

# Chapter 7. Steady state reactor models for single fluid phase

## 7.1 Adiabatic fixed bed

Process simulation programs usually include a model for an adiabatic bed. However, a model is provided here for two reasons. First, the ideal adiabatic bed model demonstrates the advantage of using mass balances that involve mass fractions as opposed to concentrations. Second, the design engineer may wish to explore more than one reactor type. Since all of the models share common physical and reaction properties, conducting the reactor exploration with one modeling system saves time.

Several assumptions may be made regarding the relevant physical processes in the reactor. The assumptions for the adiabatic bed model are discussed in the next three sections.

### **Intraparticle temperature and concentrations**

The temperature in the catalyst is normally nearly isothermal, which is the assumption for this book. Support for this assumption may be found in Carberry (1975), Kehoe and Butt (1972), and Carberry and Wendel (1963).

The composition will vary significantly with the radial position within the catalyst. However, the reaction rate expressions developed for the models are based on the whole particle performance as discussed in Chapter 6 and demonstrated in Example 4. This performance is related to the fluid composition at the surface of the particle and the particle temperature.

### **Interphase temperature and concentration gradients**

A stagnant film of fluid surrounds the catalyst particle. Reactants and products cross this film by diffusion. Similarly, heat is exchanged between the particle and the bulk fluid by conduction. Thus, there will be a difference in concentration and temperature between the catalyst surface and the bulk moving fluid. The size of these differences depend on both the rate and heat of reaction and the thickness of the stagnant film. The latter is a function of the velocity of the bulk fluid.

Mass transfer via diffusion is orders of magnitude greater than heat transfer by conduction. This assertion is based on the ratio of the Schmidt number to the Prandtl number. Thus, heat transfer resistance is more likely to be significant than mass transfer resistance. For commercial gas reactors, the mass transfer resistance may be ignored, Lee (1985). This assumption may not be valid for small, laboratory reactors. In that case, the mass balances may be modified to include the mass transfer resistance in the same manner as with the heat transfer resistance in the heat balance, discussed below.

The film resistance to heat transfer is often not significant in commercial reactors, but there are cases where this assumption is not true. Also, the use of criteria based on inlet temperatures and compositions are not valid for other conditions within the reactor. Thus, the temperature gradient may be insignificant at the reactor inlet and outlet, yet be very significant at a hot or cold spot. Also, gradients may increase during transient conditions. Ignoring those transient gradients could result in significant error.

The pseudohomogeneous model for an adiabatic bed is presented in this section as an introduction to the weight fraction method. This model can be used for those cases where the interphase temperature difference meets a criteria presented in eq (7.21a).

### Axial dispersion

In most cases, axial dispersion of mass and heat are insignificant. The exception is very short beds, such as metal gauze reactors. During startup or a change in feed temperature or flow rate, catalyst beds may appear to have axial dispersion. This is caused by the heat capacity of the catalyst and the heat transfer resistance between the catalyst and the fluid. If a heat balance is included for the catalyst, no additional axial dispersion term is needed.

A general criterion for the significance of axial mixing is given by Rase (1990). Axial dispersion is not significant when

$$\frac{L}{d_p} \geq 50 \qquad \begin{array}{l} L = \text{reactor length} \\ d_p = \text{catalyst particle diameter} \end{array} \qquad (7.1)$$

Each catalyst particle and the surrounding fluid may be considered a stirred tank. Thus, the criterion above states that 50 tanks in series will equate to an ideal (i.e. without axial dispersion) plug flow reactor.

The significance of axial dispersion depends upon the relative sizes of the reaction and dispersion terms. Belfiore (2002) studied this relationship for mass dispersion and determined the critical Peclet number for various reaction rates and orders (Tables 22-3 and 22-4 in Belfiore). Rase (1990) provided another criterion that indirectly relates the dispersion term and the reaction rate, as shown in Eq (7.2).

$$\frac{L}{d_p} > \frac{20 \cdot n}{Pe_{a\_M}} \cdot \ln\left(\frac{C_{A0}}{C_{Ae}}\right) \qquad (7.2)$$

$$Pe_{a\_M} = \frac{v \cdot d_p}{D_{e\_a}} \qquad \text{axial mass Peclet number based on particle diameter, not L}$$

$v$  = mass average velocity

$D_{e\_a}$  = effective axial dispersion coefficient

$C_{A0}$  and  $C_{Ae}$  = inlet and outlet reactant concentrations

$n$  = reaction order  $> 0$

Axial dispersion will not be included in the examples for the reasons given above.

