

# Example 5: Adiabatic Fixed Bed Reactor (steady state)

Partial oxidation of methanol to formaldehyde



This example is based on Example 11 in Rase (1990). The rate expressions have been changed, and the flow rate and reactor length have been changed to represent a commercial reactor instead of a pilot plant. The pilot plant modeled by Rase was a tubular reactor with cooling. The adiabatic bed model here must have a lower catalyst activity to prevent a "runaway" at the exit. The conditions used in the example are not based on an actual design. For this system, the tubular reactor is the better option, and that option will be modeled in Example 7.

The model assumes that both mass and energy balances are pseudohomogeneous. The pseudohomogeneous assumption for the energy balance is checked using the simulation results.

*miscellaneous constants*

$$R_g := 1.987 \cdot \frac{\text{cal}}{\text{mol} \cdot \text{K}} \quad \text{gas law constant}$$

## Thermophysical properties

$$A_w := \begin{pmatrix} 12 \\ 1 \\ 16 \\ 14 \end{pmatrix} \cdot \frac{\text{gm}}{\text{mol}} \quad \begin{matrix} \text{C} \\ \text{H} \\ \text{O} \\ \text{N} \end{matrix}$$

$$Atom := \begin{pmatrix} 1 & 4 & 1 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 2 & 1 & 0 \\ 1 & 0 & 1 & 0 \\ 1 & 2 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \quad NC := \text{rows}(Atom) = 6$$

C, H, O, N atoms

*molecular weights*

methanol	$M_w := Atom \cdot A_w = \begin{pmatrix} 0.032 \\ 0.032 \\ 0.018 \\ 0.028 \\ 0.03 \\ 0.028 \end{pmatrix} \frac{kg}{mol}$
oxygen	
water	
CO	
CH <sub>2</sub> O	
N <sub>2</sub>	

*heats of formation*

$$\Delta H_f := \begin{pmatrix} -48.08 \\ 0 \\ -57.8 \\ -26.416 \\ -27.7 \\ 0 \end{pmatrix} \cdot 10^3 \cdot \frac{cal}{mol}$$

*free energies*

$$\Delta F_f := \begin{pmatrix} -38.84 \\ 0 \\ -54.635 \\ -32.781 \\ -26.27 \\ 0 \end{pmatrix} \cdot 10^3 \cdot \frac{cal}{mol}$$

## Feed conditions

$T_0 := 525 \cdot K$       inlet temperature

$P_{tot} := 5 \cdot atm$       inlet pressure

$G := .8 \cdot \frac{gm}{cm^2 \cdot s}$       mass flux

$$molf := \frac{molf}{\sum molf}$$

$M_f := molf \cdot M_w$       molecular weight of feed mixture

*moles or mole fractions in feed*

$$molf := \begin{pmatrix} .0901 \\ .0991 \\ 0.0132 \\ 0.0051 \\ .0006 \\ .7918 \end{pmatrix}$$

$$\sum molf = 1$$

normalized

$$M_f = 0.029 \frac{kg}{mol}$$

$$\omega_0 := \frac{\overrightarrow{(molf \cdot Mw)}}{M_f}$$

convert mole fractions to weight fractions

$$\theta_0 := 1$$

temperature

$$p_0 := 1$$

pressure

## Reactor geometry and type

$$L := 2 \cdot m$$

reactor length

$$fluid := "gas"$$

fluid is "gas" or "liquid"

## Catalyst properties

$$d_p := 2.5 \cdot mm$$

equivalent particle diameter  
(diameter of sphere with same  
surface area of particle)

$$Cp_c := .25 \cdot \frac{cal}{gm \cdot K}$$

catalyst heat capacity

$$\varepsilon := .496$$

bed void fraction

$$shape := "cylinder"$$

catalyst shape, "cylinder" or  
"sphere"

$$\rho_c := 53 \cdot \frac{lb}{ft^3}$$

catalyst bulk density

$$smooth := "yes"$$

catalyst surface is smooth,  
"yes" or "no"

## Gas properties

The properties for nitrogen, the dominate component, will be used for gas properties.

$$\sigma := 3.798 \cdot Angstrom$$

Lennard-Jones parameter for nitrogen

gas viscosity

$$\mu(T) := \frac{2.67 \cdot 10^{-5} \cdot \sqrt{\frac{MwNC-1}{\frac{gm}{mol}} \cdot \frac{T}{K}}}{\left(\frac{\sigma}{Angstrom}\right)^2} \cdot \frac{gm}{cm \cdot s}$$

