An Accurate One-Dimensional Model for Nonadiabatic Annular Reactors

J. Carl Pirkle, Jr., Haroon S. Kheshgi, and Patrick S. Hagan
Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, NJ 08801

Many pilot plant reactors designed to simulate commercial reactors are instrumented so that temperature can be measured along the length of the reactor tube. A favorite configuration consists of placing a small tube concentrically into the reactor tube as shown in Figure 1. Within the smaller tube, several thermocouples are placed at different positions along the axis. The interior tube, called the thermowell, is designed to be thin enough that the temperatures measured by the thermocouples are representative of the temperatures of the reacting mixture near the outside wall of the thermowell. Not only do pilot-plant reactors often have this design, but several tubes (out of the many thousands of tubes) in commercial nonadiabatic reactors have thermowells to monitor the axial temperature profiles.

In this study we extend the asymptotic analysis used to model radial heat transfer in a nonadiabatic reactor tube (Pirkle et al., 1987; Hagan et al., 1988a,b; Kheshgi et al., 1988) to those with a thermowell—an annular reactor with an insulating core. This asymptotic analysis is used to approximate two-dimensional reactor modeling equations (the two dimensions being the axial and radial position in the reactor) as one-dimensional equations (the axial position) which we refer to as the *α-model.* Of course, this significantly reduces computer simulation time and cost, since one-dimensional models require much less CPU time than two-dimensional models. This is especially valuable if we are trying to estimate kinetic rate constants and transport parameters from pilot-plant data.

Mathematical Model of a Nonadiabatic Tubular Reactor

The continuity and energy equations, with the appropriate boundary conditions, describing a single exothermic reaction occurring in a tubular reactor with heat exchange are given in dimensionless form by Hagan et al. (1988a) as Eqs. 2.6a–2.7d. Modified for the presence of a thermowell, these equations for continuity and balance of energy are:

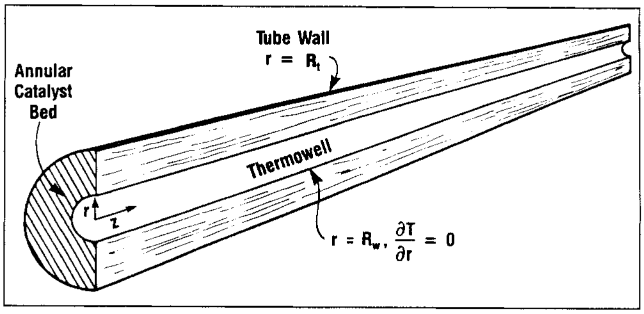

Figure 1. Reactor tube with thermowell.

$$X_Z = \frac{1}{\eta Le}(X_{rr} + \frac{1}{r} X_r) + S(X,T)$$

with

$$X_r = 0 \text{ at } r = \delta \text{ and } r = 1 \tag{1}$$

$$\eta T_z = T_{rr} + \frac{1}{r} T_r + QS(X,T)$$

with

$$T_r = 0 \text{ at } r = \delta \text{ and}$$

$$T_r = -Bi(T - T_c) \text{ at } r = 1 \tag{2}$$

where the boundary condition at $r = \delta \equiv R_w/R_t$ assumes that there is negligible heat flux into the thermowell.

Following the procedure introduced by Hagan et al. (1988a), we ignore the convection term in the energy equation and then approximate the reaction rate function $S(X,T)$ by

$$S(X,T) = S(X,T_m) \exp[A(T-T_m) + B(T-T_m)^2 + \cdots]. \tag{3}$$

Neglecting the $B(T-T_m)^2 + \cdots$ terms gives the approximate equation

$$T_{rr} + \frac{1}{r} T_r + Q\, S(X,T_m)\exp[A(T-T_m)] = 0, \quad \delta < r < 1. \tag{4}$$

Present address of J. C. Pirkle, Jr.: Exxon Research and Development Laboratories, 4999 Scenic Highway, Baton Rouge, LA 70821.
Present address of P. S. Hagan is Los Alamos Scientific Laboratory, Los Alamos, NM 87544.

Solution of this system of equations can be used as a zero-order approximation to the full energy equation, which includes a convection term. Energy balance (Eq. 4) and boundary conditions (Eq. 2) resemble the "explosion" problem (Thomas, 1958) except that we now have an annular shaped medium instead of the more familiar cylindrical shape.

Solution of "Explosion" Problem for Annulus

The "explosion" problem for a cylindrical region has been solved analytically and involves a tricky substitution (Chambre, 1952). The problem for the annulus is even more difficult due to the boundary condition at $r = \delta$.

