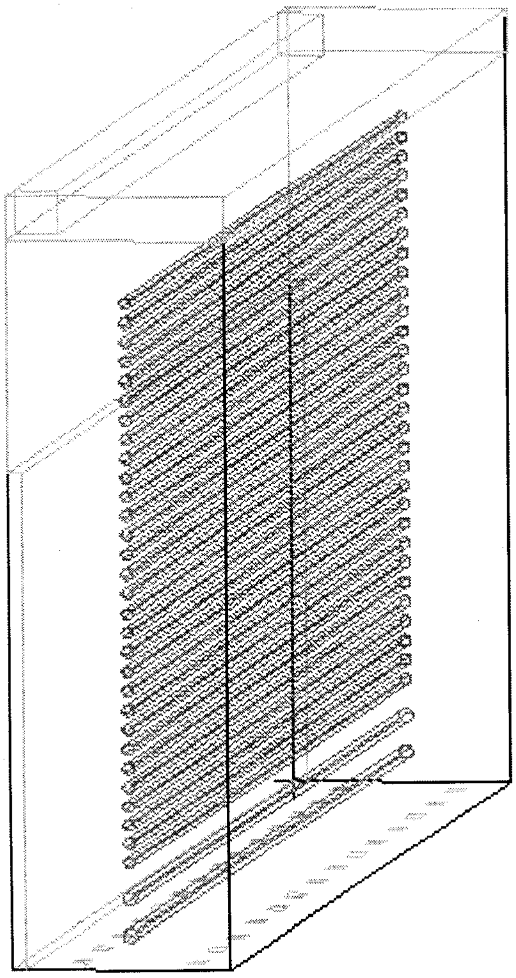

Figure 16.Industrial Radiant Furnace Geometry

The 3D furnace model and the 1D process tube model are coupled through the heat flux. The equations governing the process tube model are

$$\frac{\dot{m}\, C_p}{A_{cs}} \frac{dT}{dz} = h\, a\,(T_o - T) + (-\Delta H_{rxn}) R$$

$$\frac{1}{A_{cs}} \frac{dF_i}{dz} = \upsilon_i R, \quad \frac{dp_t}{dz} = \rho \left(g_y \frac{dy}{dz} + u^2\, Fr + u \frac{du}{dz} \right)$$

$$Fr = \frac{f}{2\, d_t} + \frac{1.4}{\pi R_b} \left(0.051 + 0.19 \frac{d_t}{R_b} \right)$$

The reaction is

$$\text{Resid(l)} \text{−>} 0.742\ \text{HCGO(l)} + 0.742\ \text{LCGO(g)} + \\ + 0.725\ \text{Naphtha(g)} + 1.82\ \text{LG(g)}$$

Since some of the products are vapor, physical properties for the two phase mixture were taken as an average

$$\frac{1}{\mu} = \frac{\text{fraction vapor}}{\mu_v} + \frac{\text{fraction liquid}}{\mu_l}$$

The process tube model is coupled with the CFD model through a FORTRAN routine that the CFD model calls. The same principles discussed above apply here: one must check the FORTRAN program, and then one must test the use of the FORTRAN program in the CFD model to insure that it is being used correctly. But, how good is the 1D model? One can do all the testing and find the computer work is satisfactory, but if a truly 2D process tube model is necessary incorrect results will be given by the 1D model. This is an ideal application for CRDT, since once the 1D model is done, the 2D model is easily solved. Unfortunately, the CRDT is limited to one phase, so a special purpose program was written to compare 1D and 2D models, using the same approach taken in CRDT, namely using the orthogonal collocation method (Finlayson, 1980) to model radial dispersion of energy and mass. For the purpose of this test, only one tube was modeled, and the pressure was taken as constant in that tube. The boundary condition at the tube wall was that an applied flux was specified (i.e. the 1D and 2D models were tested outside of the CFX program).