Bird et al (2002), Eq 1.4-14

$$\mu(500 \cdot K) = 2.19 \times 10^{-4} \cdot poise$$

molar heat capacities from Reid et al (1977)

each row contains the parameters for one component

$$cp := \begin{pmatrix} 5.052 & 1.694 \cdot 10^{-2} & 6.179 \cdot 10^{-6} & -6.811 \cdot 10^{-9} \\ 6.713 & -.879 \cdot 10^{-6} & 4.170 \cdot 10^{-6} & -2.544 \cdot 10^{-9} \\ 7.701 & 4.59 \cdot 10^{-4} & 2.521 \cdot 10^{-6} & -.859 \cdot 10^{-9} \\ 7.373 & -.307 \cdot 10^{-2} & 6.662 \cdot 10^{-6} & -3.037 \cdot 10^{-9} \\ 5.607 & 7.540 \cdot 10^{-3} & 7.130 \cdot 10^{-6} & -5.494 \cdot 10^{-9} \\ 7.440 & -.324 \cdot 10^{-2} & 6.4 \cdot 10^{-6} & -2.79 \cdot 10^{-9} \end{pmatrix} \cdot \frac{cal}{mol \cdot K}$$

methanol  
oxygen  
water  
CO  
CH2O  
N2

$$CpTf(T) := \left[ 1 \quad \frac{T}{K} \quad \left(\frac{T}{K}\right)^2 \quad \left(\frac{T}{K}\right)^3 \right]^T$$

heat capacity temperature functions

$$Cp(\omega, \theta) := cp \cdot CpTf(\theta \cdot T_0) \cdot \frac{\omega}{Mw}$$

heat capacities on a mass basis as a function of state variables

$$Mwt(\omega) := \frac{1}{\sum \frac{\omega}{Mw}}$$

molecular weight of mixture

$$Mwt(\omega_0) = 0.029 \frac{kg}{mol}$$

$$\rho_f(\omega, \theta, p) := \frac{p \cdot Ptot \cdot Mwt(\omega)}{Rg \cdot T_0 \cdot \theta}$$

density

$$\rho_f(\omega_0, \theta_0, p_0) = 3.321 \frac{kg}{m^3}$$

$$D_f := \frac{\mu(T_0) \cdot \frac{3}{8}}{\rho_f(\omega_0, \theta_0, p_0) \cdot \frac{5}{16}}$$

diffusivity, Bird et al, p 861

$$D_f = 8.11 \times 10^{-6} \frac{m^2}{s}$$

$$C_v := \frac{(Cp(\omega_0, \theta_0) \cdot M_f - Rg)}{M_f}$$

heat capacity at constant volume, mass basis

$$C_v = 204.502 \frac{1}{kg} \cdot \frac{cal}{K}$$

$$k_f := \frac{\mu(T_0)}{\frac{5}{16}} \cdot \frac{25}{32} \cdot C_v$$

gas thermal conductivity, Bird et al, p 861

$$k_f = 0.011 \frac{1}{K \cdot s \cdot m} \cdot cal$$

## Liquid Properties

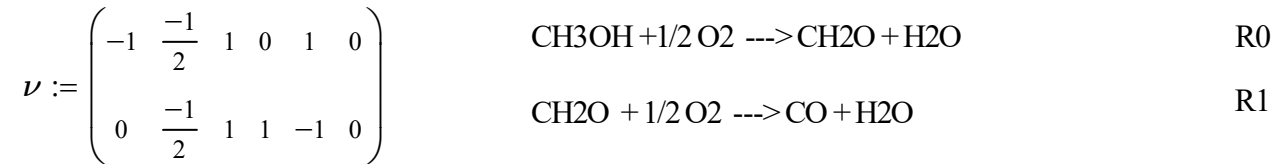
The coefficient of expansion of a liquid is needed even for a gas system in order for an "if" statement later in the program to work properly. For a liquid system, update for the liquid if known. For a gas system, the value below has no bearing on the computations.

$$\beta := \frac{2 \cdot 10^{-4}}{K}$$

coefficient of expansion of water

# Stoichiometry

rows are reactions, columns are components



$$NR := \text{rows}(\nu)$$

number of reactions

*check stoichiometry and Mw*

$$\frac{\nu \cdot Mw}{\frac{kg}{mol}} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

This vector should be null if Mw and  $\nu$  are correct.