To solve Eq. 4, we first let $\theta \equiv AT$ so that we have

$$\theta_{rr} + \frac{1}{r}\theta_r = -\Gamma \exp(\theta) \tag{5}$$

with $\theta_r = 0$ at $r = \delta$ and $\theta_r = -Bi(\theta - \theta_c)$ at $r = 1$

where $\Gamma = AQS \exp(-AT_m)$. Make the substitution of variables made by Chambre (1952) for the cylindrical problem:

$$u = r^2 \exp(\theta) \text{ and } w = r d\theta/dr. \tag{6}$$

Substitution of Eq. 6 into Eq. 5 yields

$$dw/du = -\frac{\Gamma}{(2+w)} \tag{7}$$

which has the solution

$$w^2 + 4w + D = -2\Gamma u \tag{8}$$

where D is an arbitrary constant.

Substitution of the original variables into Eq. 8 gives

$$\theta_{rr} - \frac{1}{r}\theta_r - \frac{1}{2}(\theta_r)^2 + E/r^2 = 0 \tag{9}$$

where E is an arbitrary constant. If we let $\psi = \theta_r$, we get a Ricatti equation

$$\psi_r = \frac{1}{r}\psi + \frac{1}{2}\psi^2 - E/r^2. \tag{10}$$

Following the procedure outlined in Bender and Orszag (1978), we solve the Ricatti equation to get

$$\psi = -\frac{2(1+F)}{r} + \frac{1}{C_1 r^{1+2F} + r/(4F)} \tag{11}$$

where C_1 and F are arbitrary constants.

Since $\psi = \theta_r$, we now have

$$d\theta/dr = -\frac{2(1+F)}{r} + \frac{F}{(C_1 r^{2F} + 1/4)r} \tag{12}$$

where C_1 is a new arbitrary constant (the old C_1 multiplied by F). We can use the condition $\theta_r = 0$ at $r = \delta$ to get C_1 in terms of F:

$$C_1 = \frac{1}{\delta^{2F}}\left\{\frac{F}{2(1+F)} - \frac{1}{4}\right\}. \tag{13}$$

For convenience, we retain C_1 in Eq. 12 for shorter notation until later.

Now, we integrate Eq. 12 by separation of variables to get

$$\theta = -2(1+F)\ln(r) - 2\ln(C_1 r^{2F} + 1/4) + 2\ln r^{2F} + C_2. \tag{14}$$

We can obtain the arbitrary constant C_2 in terms of F and C_1 by substituting the above expression for θ into the original differential equation. This yields

$$C_2 = \ln(2F^2 C_1/\Gamma) \tag{15}$$

which, when substituted into Eq. 14 gives

$$\theta = \ln[r^{-2(1+F)}] + \ln(C_1 r^{2F} + 1/4)^{-2} + \ln r^{4F} + \ln(2F^2 C_1/\delta). \tag{16}$$

Applying condition $\theta_r = -Bi(\theta - \theta_c)$ at $r = 1$, allows us to obtain

$$\ln(2F^2C_1/\Gamma) = 2(1+F)/Bi - F/[Bi(C_1 + 1/4)] + \ln(C_1 + 1/4)^2 + \theta_c. \tag{17}$$

Substituting $\theta \equiv AT$ and Eq. 17 into Eq. 16 gives

$$AT = \frac{2(1+F)}{Bi} - \frac{F}{Bi(C_1 + 1/4)} + AT_c - 2\ln(r^{1+F}) - 2\ln(C_1 r^{2F} + 1/4) + 2\ln(r^{2F}) + 2\ln(C_1 + 1/4). \tag{18}$$

Substituting Eq. 13 for C_1 into Eq. 18 gives, after considerable manipulation,

$$T = T_c + \frac{1}{A}\left\{\frac{2(F^2-1)(1-\delta^{2F})}{Bi[F-1+(F+1)\delta^{2F}]} - 2\ln\left[\frac{(F-1)r^{F+1} + (F+1)\delta^{2F} r^{1-F}}{F-1+(F+1)\delta^{2F}}\right]\right\}. \tag{19}$$

Now, substitution of Eq. 13 for C_1 into Eq. 17, the equation obtained from the boundary condition at $r = 1$, yields, after some rearrangement

$$\frac{2}{Bi}\left\{\frac{F^2 - 1 - (F^2-1)\delta^{2F}}{(F-1)+(F+1)\delta^{2F}}\right\} = \ln\left\{\frac{8\delta^{2F}(F^2-1)F^2}{[(F-1)+(F+1)\delta^{2F}]^2\Gamma}\right\} - AT_c. \tag{20}$$