### *axial dispersion for short reactors*

For short reactors that have significant axial dispersion, correct boundary conditions are needed. The conditions by Bischoff (1961) are shown below with the assumption that there is no axial dispersion in the inlet pipe.

$$c_{inlet\_pipe} = c(0) \quad \text{concentration is continuous at inlet} \quad (7.3)$$

$$v \cdot c_{inlet\_pipe} = v \cdot c(0) - \frac{1}{Pe_{a\_M}} \cdot \left( \frac{d}{dz} c(z) \right) \quad \text{total flux at inlet is continuous at inlet} \quad (7.4)$$

at  $z=0$

Using Eq(7.3), the second condition becomes:

$$\frac{d}{dz} c(z) = 0 \quad \text{at } z=0 \quad (7.5)$$

The above boundary conditions eliminate the split boundary conditions that exit boundary conditions impose. However, these inlet boundary conditions still do not eliminate the instability that may occur when solving the conservation equations with an algorithm for ordinary differential equations. The instability problem is usually resolved by using a dynamic model involving partial differential equations.

The boundary conditions for the energy balance with axial dispersion are similar to those for the mass balance , with temperature replacing concentration.

### **Mass balance for component i**

With the above assumptions, the pseudohomogeneous model for an adiabatic bed consists of accumulation, advection, and reaction (source) terms as shown in Eq(7.6).

$$\frac{d}{dt}(\rho \cdot \omega_i) + \frac{d}{dZ}(\rho \cdot v \cdot \omega_i) = S_i$$

or

$$\frac{d}{dt}(\rho \cdot \omega_i) + G \cdot \frac{d}{dZ} \omega_i = S_i \quad (7.6)$$

$\omega_i$  = mass fraction of  $i$

$\rho$  = fluid density

$S_i$  = source of  $i$

$t$  = time

$Z$  = axial distance

$G$  = mass flux, mass/area/time,  $\rho \cdot v$

For the steady state condition the accumulation term can be ignored, resulting in the following:

$$\left(\frac{d}{dZ}\omega_i\right) = \frac{S_i}{G} \quad (7.7)$$

To make dimensionless, let  $z = \frac{Z}{L}$

$$\frac{d}{dz}[\omega_i(z)] = S_i \cdot \left(\frac{L}{G}\right) \quad \omega_i(0) = \omega_{0_i} \quad \omega_0 = \text{feed composition} \quad (7.8)$$

The performance, or conversion, in reactors of different length will be equivalent if the mass flux, G, is adjusted to keep  $\frac{L}{G}$  constant.

The advection term is the reason molar concentration balances present a problem. When molar concentrations are used, the advection term becomes

$$\frac{d}{dZ}(c \cdot v \cdot x_i) \quad \begin{array}{l} x_i = \text{mole fraction of component } i \\ c = \text{total molar concentration} \end{array}$$

Unlike  $(\rho \cdot v)$ ,  $(c \cdot v)$  is not constant with respect to Z due to the molar change with reaction. Mass balances using molar concentrations can be developed, but the molar change with extent of reaction must be explicitly included in the model. This is a step not needed with the mass fraction approach.

### *source term for mass balances*

The source term in the mass balance is the production rate of each species.

$$S_i = Rxn(\omega, \theta, p, act)_i \cdot Mw_i \quad (7.9)$$

where

$$Rxn(\omega, \theta, p, act) = \left( \nu^T \cdot rxn(\omega, \theta, p, act) \right)$$

$\omega$  = vector of mass fractions in bulk fluid

$\theta$  = dimensionless temperature,  $\frac{T}{T_0}$

$T_0$  = reference temperature, usually the inlet

$p$  = dimensionless pressure,  $P/P_{tot}$

$act$  = activity of catalyst

$Rxn$  = vector function of net production from all reactions

$rxn$  = vector function of reaction rates of limiting reactants

$\nu$  = stoichiometric matrix

$Mw_i$  = molecular weight of component  $i$

The general form of a rate expression for  $j$ th  $rxn$  is as follows:

$$rxn(\omega, \theta, p, act)_j = act \cdot \rho_c \cdot \left( K0_j \cdot \exp\left(-\frac{E_j}{R_g \cdot \theta \cdot T_0}\right) \right) \cdot kinetic\_terms \cdot equilibrium\_term \quad (7.10)$$

where  $K0$  and  $E$  are vectors for the pre-exponential constant and the activation energy, respectively, and  $\rho_c$  is the catalyst *bulk* density, mass/volume of reactor. The  $K0$  vector has units that depend upon the *kinetic\_terms* and the *equilibrium\_term*. The reaction rate,  $rxn$ , has units of mol/vol/s.

The kinetic and equilibrium terms may have various forms, but all will involve local gas or liquid concentrations. These are readily obtained from the mass fractions used as the state variables as shown below.

### **gas concentrations**

Concentrations in gases are normally expressed as partial pressures, using the total pressure,  $P_{tot}$ .

$$P_i = \frac{\frac{\omega_i}{Mw_i} \cdot P_{tot}}{\sum_{j=0}^{NC-1} \frac{\omega_j}{Mw_j}} = \frac{\frac{\omega_i}{Mw_i} \cdot P_{tot}}{\sum \frac{\omega}{Mw}} \quad (7.11)$$

The total pressure may change along the length of a fixed bed reactor. This effect is modeled with the Ergun equation to be discussed later.

