Accurate One-Dimensional Fixed-Bed Reactor Model Based on Asymptotic Analysis

M. Herskowitz
Dept. of Chemical Engineering
Ben Gurion University of the Negev
Beer Sheva, Israel

P. S. Hagan
Theoretical Division
Los Alamos National Laboratory
Los Alamos, NM 87545

Radial and axial temperature and concentration profiles measured in nonadiabatic, nonisothermal fixed-bed reactors are simulated by solving the two-dimensional (2-D) mass and energy balances. The 2-D (pseudohomogeneous) model includes two radial heat transfer resistances: one in the bed and the other near the wall. The ratio of the two defines the Biot number (Froment, 1984; Hofmann, 1979).

The modeling of fixed-bed reactors has been reviewed recently (Doraiswamy and Sharma, 1984; Eigenberger and Ruppel, 1986; Paterson and Carberry, 1983; Periera Duarte and Lemcoff, 1984). One of the basic assumptions in the development of the models is plug flow. Ahmed and Fahien (1980) and Vortmeyer and Winter (1984) introduced a radial velocity gradient created by the radial porosity gradient of the bed. Hoffmann (1979) reviewed several cases and found that the two-dimensional plug flow model predictions were in excellent agreement with the detailed radial and axial temperature and concentration profiles. The pseudohomogeneous 2-D model with radially constant velocities is the basis for the derivations in this paper.

The numerical solution of the 2-D model, especially in dynamic analyses where time is an additional independent variable, can be difficult and time-consuming (Bonvin et al., 1983). Hence efforts have been made to develop accurate one-dimensional (1-D) models that can replace the 2-D model. Additionally, 1-D models can be analyzed further to find, for example, reactor runaway criteria.

Combining the two radial heat transfer resistances of the 2-D model in series gives a constant overall heat transfer coefficient, which is the basis of the standard 1-D model. The approximation of a constant overall heat transfer coefficient is excellent when the radial temperature differences are small. This is the case for reactors far from runaway or with small Biot numbers. However, as the temperature gradients in the bed increase, the much higher rate of heat generation at the centerline distorts the radial temperature profile. In essence, the average path for heat transfer in the bed increases as the radial temperature gradients in the bed increase. This increase causes a decrease of the overall heat transfer coefficient. Therefore, if this coefficient is kept constant, the temperatures predicted by the 1-D model will be lower than the temperatures predicted by the 2-D model.

This is borne out by Froment (1967), who showed that as the reactor is operated at conditions closer to a runaway, the discrepancy between the 2-D and 1-D models increases. Marek and Hlavacek (1967) and Mears (1971) derived criteria defining the conditions where the 1-D model may be used. However, in practice many reactors operate at near runaway conditions, which makes it necessary to use the 2-D model or to develop a better 1-D model.

Recently Hagan et al. (187) derived an important 1-D model called the α model. They showed that the α model predicts temperature and concentration profiles that are very close to the 2-D model predictions, even near runaway. However, all the examples considered were chosen to be mathematically simple, without regard to their physical relevance. The purpose of this investigation is to determine whether the α model is also accurate for realistic kinetic schemes.

α Model

The α model is based on an asymptotic analysis of the 2-D model, assuming that the maximum temperature rise from the

Table 1. Reactor and Reaction Parameters in Two Studies

	Valstar et al. (1975)	Emig et al. (1980)		
Reactor dia., m	0.041	0.05		
Reactor length, m	1.0	1.44		
Catalyst dia., m	0.0033	0.004		
r_0, kmol/m^3 · s	$\dfrac{2.8 \times 10^6 \exp(-10{,}210/T) P_{Ac}{}^{*,**}}{1 + 198 \times 10^{-4} \exp(3{,}780/T) P_{HAc} + 2.6 P_{VA}}$	$\dfrac{4.92 \times 10^6 \exp(-9{,}160/T) P_{Ac}{}^{**}}{RT}$		
$(-\Delta H)$kJ/kmol	1.06×10^5	1.06×10^5	—	—
C_p, kJ/kg · K	1.7	1.7–1.9	—	—
G, kg/m^2 · s	0.242	0.05	0.10	0.15
λ_{er}†, J/m · s · K	0.44	0.26	0.35	0.40
h†, J/m^2 · s · K	155	103	116	119
Bi	7.22	10.0	8.33	7.43

*For molar, a ratio of acetylene to acetic acid of 1.5

**Partial pressure given in atm

†Calculated for Valstar et al. (1975) data and Dixon (1985) correlation

wall to the centerline of the reactor is much smaller than the adiabatic temperature rise. This analysis yielded an analytical expression for the radial temperature profile. Substituting this profile into the 2-D mass and energy balances and averaging over the reactor cross section then yielded the α model equations. The details are given elsewhere (Hagan et al., 1987).