For the test done here, the term h (T_o - T) is replaced by q, the average heat flux in the furnace. For the 2D model the equations are changed to

$$\frac{m\, C_p}{A_{cs}} \frac{\partial T}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(k\, r \frac{\partial T}{\partial r} \right) + (-\Delta H_{rxn}) R$$

$$\frac{1}{A_{cs}} \frac{\partial F_i}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(D\, r \frac{\partial C_i}{\partial r} \right) + \upsilon_i R$$

$$\left.\frac{\partial T}{\partial r}\right|_{r=0} = 0, \left.\frac{\partial c}{\partial r}\right|_{r=0} = 0, -k \left.\frac{\partial T}{\partial r}\right|_{r=R} = q, \left.\frac{\partial c}{\partial r}\right|_{r=R} = 0$$

This 2D model is not the complete story, since the wall temperature is excluded, but it is sufficient to test the need for a 2D model.

First consider the standard tests for the importance of radial dispersion. Mears (1971) gives a test (derived for packed bed reactors) that is based on the principle that radial variation of temperature and concentration is unimportant when the radially averaged reaction rate differs from the local reaction rate at the wall by less than 1%. This is definitely not satisfied here, since the difference between the wall temperature and fluid temperature can up as large as 100 K. Another rule of thumb is that radial variations are important if the Biot number, $Bi_w = h\, R_t / k$, is greater than 10 (Rosendall and Finlayson, 1995) Here it is typically 500. Thus, both standard *a priori* tests (admittedly derived for packed beds) say radial variations are important. However, it is the author's experience in modeling chemical reactors that if the temperature profile is approximately quadratic, then a one-term orthogonal collocation solution gives results as good as a six-term collocation solution (including all radial variations), and the one-term orthogonal collocation solution is the same as the 1D model. The only difference is that one is solving for the temperature at the collocation point rather than the average temperature. That is indeed what happened.. 17 shows the temperature profile for the 1D model and the temperature profile at two radial positions for the 2D orthogonal collocation model. While there is a radial variation in temperature, the average properties are very close to each other. Thus, the 2D model is quite appropriate for this industrial radiant furnace model.

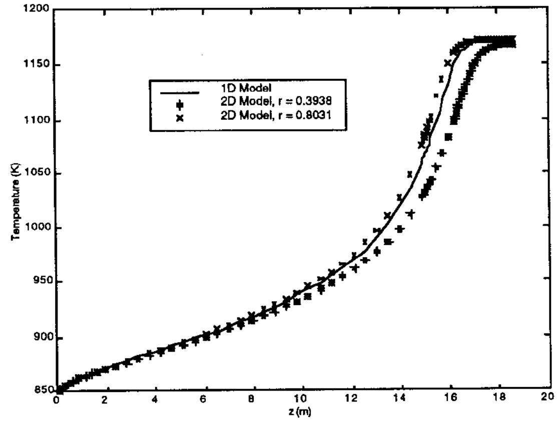

Figure17. Temperature in One Tube, Comparing a 1D and 2D model

Use of CFD programs by undergraduates.

When undergraduates use a CFD program, the same principles discussed here apply. One needs to verify your use of the code by solving problems with known solutions.

The first author usually has them do problems where we can use a mesh from an example problem. At the University of Washington we use the finite element program FIDAP, from Fluent Corporation, since that is available for a research study. In CFD, however, there are two important questions that the students have no experience with: upwinding and turbulence modeling.

Shown in Fig. 18 are two cases, one an accurate one [derived using methods from the book by Finlayson (1992)] and one using upwinding. In the simplest case, an upwinding finite difference derivative would use:

$$\left.\frac{du}{dx}\right|_i \approx \frac{u_{i+1}-u_{i-1}}{2\,\Delta x} \approx \frac{u_i-u_{i-1}}{\Delta x}$$

The net effect of this change is to minimize unwanted oscillations in the solution and allow the solution to be obtained much faster. Yet, to the student, it is simply a word entered onto a data set when using a CFD gui. If the upwinding is used for a conserved quantity (as in Fig. 18) then the effect of upwinding is to spread the material out, lowering the peak value. If the phenomenon depends on the concentration in a non-linear way, then obviously one will get incorrect results. For example, in chemical flooding of an oil field, the phenomenon depends on reaching a certain concentration level. The use of upwinding could cause the model to never reach that level. Every user of CFD needs to know this.