### **liquid concentrations**

The concentrations in liquids may also be expressed with mass fractions,

$$C_i = \frac{\omega_i}{Mw_i} \cdot \rho \quad (7.12)$$

Normally, the mass density of liquids may be assumed constant. When that assumption is invalid, the density of the non-ideal liquid must be determined by correlation, usually from an equation of state. This density correlation will be a function of the state variables,  $\omega$ ,  $\theta$ , and  $p$ .

### **Pressure equation**

A modified Ergun equation, MacDonald et al (1979), is used to calculate the axial pressure profile. In dimensionless form,

$$\frac{d}{dz}p = \frac{-f_k \cdot G^2 \cdot L}{d_p \cdot \rho_f(\omega, \theta, p) \cdot P_{tot}} \cdot \left( \frac{1 - \epsilon}{\epsilon^3} \right) = -friction\_loss \quad (7.13)$$

with

$$Rey_p = \frac{G \cdot d_p}{\mu}$$

$$f_k = \beta_P + \alpha_P \cdot \frac{(1 - \epsilon)}{Rey_p}$$

$\rho_f$  = fluid density function

$\mu$  = fluid viscosity

$Rey_p$  = particle Reynolds number

$\alpha_P = 180$        $\beta_P = 1.8$       smooth pellets

$\beta_P = 4.0$       rough pellets

The Ergun equation is a mechanical energy balance that ignores the change in kinetic energy with  $z$ . The term on the right side of the equation is a friction loss term, not a difference in kinetic energy.

## Fluid heat balance

A total energy balance, including kinetic energy, is used as the starting point. Following Bird et al (2002), p336-337, the mechanical energy balance is subtracted from the total energy balance. Kinetic energy is still included at this point in the derivation. Assuming steady state and converting from internal energy to enthalpy, the equation below is obtained.

$$C_p \cdot G \cdot \frac{d}{dZ} T_f = Q_r - \left( \rho \cdot \frac{dH}{dP} \right) \cdot \left( v \cdot \frac{dP}{dZ} \right) + v \cdot \left( \frac{dP}{dZ} \right) + v \cdot friction\_loss - del \cdot (\tau \cdot v) \quad T_f(0) = T_0 \quad (7.14)$$

$H$  = enthalpy per unit mass

$T_0$  = feed temperature

$C_p$  = heat capacity of fluid (a function of composition and temperature)

$T_f$  = fluid temperature

$Q_r$  = source of heat from reactions in catalyst phase

$\tau$  = stress tensor

$P$  = pressure

The  $v \cdot \left( \frac{dP}{dZ} \right)$  term and the friction loss term cancel each other due to Eq (7.13). The last term is the viscous work on the fluid, which is ignored.

Because the Ergun equation ignored the change in kinetic energy, the resulting equation also ignores that term. If the Ergun equation had included a change in kinetic energy, the kinetic energy term would "reappear" in the energy balance when the substitution for  $v \cdot \left( \frac{dP}{dZ} + friction\_loss \right)$  in Eq. (7.14) is made.

The  $dH/dP$  partial derivative in Eq (7.14) is at constant T and composition. For an ideal gas, the  $dH/dP$  term is zero, and for a liquid it is nearly zero. For a non ideal gas,

$$\frac{d}{dP} H = -C_p \cdot \kappa \quad \kappa = \text{Joule-Thompson coefficient} \quad (7.15)$$

Making the substitution above and canceling the terms, Eq (7.14) becomes

$$C_p \cdot G \cdot \frac{d}{dZ} T_f = Q_r + G \cdot C_p \cdot \kappa \cdot \left( \frac{dP}{dZ} \right) \quad (7.16)$$

with  $\kappa = 0$  for ideal gases and liquids

For a non reacting fluid, Eq (7.16) leads to the definition of  $\kappa$ :

$$\frac{d}{dP} T_f = \kappa \quad \text{at constant H} \quad (7.16a)$$

Converting Eq (7.16) to dimensionless form,

$$\frac{d}{dz} \theta = \frac{Q_r}{C_p(\omega, \theta) \cdot T_0} \cdot \frac{L}{G} + \frac{\kappa \cdot P_{tot}}{T_0} \cdot \left( \frac{d}{dz} p \right) \quad \theta(0) = \theta_0 \text{ , dimensionless feed temperature} \quad (7.17)$$

The form given in Eq (7.17) may be used if  $\kappa$  is known. For a mixture, the approach below may be used to determine  $\kappa$ .

$$\kappa = \frac{R_g \cdot T_0}{P_{tot} \cdot C_p \cdot M_w} \cdot T_r \cdot \left( \frac{d}{dT_r} Z_c \right) \quad \text{per Reid et al (1977), p 127 and 134} \quad (7.18)$$