The final mass and energy balances of the α model, expressed in *dimensional* form, are

$$(G y_{A0}/M_0) \frac{dX_A}{dz} = r_0(X_A, T_r) \tag{1}$$

$$G C_p \frac{dT_r}{dz} = -(\lambda_{er}/r_t^2) \frac{8\alpha}{A} + (-\Delta H) r_0(X_A, T_r) \tag{2}$$

Here T_r is the reaction-averaged temperature defined as

$$\exp(-E/RT_r) = \int_0^1 \exp(-E/RT) 2\rho \, d\rho \tag{3}$$

and α must be calculated from

$$A(T_r - T_w) = 4\alpha/Bi - \ln(1 - \alpha) + B \ln^2(1 - \alpha)/3A^2 \tag{4}$$

at each point z. Once Eqs. 1–4 have been solved, the 2-D concentration and temperature are given by

$$\begin{aligned} X_A(z, r) = X_A(z), \quad T(z, r) &= T_w \\ &+ [4\alpha/Bi - 2 \ln(1 - \alpha + \alpha r^2/r_t^2)]/A \end{aligned} \tag{5}$$

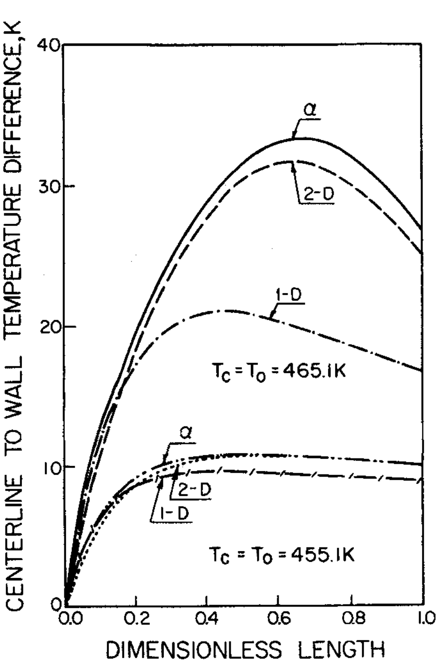


Figure 1. Predicted axial temperature profiles for Valstar et al. (1975) kinetics.

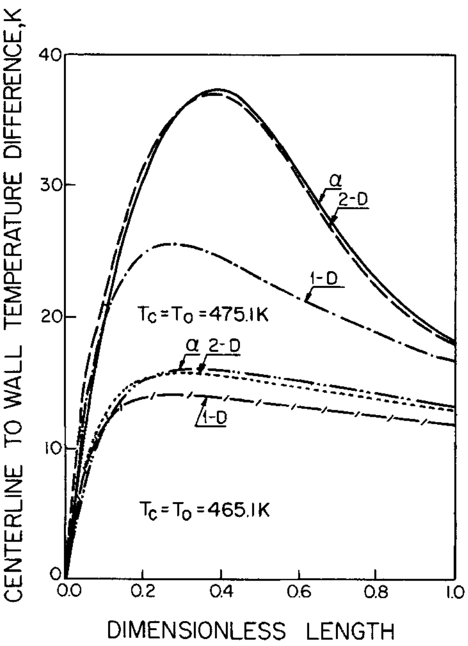


Figure 2. Predicted axial temperature profiles for Emig et al. (1980) kinetics.

$G = 10$ kg/m^2 · s

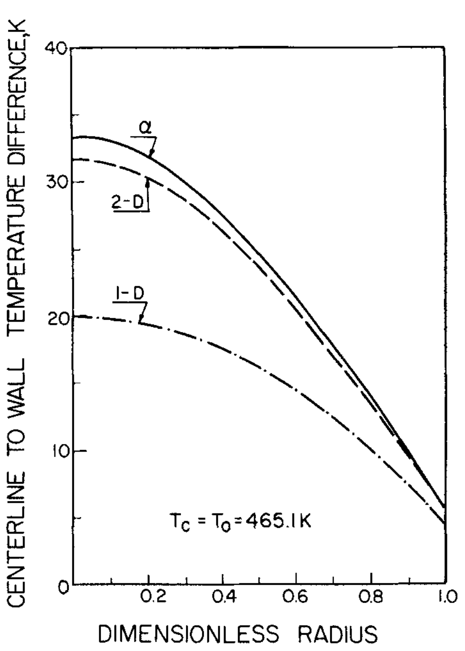


Figure 3. Predicted radial temperature profile for Emig et al. (1975) kinetics.