## Heats of reaction

$$\Delta H_o := \nu \cdot \Delta H_f$$

$$\Delta H_o = \begin{pmatrix} -1.567 \times 10^5 \\ -2.366 \times 10^5 \end{pmatrix} \frac{J}{mol} \quad \text{standard state, at 298 K}$$

$$\Delta Cp := \nu \cdot cp$$

$$DHT(t) := \left( t \frac{t^2}{2 \cdot K} \frac{t^3}{3 \cdot K^2} \frac{t^4}{4 \cdot K^3} \right)^T$$

integrate the heat capacity function to obtain the enthalpy functions

$$\Delta H(T) := \Delta H_o + \Delta Cp \cdot (DHT(T) - DHT(298 \cdot K)) \quad \text{heat of reaction at } T$$

$$\Delta H(T_0) = \begin{pmatrix} -1.552 \times 10^5 \\ -2.346 \times 10^5 \end{pmatrix} \frac{J}{mol}$$

# Equilibria

$$\Delta F_o := \nu \cdot \Delta F_f$$

free energy change at standard state and 298 K

$$\Delta F_o = \begin{pmatrix} -4.206 \times 10^4 \\ -6.115 \times 10^4 \end{pmatrix} \frac{I}{mol} \cdot cal$$

$$\ln K(TK, rj) := \text{if} \left( NR > 1, \frac{1}{Rg} \cdot \int_{298 \cdot K}^{TK} \frac{\Delta H(t)_{rj}}{t^2} dt - \frac{\Delta F_o_{rj}}{Rg \cdot 298 \cdot K}, \frac{1}{Rg} \cdot \int_{298 \cdot K}^{TK} \frac{\Delta H(t)}{t^2} dt - \frac{\Delta F_o}{Rg \cdot 298 \cdot K} \right)$$

$$Keq(T, rj) := e^{\ln K(T, rj)}$$

$$Keq(T_0, 0) = 1.1 \times 10^{19}$$

equilibrium is not at factor with either reaction

$$Keq(T_0, 1) = 9.974 \times 10^{26}$$

# Reaction rate expressions

The data given in Rase (1990) Ex 11 were fit to power law rate expressions, which are used below.

*pre-exponential rate constants*

$$K0 := \begin{pmatrix} 6.524 \\ 0.143 \end{pmatrix} \cdot \frac{mol}{gm \cdot s}$$

*activation energies*

$$Ea := \begin{pmatrix} 12.102 \\ 13.689 \end{pmatrix} \cdot \frac{kcal}{mol}$$

$$rxn(\omega, \theta, p, act) := act \cdot \rho_c \cdot \left[ \begin{array}{c} K\theta_0 \cdot \exp\left(\frac{-Ea_0}{Rg \cdot T_0 \cdot \theta}\right) \cdot \left(\frac{\frac{\omega_0}{Mw_0} \cdot \frac{p \cdot Ptot}{atm}}{\sum \frac{\omega}{Mw}}\right)^{0.9} \\ K\theta_1 \cdot \exp\left(\frac{-Ea_1}{Rg \cdot T_0 \cdot \theta}\right) \cdot \left(\frac{\frac{\omega_4}{Mw_4} \cdot \frac{p \cdot Ptot}{atm}}{\sum \frac{\omega}{Mw}}\right) \cdot \left(\frac{\frac{\omega_2 + 10^{-9}}{Mw_2} \cdot \frac{p \cdot Ptot}{atm}}{\sum \frac{\omega}{Mw}}\right)^{-.65} \end{array} \right]$$

$$rxn(\omega_0, \theta_0, p_0, 1) = \left( \frac{24.744}{4.262 \times 10^{-3}} \right) \frac{mol}{s \cdot m^3} \quad \text{initial reaction rates with } act = 1$$

## Net mass and heat production rates

$$Rxn(\omega, \theta, p, act) := \nu^T \cdot rxn(\omega, \theta, p, act) \quad \text{mass}$$

$$Qr1(\omega, \theta, p, act) := (-\Delta H(\theta \cdot T_0)) \cdot rxn(\omega, \theta, p, act) \quad \text{energy}$$

The following operation is needed to convert Qr1 from a vector with 1 element to a scalar when there is only one reaction.

$$Qr(\omega, \theta, p, act) := \text{if}(NR = 1, \text{tr}(Qr1(\omega, \theta, p, act)), Qr1(\omega, \theta, p, act))$$