$Z_c$  = compressibility factor of gas mixture

$T_r$  = reduced temperature of mixture

$P_r$  = reduced pressure of mixture

derivative of  $Z_c$  is at constant  $P_r$

Substituting Eq (7.18) into the last term in Eq (7.17) results in the following:

$$\frac{d}{dz} \theta = \frac{Q_r}{C_p \cdot T_0} \cdot \frac{L}{G} + \frac{R_g}{C_p \cdot M_w} \cdot T_r \cdot \left( \frac{d}{dT_r} Z_c \right) \cdot \left( \frac{d}{dz} p \right) \quad (7.19)$$

A comparison of the Joule-Thompson term with various heats of reaction shows that it can be significant if the system is near the critical pressure where the derivative of  $Z_c$  is greatest. This is true even for reactions with large heat of reaction. In the examples in this book, ideal gases are assumed so the second term in Eq (7.19) is not used. If the Joule-Thompson term is included, the reaction rate expressions should also include the fugacity coefficients because of the non-ideal fluid.



### *source term for heat balance*

The source term is positive for exothermic reactions, negative for endothermic.

$$Qr(\omega, \theta, p) = -\Delta H(\theta \cdot T_0) \cdot rxn(\omega, \theta, p) \quad (7.20)$$

### **Temperature difference from particle energy balance**

As mentioned above, the difference between particle and fluid temperatures should be calculated after solving the model. The temperature difference may be calculated using the particle heat balance below. The pseudohomogeneous dimensionless temperature is used in place of the unknown particle temperature in the heat source term.

$$h_s \cdot a_p \cdot \Delta\theta \cdot T_0 - Qr(\omega, \theta, p) = 0 \quad (7.21)$$

$h_s$  = heat transfer coefficient between particle and fluid

$a_p$  = surface area/reactor volume,  $\frac{6}{d_p} \cdot (1 - \varepsilon)$

$\varepsilon$  = bed void fraction

$\theta_p$  = dimensionless particle temperature

$\Delta\theta$  = dimensionless temperature difference,  $\theta_p - \theta_f$

A temperature difference given by the formula in Eq (7.21a) will cause a 10% difference in the reaction rate depending upon which temperature is used, that of the fluid or of the catalyst.

$$\Delta T_c = Rg \cdot \frac{T^2}{E} \cdot \ln(1.1) \quad (7.21a)$$

### **Example 5: Adiabatic Bed**

The partial oxidation of methanol to formaldehyde is used to demonstrate the adiabatic bed model. Please go to the **Example 5** file.

## Scaling relations for adiabatic fixed bed

The ratio  $L/G$  may be used to scale this type of reactor provided the pressure is fairly constant through the reactor. Normally, pressure drop is about 10% of the inlet pressure in the commercial reactor. In the shorter pilot plant, the pressure drop will be smaller. Therefore, the differences in reaction rates between the two reactors that is due to pressure will be less than 10%

The interphase temperature difference will be kept constant between the pilot plant and commercial scales if the catalyst size and  $G$  are kept constant. Keeping  $G$  and  $L/G$  both constant would mean a constant  $L$ , i.e. no change in scale. However,  $G$  may be lowered for the pilot plant if the interphase temperature difference, as predicted by the model, remains within a reasonable range. The use of a heterogeneous model reduces the risk associated with this deviation from a strict adherence to scaling relationships.

### Radial bed

For beds that are short because of either pressure drop or temperature constraints, a radial flow reactor provides a larger cross section for flow than an axial flow reactor. The change in flow direction increases the amount of fluid that can be processed in the same size of vessel, reducing the capital cost. The mass flux varies with the radius as shown below:

$$G(r) = \frac{G_0 \cdot r_0}{r} \quad (7.22)$$

A shell balance leads to the following material balance,

$$\frac{d}{dr} (r \cdot G(r) \cdot \omega(r)_i) = S_i \cdot r$$
$$\frac{d}{dr} (G_0 \cdot r_0 \cdot \omega(r)_i) = G_0 \cdot r_0 \cdot \left( \frac{d}{dr} \omega(r)_i \right) = S_i$$

or

$$\frac{d}{dr} \omega(r)_i = \frac{S_i \cdot r}{G_0 \cdot r_0} \quad (7.22a)$$

Converting Eq (7.22a) to dimensionless form:

$$\eta = \frac{r - r_0}{r_1 - r_0} \quad \begin{array}{l} r_0 \text{ radius at entrance} \\ r_1 \text{ radius at exit} \end{array}$$

$$r = \eta \cdot (r_1 - r_0) + r_0$$

$$\frac{d}{d\eta} \omega_i = \frac{S_i \cdot [\eta \cdot (r_1 - r_0) + r_0] \cdot (r_1 - r_0)}{G_0 \cdot r_0} \quad \omega_i(0) = \omega_{0_i} \quad (7.23)$$