A is the effective activation energy

$$A = \frac{\partial}{\partial T}\ln(r_0) \quad \text{at } T = T_r \tag{6}$$

and B is a correction factor

$$B = \frac{1}{2}\frac{\partial^2}{\partial T^2}\ln(r_0) \quad \text{at } T = T_r \tag{7}$$

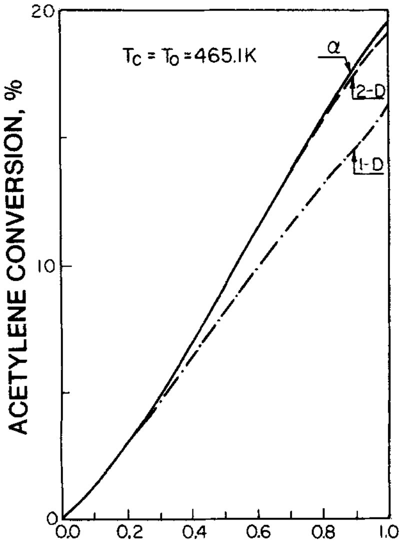


Figure 4. Predicted acetylene conversion for Valstar et al. (1975) kinetics.

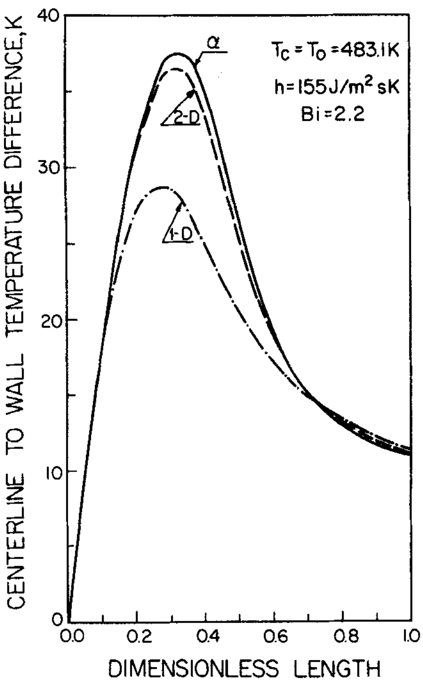


Figure 5. Effect of Biot number on agreement among the three models.

The difference between Eq. 2 of the α model and the energy balance of the (standard) 1-D model is the heat removal term. Comparing the two terms, we see that the equivalent heat transfer coefficient U for the α model is

$$U = (\lambda_{er}/r_t)\frac{4\alpha}{A(T_r - T_w)} \tag{8}$$

Substituting α from Eq. 4 and expanding yields

$$(\lambda_{er}/r_t)\frac{1}{U} = \frac{1}{Bi} - (\lambda_{er}/r_t)\frac{1}{U\phi_r} \cdot \ln\left[1 - (r_t/4\lambda_{er})U\phi_r\right] + \cdots \tag{9}$$

where $\phi_r = A(T_r - T_w)$. From Eq. 9 two extreme values of U can be calculated:

$$(\lambda_{er}/r_t)\frac{1}{U} = \frac{1}{Bi} + \frac{1}{4} \quad \text{as } \theta_r \to 0 \tag{10}$$

$$(\lambda_{er}/r_t)\frac{1}{U} = \frac{1}{Bi} + \frac{1}{3} \quad \text{at runaway} \tag{11}$$

Finlayson (1980) derived Eq. 11 by applying the orthogonal collocation method to the 2-D energy balance at one point. Equation 10 gives an upper bound on U, while Eq. 11 gives a lower bound. The difference between the two can be as high as 25% for $Bi \gg 1$.