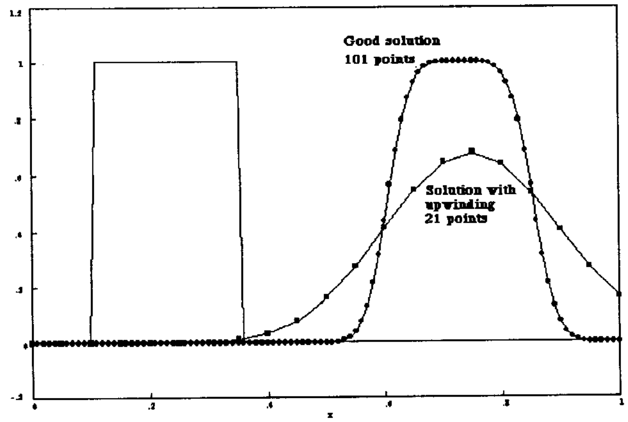

Figure 18. Concentration Profile for Flow Through a Packed Bed. One curve uses upwind differencing (and is faster to calculate); the other uses the random choice method.

At the University of Washington we have an Undergraduate Fuel Cell project, whose goal is to design and build an amusement-park sized fuel-cell powered locomotive. This is an interdisciplinary, multi-campus project. The design of the fuel cell plate is complicated, since it is necessary for the fuel to go along very small channels, looping back and forth. One design question is: how small should the cross section of those channels be? If they are smaller, then the velocity is larger, and the mass transfer is better, which is desirable. However, if they are smaller, the pressure drop is larger, which is undesirable. The pressure drop at the corners of the loops is also important. One example, provided by Karen Fukuda, is shown in Fig. 19. In this example the flow is laminar, but the flow around the ends of the loops, and the pressure drop, can be obtained

Another case where the CFD capabilities exceed the knowledge base of students is when turbulent flow is modeled. Many programs, including FIDAP, use a k-ε model of turbulence. The parameters needed for the model have been measured in special situations, such as wall shear, free shear, etc., and must be used carefully in 2D and 3D situations that have more than one type of shear flow.

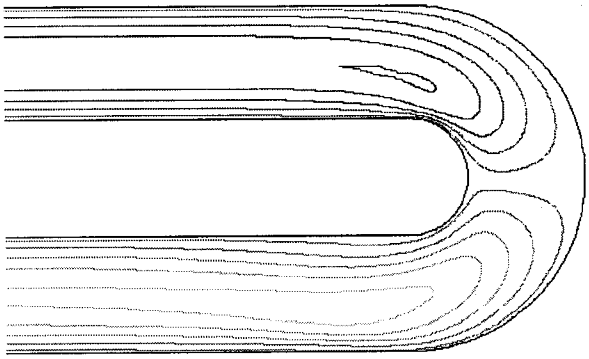

Figure 19. U_x Velocity for One-phase Flow in Fuel Cell Plate (due to Karen Fukuda)

Use of Natural Boundary Conditions in the FEM

One advantage of the finite element method is the use of natural boundary conditions, and these allow students to solve problems in semi-infinite geometries without having to extend the mesh to infinity. The example chosen here is the solution to the nonlinear Poisson-Boltzmann equation that arises in colloidal chemistry.

$$\nabla^2 \psi = -\frac{1}{A}\,\sinh(A\,\psi)$$

For the case of a charged sphere inside a cylinder with zero potential, the solution using natural boundary conditions is shown in Fig. 20. The boundary condition along the top surface is just no applied flux (the natural boundary condition for the Galerkin method). Notice that the contours need not be perpendicular to the boundary, as they would be if we enforced a condition $\partial \psi/\partial n = 0$ or $\psi = 0$. While this is true far from the sphere, a much larger domain would be necessary to reach the position where this is true. The same principle applies to Stokes flow around a sphere or cylinder - one doesn't have to use a mesh covering the entire space to eliminate the effect of the wall; one just uses natural boundary conditions and specifies no applied mass flux on those outer boundaries. For additional information about the use of natural boundary conditions, see Finlayson (1992).