Similarly, the heat balance becomes,

$$\frac{d}{d\eta} \theta = \frac{Qr \cdot [\eta \cdot (r_1 - r_0) + r_0] \cdot (r_1 - r_0)}{G_0 \cdot r_0 \cdot Cp(\omega, \theta) \cdot T_0} \quad \theta(0) = 1 \quad (7.24)$$

The pressure drop equation also must be modified to accommodate the radial variation in G.

$$f_k(\eta) = \beta + \alpha \cdot \left[ \frac{1 - \varepsilon}{\frac{d_p \cdot G_0 r_0}{\mu \cdot [\eta(r_1 - r_0) + r_0]}} \right] = \beta + \alpha \cdot \frac{(1 - \varepsilon) \cdot \mu \cdot [\eta \cdot (r_1 - r_0) + r_0]}{(d_p \cdot G_0 \cdot r_0)} \quad (7.25)$$

$$\frac{d}{d\eta} p = \frac{-f_k(\eta) \cdot (G_0 \cdot r_0)^2 \cdot (r_1 - r_0)}{d_p \cdot \rho_f(\omega, \theta, p) \cdot P_{tot} \cdot [\eta \cdot (r_1 - r_0) + r_0]^2} \cdot \left( \frac{1 - \varepsilon}{\varepsilon^3} \right) \quad (7.26)$$

## Example 6: Adiabatic Radial Flow Reactor

The adiabatic model used for Example 5 was modified using Eq (7.23) through Eq (7.26). Please consult the files for [Example 6](#).

### Scaling relations for radial bed

A radial bed may not be used in the pilot plant even though a radial bed is planned for the commercial reactor. Instead, a traditional, axial flow bed is often used. The length of this bed corresponds to the difference in the radii of the radial bed, but the decrease in  $G$  through the commercial radial bed ends the similarity between the two reactors. The decrease in  $G$  causes the temperature profile to steepen (for exothermic reactions) more than with the axial flow reactor. The model can be used to translate results from the cylindrical bed to a radial bed. See also the comments made for scaling the adiabatic bed regarding the interphase temperature difference and  $G$ . Those comments are true for the radial bed also.

## 7.2 Tubular Reactor

Tubular reactors are used for both exothermic and endothermic systems. For endothermic systems, multiple tubes with catalyst are heated in a furnace, or with a hot fluid such as a heating oil or molten salt. Cooling for exothermic systems is usually with a liquid, which may or may not be boiling. Tubular reactors allow reactions to proceed to higher conversions without limitation by either equilibrium or a temperature "runaway".

In the early days of computer simulation, tubular reactors were modeled as a one 1D system. The radial temperature and composition profiles are ignored in a 1D model. Instead, the 1D model predicts the axial profile of the bulk temperature and composition. The bulk properties are sometimes referred to as the mixing cup values, because the value is what would result if flow from the entire reactor cross section were collected and mixed. The formula for the bulk temperature is shown in Eq (7.27).

$$T_b = \frac{\int_0^R T(r) \cdot v(r) \cdot r \, dr}{\int_0^R v(r) \cdot r \, dr} \quad R = \text{tube inside radius} \quad (7.27)$$

The axial velocity is usually assumed to be independent of  $r$ , i.e. plug flow. Although the higher void fraction near the tube wall allows higher velocity at the wall, this effect is usually ignored. In the model developed below, the mass flux is assumed constant throughout the reactor. However, the density and therefore velocity change with temperature and molecular weight. Thus, for calculation of the bulk properties, the velocity variation with  $r$  is included. For example, the formula below is used to compute the bulk average dimensionless temperature (either fluid or catalyst):

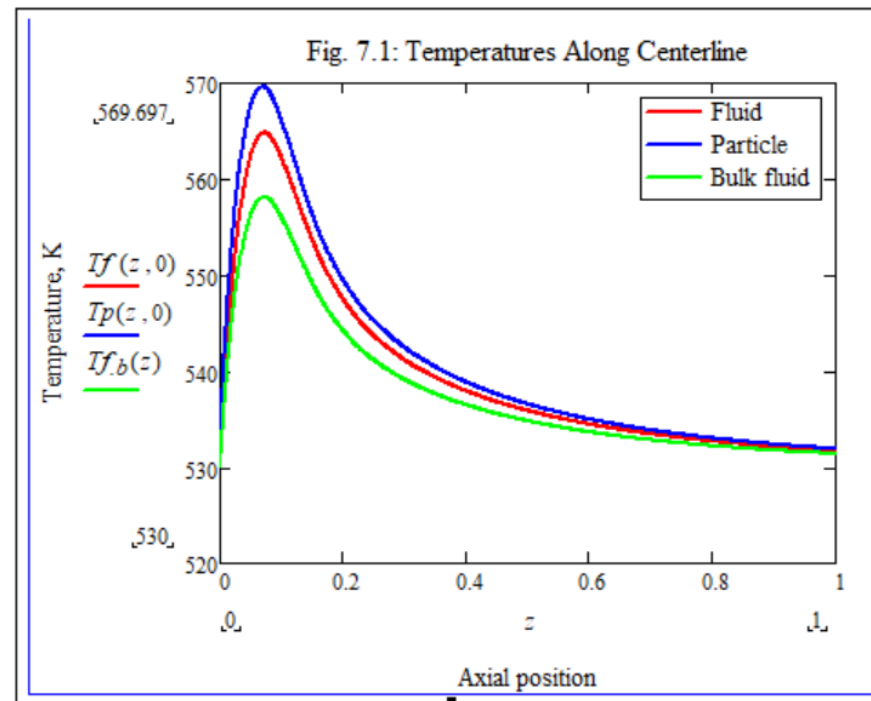
$$\theta_{ave}(\omega, \theta, p) = \frac{\sum_{j=0}^N (Wq_j \cdot \theta_j \cdot v(\omega, \theta_j, p))}{\sum_{j=0}^N (Wq_j \cdot v(\omega, \theta_j, p))}$$