The α model can be extended to cover multiple-reaction systems (Hagan et al., 1987). The only other modification needed for the multiple-reaction case is that A and B must be defined

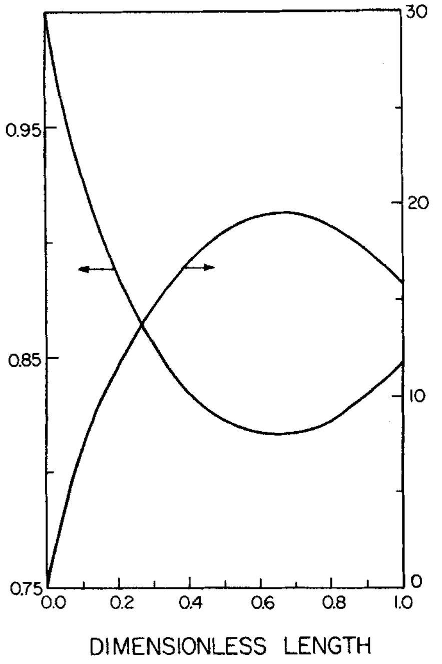


Figure 6. Effect of temperature gradient on overall heat transfer coefficient.

as

$$A = \frac{\partial}{\partial T}\ln(H) \quad B = \frac{1}{2}\frac{\partial^2}{\partial T^2}\ln(H) \quad \text{at } T = T_r \tag{12}$$

where

$$-R_j = -\sum_{i=1}^{N} s_{ij} r_{0,i} \tag{13}$$

$$H = \sum_{i=1}^{N} (-\Delta H)_i r_{0,i} \tag{14}$$

With these values of A and B, Eqs. 1–4 are solved as in the single-reaction case.

Comparison of the Three Models

The predictions of the three models were compared for the vinyl acetate synthesis reaction from acetylene and acetic acid, using the kinetic schemes published by Valstar et al. (1975) and Emig et al. (1980). The former is a non-Arrhenius type expression while the latter is of Arrhenius form. They are listed in Table 1 along with the heat transfer parameters measured by Valstar et al. (1975).

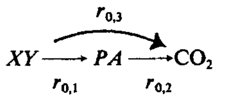
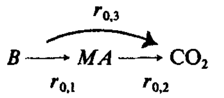
The radial temperature profile at each axial position was calculated from Eq. 5 for the α model, while a parabolic profile was assumed for the (standard) 1-D model:

$$T = T_a + \frac{Bi}{Bi + 4}(T_a - T_w)(1 - 2\rho^2) \tag{15}$$

Figures 1 and 2 graph the predicted centerline temperature rise $T(z, 0) - T_w$ against the axial position z. Figure 3 shows the predicted radial temperature profile at a position close to the hot spot in Figure 1. Axial conversion (of acetylene) profiles are shown in Figure 4.

For both kinetic schemes, the predictions of the α model are very close to the 2-D model predictions, even at near runway conditions. On the other hand, predictions based on the 1-D model deviate substantially from the 2-D model predictions, especially as conditions approach runaway and the temperature gradients get larger. The agreement of the 1-D model with both the 2-D and α models improves as the Biot number decreases. An example is shown in Figure 5.

Table 2. Reactor and Reactions Parameters for Phtalic Anhydride and Maleic Anhydride Synthesis

	Reaction System	
	Phthalic Anhydride	Maleic Anhydride
Reaction scheme	 $r_{0,3}$ $XY \xrightarrow{} PA \xrightarrow{} CO_2$ $r_{0,1}$ $r_{0,2}$	 $r_{0,3}$ $B \xrightarrow{} MA \xrightarrow{} CO_2$ $r_{0,1}$ $r_{0,2}$
Kinetic Expressions	Froment (1967)	Centi et al. (1985)
$r_{0,1}$ kmol/m$^3 \cdot$ s	$3.1 \times 10^7 \exp(-13{,}600/T) y_{Xy}$	$89 \exp(-5{,}440/T) y_B/(1 + 52.9 y_B)$
$r_{0,2}$ kmol/m$^3 \cdot$ s	$8.6 \times 210^7 \exp(-15{,}600/T) y_{PA}$	$3.8 \times 10^{-3} \exp(-6{,}900/T) y_{MA}/y_B^{1.15}$
$r_{0,3}$ kmol/m$^3 \cdot$ s	$1.3 \times 10^7 \exp(-14{,}400/T) y_{Xy}$	$1.9 \times 10^{-3} \exp(-13{,}200/T)$
Heat of Reaction		
$(-\Delta H)_1$, kJ/kmol	1.09×10^6	1.24×10^6
$(-\Delta H)_2$, kJ/kmol	3.24×10^6	1.42×10^6
$(-\Delta H)_3$, kJ/kmol	4.18×10^6	2.66×10^6
C_p, kJ/kg $\cdot$ K	1.05	1.05
y_{Xy}, y_B	0.0093	0.0093
G, kg/m$^2 \cdot$ s	1.30	1.30
Reactor dia., m	0.025	0.025
Reactor length, m	3.0	3.0
Catalyst dia., m	0.003	0.003
λ_{er}*, J/m $\cdot$ s $\cdot$ K	0.51	0.51
h*, J/m$^2 \cdot$ s $\cdot$ K	200	200