Raising both sides of the above equation as exponentials of e gives, after substituting for Γ,

$$AQS\exp[-A(T_m-T_c)]=\frac{8F^2\delta^{2F}(F^2-1)}{[F-1+(F+1)\delta^{2F}]^2}\exp\left[-\frac{2}{Bi}\frac{(F^2-1)(1-\delta^{2F})}{(F-1)+(F+1)\delta^{2F}}\right] \quad (21)$$

which can be solved to get values of F corresponding to given values of A, T_c, T_m, δ, Q, S, and Bi. Substituting these values into Eq. 19 completes the solution to the original "explosion" problem Eq. 4. This provides a radial temperature profile that can be used as a zero-order solution to the complete reactor problem (Eqs. 1 and 2) which includes convection.

Inclusion of Convection Term

Define the radially averaged conversion X_m and the reaction averaged temperature T_m in the reactor by

$$X_m(z)=\frac{1}{(1-\delta^2)}\int_\delta^1 2rX(z,r)dr, \quad (22)$$

$$S(X_m,T_m)=\frac{1}{1-\delta^2}\int_\delta^1 S[X_m,T(z,r)]2rdr. \quad (23)$$

Let the radially averaged value of any function $f(r)$ be represented by

$$\langle f(r)\rangle=\frac{1}{1-\delta^2}\int_\delta^1 2f(r)rdr. \quad (24)$$

Taking the cross-sectional average of the two-dimensional equations (Eqs. 1 and 2) yields

$$dX_m/dz=S_m(X_m,T_m) \quad (25)$$

$$\eta dT_m/dz=\left\langle T_{rr}+\frac{1}{r}T_r\right\rangle+QS_m(X_m,T_m) \quad (26)$$

where we have approximated the radially averaged temperature gradient $\langle dT/dz\rangle$ by dT_m/dz following the arguments of Hagan et al. (1988a).

The heat loss term $\langle T_{rr}+T_r/r\rangle$ can be related to the reaction temperature T_m. At each axial position z, we demand that $T(z,r)$ is of the form Eq. 19 for some value of the parameter F which depends on z. Then

$$\left\langle T_{rr}+\frac{1}{r}T_r\right\rangle=\frac{2}{1-\delta^2}\int_\delta^1 (rT_r)_r dr=\frac{2}{1-\delta^2}T_r|_{r=1} \quad (27)$$

where we have used the condition $T_r=0$ at $r=\delta$. Substituting Eq. 19 into the right side of Eq. 27, we get

$$\left\langle T_{rr}+\frac{1}{r}T_r\right\rangle=-\frac{8\alpha}{A(1-\delta^2)} \quad (28)$$

with

$$\alpha=\frac{1}{2}\frac{(F^2-1)(1-\delta^{2F})}{F-1+(F+1)\delta^{2F}}. \quad (29)$$

Here α is similar to the parameter in the α-model for radial heat transport in a cylindrical tube except for the factor $(1-\delta^2)$ that appears on the right side of Eq. 28. Equation 21 can now be simplified by substituting Eq. 29 into the argument of the exponential on the right side of the equation:

$$AQS\exp[-A(T_m-T_c)]=\frac{8F^2\delta^{2F}(F^2-1)}{[F-1+(F+1)\delta^{2F}]^2}\exp\left(-\frac{4\alpha}{Bi}\right). \quad (30)$$

To relate α in the heat loss expression Eq. 28 to the reaction-averaged temperature T_m, we derive an expression for T_m in terms of α. Substituting the expansion (Eq. 3) into the definition Eq. 23 of T_m yields

$$1=\langle\exp[A(T-T_m)][1+B(T-T_m)^2+\ldots]\rangle \quad (31)$$

or

$$1=\langle\exp[A(T-T_m)]\rangle+B\langle\exp[A(T-T_m)][A(T-T_m)]^2\rangle. \quad (32)$$

It can be shown that the last term in Eq. 32 is a small correction when $\delta=0$. Although it is not readily apparent from Eq. 19 and Eq. 21, the equilibrium profile is of the form

$$T=T_0(r)+\delta^2T_1(r)+\ \ldots.. \quad (33)$$

where $T_0(r)$ is the equilibrium profile for the $\delta=0$ (no thermowell) case. Thus, we choose to work out the first term in Eq. 32 through $0(\delta^2)$, and use the result from the $\delta=0$ case for the last term.