$\theta$  = fluid or catalyst dimensionless temperature

$Wq_j$  = collocation weights for each collocation point, j

(7.28)

A 1D model can simulate the bulk fluid temperature with accuracy provided the wall heat transfer coefficient was determined using the bulk temperature. However, the temperatures along the centerline are either higher or lower than the bulk temperature depending upon whether the reactions are exothermic or endothermic, respectively. In the example shown in Fig. 7.1, the fluid temperatures along the centerline are 7 K higher than the bulk temperature in the hot spot. The catalyst temperature is 12 K higher than the bulk peak temperature. Catalysts normally lose activity above a maximum temperature. Also, decomposition reactions usually have high activation energies. Thus, the loss of reactant and product to decomposition is greater in hot spots. Without full knowledge of the temperature profile, reactor performance can be adversely affected.



Criteria have been developed to determine whether or not a 2D model is needed for accuracy. One criteria [see Example 7 in Rase (1990)], was applied to the example used for Fig 7.1. Based on that criteria, a 2D model was not required. That is the correct recommendation, provided only bulk temperatures and compositions are of interest. However, the more complete result provided by the 2D model is recommended for design.

A better criterion for choosing a design model is to use a 2D model when a fixed bed or a homogeneous, laminar flow system is being heated or cooled at the wall. This criterion excludes models for (1) process control, and (2) homogeneous turbulent flow which is essentially plug flow. With today's computers, no other criterion is needed.

Full 2D models of tubular reactors are not commonly found in process simulation packages, so they have to be created independently. This can be a formidable task. However, once created using the methods in this book, the program can be reused for other reaction systems. The task of creating a 2D reactor model has already been made much easier by the elimination of the need for effectiveness factors or the solution of the intraparticle diffusion problem. The second task that may discourage the development of a 2D model is the selection and programming of the numerical integration routine.

### Mass balance

The mass balance for the 2D model is obtained by adding the radial dispersion term to the 1D model.

$$\frac{d}{dz} \omega_i(\eta, z) = \alpha_M(\omega, \theta_f, p) \cdot \left[ \frac{1}{\eta} \cdot \left[ \frac{d}{d\eta} [\omega_i(\eta, z)] \right] + \frac{d^2}{d\eta^2} [\omega_i(\eta, z)] \right] + S_i(\omega, \theta_p, p) \cdot \frac{L}{G} \quad (7.29)$$

$$\text{BC: } \frac{d}{d\eta} \omega_i(0, z) = 0 \quad \frac{d}{d\eta} \omega_i(1, z) = 0 \quad \omega_i(\eta, 0) = \omega_{0i}$$

where

$D_e$  = effective radial dispersion coefficient for mass

$R_i$  = inside radius of reactor tube

$$\alpha_M(\omega, \theta_f, p) = \frac{\rho_f(\omega, \theta_f, p) \cdot D_e \cdot L}{R_i^2 \cdot G}$$

$$\eta = \frac{r}{R_i} \quad \text{dimensionless radial distance}$$

Update: Simulations using eq (7.29) with and without the radial dispersion term demonstrated that the dispersion term is not needed. Therefore, eq (7.8) may be used for the mass balance. The reaction source term for the tubular model must use the radial average particle temperature in order to obtain the average reaction rate across the radius.

## Energy balance for fluid phase

Froment and Bischoff (1990) and others showed that the catalyst phase in a 2D heterogeneous model must include radial dispersion or the catalyst temperature becomes unrealistically high for exothermic reactions. The model below uses a static thermal conductivity for the catalyst phase and a dynamic thermal dispersion coefficient for the fluid phase. It can be shown that a homogeneous model that uses the sum of these dispersion coefficients obtains nearly the same results as the heterogeneous model. The amount of disagreement depends upon the difference between the catalyst temperature and the fluid temperature. With significantly different fluid and catalyst temperatures, the use of an average or homogenous temperature will obviously change the results compared to those obtained with a heterogeneous model, which is the reason for using the heterogeneous model.