*De Wasch and Froment (1972)

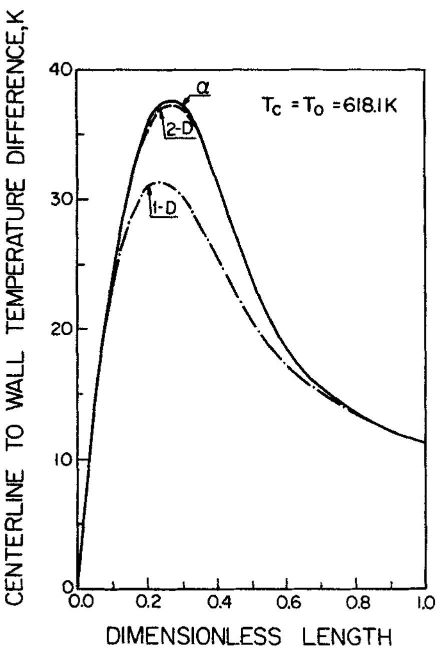


Figure 7. Predicted axial temperature profiles for phthalic anhydride system.

As mentioned earlier, the overall heat transfer coefficient is not constant, as assumed in the 1-D model, but decreases as the temperature rise increases. The value of U calculated from Eq. 8 is plotted in Figure 6 for the conditions in Figure 2.

The α model was also tested for multiple-reaction systems. Extensive simulations were carried out for the oxidation of σ-xylene and butane using the kinetics of Froment (1967) and Centi et al. (1985). The parameters are given in Table 2. The results are illustrated by Figures 7 and 8. The trend of the results is similar to those described previously for the case of single-reaction systems. Simulations of these and other systems clearly show that the α model is as accurate for multiple-reaction systems as it is for single-reaction systems.

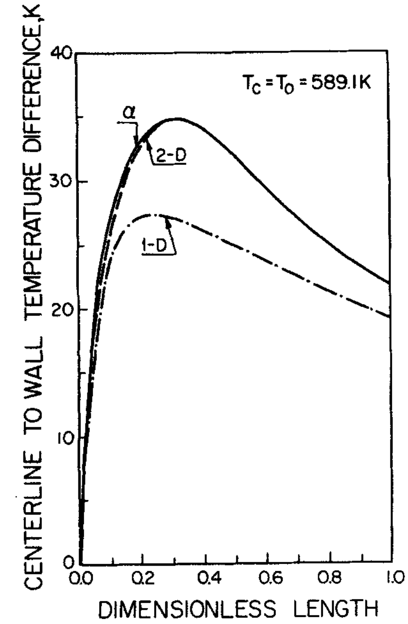


Figure 8. Predicted axial temperature profiles for maleic anhydride system.

Notation

A = parameter, Eq. 6 or 12
B = parameter, Eq. 7 or 12
Bi = Biot number, $h_w r_t / \lambda_{er}$
C_p = heat capacity, kJ/kg · K
E = activation energy, kJ/kmol
G = mass velocity, kg/m^2 · s
H = heat generated by reactions, Eq. 14, kJ/kmol
$(-\Delta H)$ = heat of reaction, kJ/kmol
$(-\Delta H)$ = heat of reaction i, kJ/kmol
h_w = wall heat transfer coefficient, kJ/m^2 · s · K
M_0 = molecular weight of feed, kg/kmol
R = universal gas constant, kJ/kmol · K
R_j = rate of change of component j, kmol/s · m^3
r = radial distance, m
r_0 = overall rate of reaction, kmol/s · m^3
$r_{0,i}$ = overall rate of reaction, i, kmol/s · m^3
r_t = reactor radius, m
s_{ij} = stoichiometric coefficient of component j in reaction i
T = temperature, K
T_a = area-averaged temperature, K
T_r = reaction-averaged temperature, K
T_w = wall temperature, K
ΔT_{ad} = adiabatic temperature rise, K
U = overall heat transfer coefficient, kJ/m^2 · s · K
X_A = conversion of key component A
X_j = conversion of component j
y_{A0} = mole fraction of component A in feed
z = axial distance, m

Greek letters

α = parameter, Eq. 4
λ_{er} = effective radial conductivity, kJ/m · s · K
ρ = dimensionless radial distance, r/r_t

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