Neglecting the last term in Eq. 32, and using Eq. 4, which is satisfied by the equilibrium profile, we obtain

$$1=\langle\exp(A(T-T_m)\rangle=-\frac{2}{QS(1-\delta^2)}T_r|_{r=1}=\frac{4(F^2-1)(1-\delta^{2F})}{QAS(1-\delta^2)[F-1+(F+1)\delta^{2F}]}. \quad (34)$$

From Eq. 30, we substitute for $QAS(X,T_m)$ and get

$$1=\frac{1-\delta^{2F}}{(1-\delta^2)\delta^{2F}}\frac{F-1+(F+1)\delta^{2F}}{2F^2}\exp(4\alpha/Bi)\exp[-A(T_m-T_c)]. \quad (35)$$

Equations 21 and 35 can be solved for $F(z)$ and $\alpha(z)$ by the bisection method at the inlet of the reactor. Then, since the values of $\alpha(z)$ and $F(z)$ change smoothly with position z, they can be obtained by the Newton-Raphson method for downstream grid-points. Substitution of Eq. 28 into 26 gives the α-model energy equation for a nonadiabatic reactor with a thermowell:

$$\eta dT_m/dz=-\frac{8\alpha}{A(1-\delta^2)}+QS_m(X_m,T_m). \quad (36)$$

Table 1. Parameters and operating conditions used in the test problem for models of an annular nonadiabatic tubular reactor.

Parameter or Operating Condition	Value
Inlet (coolant) temperature, T_c	630 to 635 K
Inlet pressure, P_I	0.1014 MPa
Inlet gas velocity, V_I	5.92 $m \cdot s^{-1}$
Inlet concentration of reactant w_{1I}	4×10^{-4} $kmol \cdot kg^{-1}$
Gas phase specific heat C_{pf}	1.059 $kJ \cdot kg^{-1} \cdot K^{-1}$
Catalyst phase bulk density ρ_B	1300 $kg \cdot m^{-3}$
Tube radius R_t	0.01323 m
Thermowell radius R_w	0.00433 m
Tube length L	2.00 m
Interparticle bed voidage ϵ	0.38
Effective thermal conductivity Λ	2.804 $kJ \cdot m^{-1} \cdot h^{-1} \cdot K^{-1}$
Wall heat transfer coefficient h_w	560.9 $kJ \cdot m^{-2} \cdot h^{-1} \cdot K^{-1}$
Peclet number for radial mass transfer Pe_{mr}	8.0
Activation energy E_1	1.134×10^5 $kJ \cdot kmol^{-1}$
Pre-exponential rate constant $k_{0,1}$	1.75×10^6 $m^3 \cdot kg\ cat^{-1} \cdot s^{-1}$
Heat of reaction ΔH_1	-1.287×10^6 $kJ \cdot kmol^{-1}$

Comparison of the α-Model and 2-D Model

The straightforward test of the accuracy of the α-model is to compare its solutions with those of the two-dimensional model. Using the finite difference method, we compute solutions of the modeling equations for a first-order exothermic reaction in a nonadiabatic reactor. In these cases, inlet temperature was set equal to the coolant temperature, and the pressure drop was neglected. The chosen values for the kinetic and transport parameters and the operating conditions are given in Table 1 and are similar to those in α-model solutions for a tubular reactor reported by Pirkle et al. (1987).

For three different values of the coolant temperature, Figure 2 compares the radially-averaged temperature and conversion profiles generated by the one-dimensional α-model and the two-dimensional model. For proper coolant temperatures, the agreement between the two models is remarkable, just as in the case of reactors without thermowells (Pirkle et al., 1987; Hagan et al., 1988a,b; Kheshgi et al., 1988). For higher coolant temperatures, which are just below those leading to temperature runaway, the α-model barely overpredicts the temperature rise, making it a slightly conservative design tool. Thus, the α-model for a reactor with a thermowell is an excellent approximation to the more rigorous two-dimensional model and can be used in a variety of preliminary design and optimization calculations.

Notation

A = $\partial \ln S / \partial T$ at $T = T_m$
B = $(1/2)\ \partial^2 \ln S / \partial T^2$ at $T = T_m$
Bi = Biot number for radial heat transfer
F = implicitly defined variable in Eq. 21 needed for α
Le = Lewis number
r = dimensionless radial position
Q = dimensionless reactive heat release rate
R_t = inner radius of reactor tube
R_w = outer radius of thermowell tube
S = normalized reaction rate
T = dimensionless temperature
T_c = dimensionless coolant temperature
T_m = radially averaged dimensionless temperature
X = dimensionless concentration
z = dimensionless axial position