The homogeneous and the heterogeneous models require the same time step size, so computation time is not a factor in model selection.

advection = radial dispersion - interphase transfer

$$\frac{d}{dz} \theta_f = \alpha_{Hf} \cdot \left[ \frac{1}{\eta} \cdot \left( \frac{d}{d\eta} \theta_f \right) + \frac{d^2}{d\eta^2} \theta_f \right] - \alpha_{FP} \cdot (\theta_f - \theta_p) \quad (7.30)$$

$$\text{BC: } \frac{d}{d\eta} \theta_f(0, z) = 0 \quad -\frac{d}{d\eta} \theta_f(1, z) = Bi_w \cdot (\theta_f - \theta_w) \quad \theta_f(\eta, 0) = \theta_0$$

where

$$\alpha_{Hf} = \frac{k_{ef} \cdot L}{G \cdot Cp(\omega_0, \theta_0) \cdot Ri^2}$$

$$\alpha_{FP} = \frac{h_s \cdot a_v \cdot L}{G \cdot Cp(\omega_0, \theta_0)}$$

$$Bi_w = \frac{h_w \cdot Ri}{k_{ph}}$$

$h_w$  = heat transfer coefficient at wall

$h_s$  = interphase heat transfer coefficient

$a_v$  = catalyst external area per reactor volume

$k_{ph}$  = effective thermal radial dispersion coefficient for pseudohomogeneous model

$k_{ef}$  = effective thermal radial dispersion coefficient for fluid phase

$\theta_w$  = dimensionless wall temperature

### Energy balance for solid phase

The reaction heat term in the solid phase energy balance is a function of the catalyst temperature,  $\theta_p$ .

$$0 = \alpha_{Hp} \cdot \left[ \frac{1}{\eta} \cdot \left( \frac{d\theta_p}{d\eta} \right) + \frac{d^2\theta_p}{d\eta^2} \right] + \alpha_{FP} \cdot (\theta_f - \theta_p) + \frac{L \cdot Qr(\omega, \theta_p, p)}{G \cdot Cp(\omega_0, \theta_0) \cdot T_0} \quad (7.31)$$

$$\text{BC: } \frac{d\theta_p(0, z)}{d\eta} = 0 \qquad -\frac{d\theta_p(1, z)}{d\eta} = Bi_w \cdot (\theta_p - \theta_w)$$

$$\alpha_{Hp} = \frac{k_{es} \cdot L}{G \cdot Cp(\omega_0, \theta_0) \cdot Ri^2} \qquad k_{es} = \text{effective dispersion coefficient for solid phase}$$

The catalyst temperature at the inlet is determined by the following particle energy balance, which assumes there is no radial gradient in the solid phase at the inlet:

$$\theta_p(\eta, 0) = \theta_f(\eta, 0) + \frac{\frac{L \cdot Qr(\omega_0, \theta_0, p_0)}{G \cdot Cp(\omega_0, \theta_0) \cdot T_0}}{\alpha_{FP}} \quad (7.32)$$

### Pressure equation

The ordinary differential equation (ODE), Eq (7.13), used to calculate the pressure change in the 1D model is used also for the tubular reactor. The pressure is assumed independent of radial position and the density is evaluated at the centerline.

### The dispersion and heat transfer parameters

The model includes effective dispersion coefficients and heat transfer parameters that are determined from correlations. The correlations and references are given in Example 7. In the model, transport parameters are assumed to be constant, based on inlet conditions, unless the parameter is explicitly a function of fluid density. The density variation is included because it may be affected by the reactions in addition to temperature and pressure. Recall that density and molecular weight are the means used to follow the molar expansion without the use of extents of reaction.



### **Example 7: Fixed bed model (steady state)**

The production of formaldehyde, modeled in Examples 5 and 6, is again used for the example. **Example 7** provides the correlations for the radial dispersion parameters, and the heat transfer coefficient at the

#### ***Numerical integration method***

The model for the tubular reactor consists of a system of partial differential equations (PDE), one ODE and one nonlinear algebraic equation. The collocation method was used to convert the PDE equations to ODE type. The algebraic equation (particle energy balance) was solved by a root method within the derivative function for the system of ODE equations. The Rkadapt routine in Mathcad was used to integrate the ODEs.

#### **Scaling relations for tubular reactor**

For a true scale down (or up), the reactor radius must be kept constant to keep the radial flux in the correct proportion to the advection and source terms. The L/G ratio and the catalyst size also need to be kept constant.

Most of the transport parameters are correlated with the Reynolds number which is a function of G. The model, with these correlations, allows the pilot plant to be scaled down, reducing G and L. However, for reactions with very high heat of reaction, the commercial design may be approaching the limit on interphase temperature difference, or hot spot temperature. In that case, lowering G for the pilot plant is not advised. The pilot plant would then consist of a single tube of the same diameter and length as the commercial design. This is a common scenario.