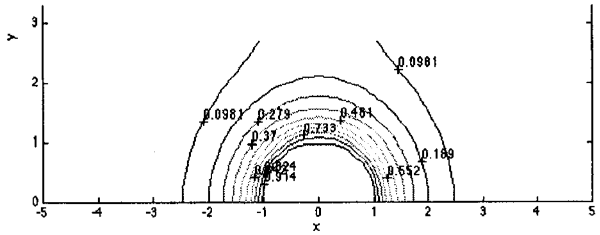

Figure 20. Potential Around Sphere in a Cylinder; Governed by the Poisson-Boltzmann Equation, A = 2.3

Conclusion.

The power of computers and computer software has made it possible for students to solve problems that could only be imagined a few years ago. This paper has shown that this requires educators to change their emphasis from the mathematics of solving the problem to the tools needed to derive a nonlinear model and assess the numerical errors. Blind acceptance of computer results benefits no one except your competitors.

References

Anklam, M.R., R. K. Prud'homme, B. A. Finlayson (1997). Ion Exchange Chromatography Laboratory. *Chem. Eng. Ed.,* **31**, 26-31.

Carberry, J. J. (1976) *Chemical and Catalytic Reaction Engineering*, McGraw-Hill, New York.

Fairbairn, A. W., H. A. Cheney, A. J. Chernaivsky (1947) Commercial Scale Manufacture of Allyl Chloride and Allyl Alcohol from Propylene. *Chem. Eng. Prog.* **43** 280-290.

Finlayson, B. A. (1992). *Numerical Methods for Problems with Moving Fronts*. Ravenna Park, Seattle.

Finlayson, B. A. (1980). *Nonlinear Analysis in Chemical Engineering.* McGraw-Hill, New York.

Hill, C. G., Jr. (1977). *Introduction to Chemical Engineering Kinetics & Reactor Design.* Wiley, New York.

Keller, H. B. (1972). *Numerical Methods for Two-Point Boundary-Value Problems*, Blaisdell, New York.

LeVeque, R. J. (1992). *Numerical Methods for Conservation Laws.* Birkhäuser Verlag, Basel.

Mears, D. E. (1971). Diagnostic criteria for heat transfport limitations in fixed bed reactors. *J. Cat.*, **20**, 127.

Mickens, R. E. (1989). Exact Solutions to a Finite-Difference Model of a Nonlinear Reaction-Advection Equation: Implications for Numerical Analysis. *Num. Methods Part. Diff. Eqn.*, **5**, 313-325.

Mitchell, A. R. and J. C. Bruch, Jr. (1985). A Numerical Study of Chaos in a Reaction-Diffusion Equation. *Num. Methods Part. Diff. Eqn.*, **1**, 13-23.

PDE Toolbox (1997). MATLAB, Mathworks, Inc.

Poulain, C. and B. A. Finlayson (1993). A Comparison of Numerical Methods Applied to Nonlinear Adsorption Columns. *Int. J. Num. Methods Fluids*, **17**, 839-859.

Rosendall, B. M. and B. A. Finlayson (1994). The Chemical Reactor Design Tool. ASEE Proceedings, pp. 2219-2222, Edmonton, Canada.

Rosendall, B. and B. A. Finlayson (1995). Transport Effects in Packed-Bed Oxidation Reactors. *Comp. Chem. Eng.*, **19**, 1207-1218.

Rosendall, B. M., Berkoe, J. M., and A. C. Heath (1998). Computational Fluid Dynamics Model of an Industrial Cracking Furnace, AIChE Annual Meeting, Miami Beach.

Smith, J. M. (1970) *Chemical Engineering Kinetics.* McGraw-Hill, New York.

Strube, J. and H. Schmidt-Traub (1998). Dynamic simulation of simulated-moving-bed chromatographic processes. *Computers Chem. Engng..* **22**, 1309-1317.

Varma, A., M. Morbidelli, and H. Wu (1998). *Parametric Sensitivity in Chemical Systems.* Cambridge University Press.

Wheeler, D. L. (1999). To Improve Their Models, Mathematicians Seek a 'Science of Uncertainty', Chronicle of Higher Education, April 16, 1999.