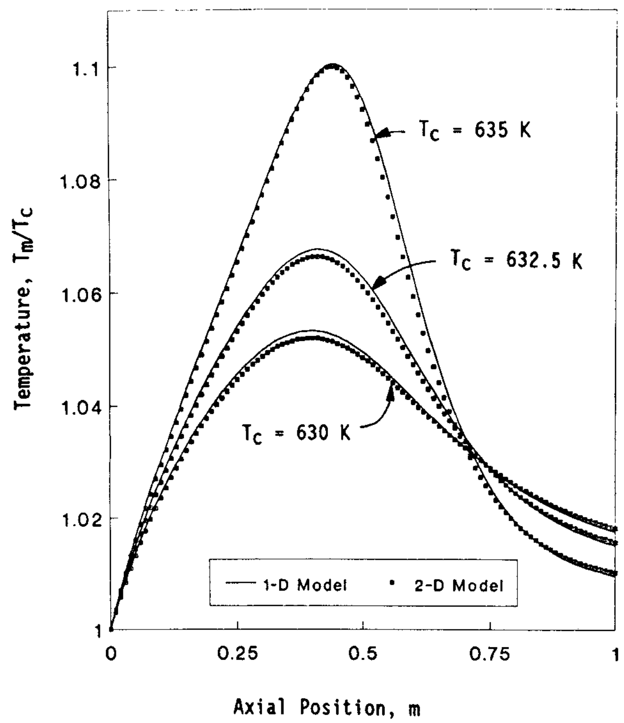

Figure 2a. Radially averaged temperature of an nonadiabatic annular reactor: 1-D α-model vs. full 2-D model.

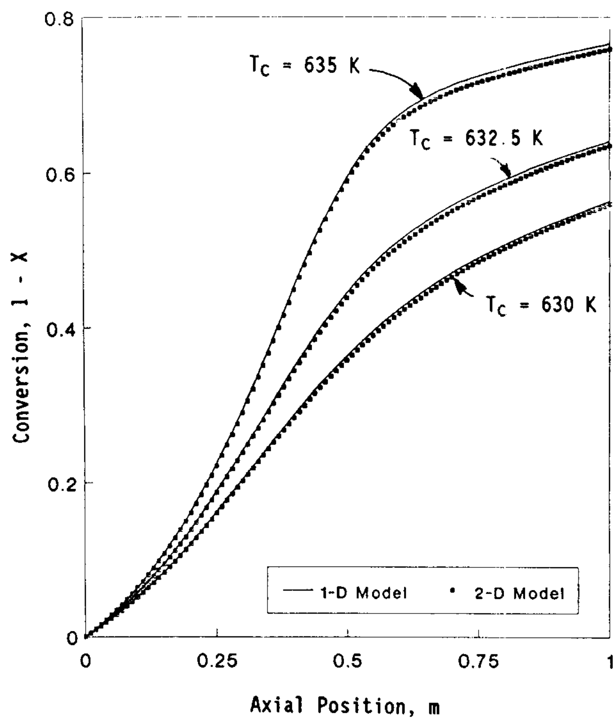

Figure 2b. Concentration solution of an nonadiabatic annular reactor: 1-D α-model vs. full 2-D model.

Greek letters

α = heat transfer parameter
δ = ratio of thermowell to reactor tube radius
η = ratio of time scales for radial transfer of heat to reactive heat release

Literature Cited

Bender, C. M., and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers*, p. 20, McGraw-Hill, New York (1978).

Chambre, P. L., "On Solution of the Poisson-Boltzman Equation with Applications to the Theory of Explosions," *J. Chem. Phys.*, **20**, 1795 (1952).

Hagan, P. S., M. Herskowitz, and J. C. Pirkle, "A Simple Approach to Highly Sensitive Tubular Reactors," *SIAM J. Appl. Math.*, **48**, 1083 (1988a).

Hagan, P. S., M. Herskowitz, and J. C. Pirkle, "Runaway in Highly Sensitive Tubular Reactors," *SIAM J. Appl. Math.*, **48**, 1437 (1988b).

Kheshgi, H. S., S. C. Reyes, J. C. Pirkle, and P. S. Hagan, "Transients in Tubular Reactors: Comparison of One- and Two-Dimensional Models," *AIChE J.*, **34**, 1373 (1988).

Pirkle, J. C., S. C. Reyes, P. S. Hagan, H. S. Kheshgi, and W. E. Schiesser, "Solution of Dynamic Distributed Parameter Model of Nonadiabatic, Fixed-bed Reactor," *Comp. Chem. Eng.*, **11**, 737 (1987).

Thomas, P. H., "On the Thermal Conduction Equation for Self-Heating Materials with Surface Cooling," *Trans. Farday Soc.*, **54**, 60 (1958).

Manuscript received May 28, 1991, and revision received June 17, 1991.