Tubular reactors are used when the absolute value of the heat of reaction is high, so there is a good chance that the scale of 1:1 is needed. However, there can be intermediate levels of heat of reaction that require the heat exchange but that may allow some scale down in the tube diameter. The model can be used to evaluate the risk of changing the diameter from that planned for the commercial unit.

### **7.3 CSTR**

Process simulation programs routinely include a CSTR model. However, if such a program is not available, or if the reader needs greater flexibility in specifying the reaction rate expressions, the model developed below may be useful. In addition, the reader may find the Mathcad parametric features more useful than the case study capabilities in the process simulation programs.

## Mass balance

$$q \cdot \rho \cdot \omega_{in_i} - q \cdot \rho \cdot \omega_{out_i} + Vr \cdot Mw_i \cdot Rxn(\omega_{out}, \theta_{out}, p)_i = 0 \quad (7.33)$$

$q$  = volumetric feed rate

$Vr$  = reactor volume

$\omega_{in}$  and  $\omega_{out}$  = feed and effluent mass fractions

$\theta_{out}$  = dimensionless effluent temperature

Convert to space time and divide by  $\rho$ ,

$$\omega_{in_i} - \omega_{out_i} + \frac{\tau_s \cdot Mw_i \cdot Rxn(\omega_{out}, \theta_{out}, p)_i}{\rho} = 0 \quad (7.34)$$

$$\tau_s = \frac{Vr}{q} \text{space time}$$

The set of nonlinear equations in Eq (7.34) are solved by a minimization routine. In order to maintain the proper material balance of both compounds and elements, the following constraints must be included.

$$1 - \sum \omega = 0 \quad \text{mass fractions sum to 1} \quad (7.35)$$

$$Atom^T \cdot (\omega_{in} - \omega_{out}) = 0 \quad \text{each element must balance} \quad (7.36)$$

$Atom$  = matrix of chemical formulas of compounds with compounds in rows and elements in columns

## Heat balance

$$q \cdot \rho \cdot (H_{in} - H_{out}) + Qx_t = -(q \cdot \rho) \cdot Del\_H + Qt = 0 \quad (7.37)$$

$H$  = fluid enthalpy per unit mass

$Qt$  = heat exchanged per unit time

$Del\_H$  = difference in stream enthalpy =  $(H_{out} - H_{in})$

Divide by  $q \cdot \rho$ ,

$$-Del\_H + \frac{Q_t}{q \cdot \rho} = -Del\_H + Q_m = 0 \qquad Q_m = \frac{Q_t}{q \cdot \rho} = \text{heat exchanged per unit mass of feed} \qquad (7.37a)$$

The heat of reaction is not needed because the enthalpy terms are based on heats of formation. For example, the enthalpy of the outlet stream is

$$H_{out} = \left[ \Delta H_f \cdot \frac{\omega_{out}}{M_w} + Cp \left( \omega_{out}, \frac{T_{out}}{T_0} \right) \cdot (DHT(T_{out}) - DHT(298 \cdot K)) \right] \qquad (7.38)$$

$T_{out}$  = effluent temperature

### Example 8: CSTR

This academic example shows how the model can be used in the design of a CSTR. The procedure is as follows:

1. Obtain a parametric solution of the mass balances, Eq(7.34) through Eq (7.36) with  $\tau_s$  and reactor temperature,  $T_{out}$ , as parameters.
2. Map the conversion and selectivity for a case study of  $\tau_s$  and  $T_{out}$ .
3. Select an optimum value of  $\omega$ ,  $\tau_s$  and  $T_{out}$  from the conversion and selectivity maps.
4. Calculate the enthalpy difference,  $Del\_H$ , (given  $\omega$  from step 3) and map as a function of  $T_{in}$  and  $T_{out}$ .
5. Use the map in step 4 to select a  $T_{in}$  and  $Q_m$  ( $T_{out}$  is known from step 3).
6. Plot  $T_{out}$  vs  $Del\_H$  and determine more precise values for the required heat exchange,  $Q_m$ , and  $T_{in}$  that provide a stable operating point at the desired  $T_{out}$ .
7. Add the heat balance, including  $Q_m$ , and re-solve model to obtain the final outlet composition and temperature for the given  $T_{in}$ ,  $\tau_s$ , and  $Q_m$ .

In the last step,  $T_{out}$  from step 3 could have been specified and the equations solved for  $\omega$  and  $Q_m$ , but the designer more often would like to specify  $Q_m = 0$  for adiabatic operation and to calculate  $T_{out}$ .

The key to this procedure is the first step which solved mass balances without a heat balance constraint. That step allowed the selection of the optimum operating region of the parameter space. Once the operating region was known, the rest of the design parameters could be obtained with additional plots. By following the above procedure, the final simulation has good initial guesses, increasing the likelihood of convergence to the desired solution.

Please read the [Example 8 file](#).