## Correlations for parameters in the model

$$a_p := \frac{6}{d_p} \cdot (1 - \varepsilon)$$

catalyst surface to reactor volume ratio

$$Rey_p := \frac{G \cdot d_p}{\mu(T_0)}$$

particle Reynolds number  $Rey_p = 891.189$

$$Pr := \frac{Cp(\omega_0, \theta_0) \cdot \mu(T_0)}{k_f}$$

Prandtl number  $Pr = 0.536$

$$\beta := \text{if}(\text{fluid} = \text{"gas"}, 0, \beta)$$

$$Gr := g \cdot \beta \cdot d_p^3 \cdot 2 \cdot K \cdot \left( \frac{\rho_f(\omega_0, \theta_0, 1)}{\mu(T_0)} \right)^2$$

Grashof number  $Gr = 0$

**Ergun equation parameters** MacDonald et al (1979)

$$\alpha_P := 180$$

$$\beta_P := \text{if}(\text{smooth} = \text{"yes"}, 1.8, 4.0)$$

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

**particle to fluid heat transfer coefficient**

$$h_{sg} := \frac{k_f}{d_p} \cdot \left( 2 + 1.1 \cdot Pr^{\frac{1}{3}} \cdot Rey_p^{.6} \right)$$

Wakao and Kaguei,(1982) gases

$$Nu_s := 2 + Pr^{\frac{1}{3}} \cdot Gr^{\frac{1}{2}}$$

static liquid Nusselt number

Baptista et al (1997) liquids

$$h_{sl} := \frac{k_f}{d_p} \cdot (Nu_s + .17 \cdot Pr^{.38} \cdot Re_{yp}^{.67}) \quad \text{for} \quad 4 \leq Re_{yp} \leq 640 \quad 70 \leq Pr \leq 5300$$

$$h_s := \text{if}(\text{fluid} = \text{"gas"}, h_{sg}, h_{sl}) \quad h_s = 1.049 \times 10^3 \frac{\text{kg}}{\text{K} \cdot \text{s}^3}$$

## Adiabatic reactor model

The model consists of ordinary differential equations for the mass, energy, and pressure change. The  $D(z, Y)$  vector below defines the derivatives in terms of a state vector,  $Y$ . The submatrix operation is used to select the  $\omega$  vector portion of the  $Y$  vector.

$$\begin{array}{l}
 \text{act} := .1 \quad \text{catalyst activity} \\
 \\
 D(z, Y) := \left[ \begin{array}{l}
 Rxn(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}, Y_{NC+1}, \text{act})_0 \cdot Mw_0 \cdot \frac{L}{G} \\
 Rxn(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}, Y_{NC+1}, \text{act})_1 \cdot Mw_1 \cdot \frac{L}{G} \\
 Rxn(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}, Y_{NC+1}, \text{act})_2 \cdot Mw_2 \cdot \frac{L}{G} \\
 Rxn(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}, Y_{NC+1}, \text{act})_3 \cdot Mw_3 \cdot \frac{L}{G} \\
 Rxn(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}, Y_{NC+1}, \text{act})_4 \cdot Mw_4 \cdot \frac{L}{G} \\
 Rxn(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}, Y_{NC+1}, \text{act})_5 \cdot Mw_5 \cdot \frac{L}{G} \\
 \\
 Qr(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}, Y_{NC+1}, \text{act}) \cdot \frac{L}{G \cdot Cp(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}) \cdot T_0} \\
 \\
 \frac{-f_k \cdot G^2 \cdot L}{d_p \cdot \rho_f(\text{submatrix}(Y, 0, NC - 1, 0, 0), Y_{NC}, Y_{NC+1}) \cdot P_{tot}} \cdot \left( \frac{1 - \epsilon}{\epsilon^3} \right)
 \end{array} \right]
 \end{array}$$

$NZ := 1000$

number of intervals in z to be saved

$Y_0 := stack(\omega_0, \theta_0, p_0)$

the initial value of Y

$S := Rkadapt(Y_0, 0, 1, NZ, D)$

ODE integration routine, the arguments are:

- initial value vector for Y
- initial value for z
- final value for z
- number of print point in axial direction
- derivative function for right hand side of ODEs

**results**

$Z := S^{(0)}$  independent variable values

$j := 0..NZ$  axial index variable

$n := 0..NC - 1$  component index

$\omega_{n,j} := (S^{(n+1)})_j$  weight fractions

$$\sum \omega^{(NZ)} = 1$$

check accuracy at reactor exit  
sum weight fractions = 1?  
even a small error may be an indication of model error

$\theta := S^{(NC+1)}$  temperature

$p := S^{(NC+2)}$  pressure

Fig E5.1: Temperature

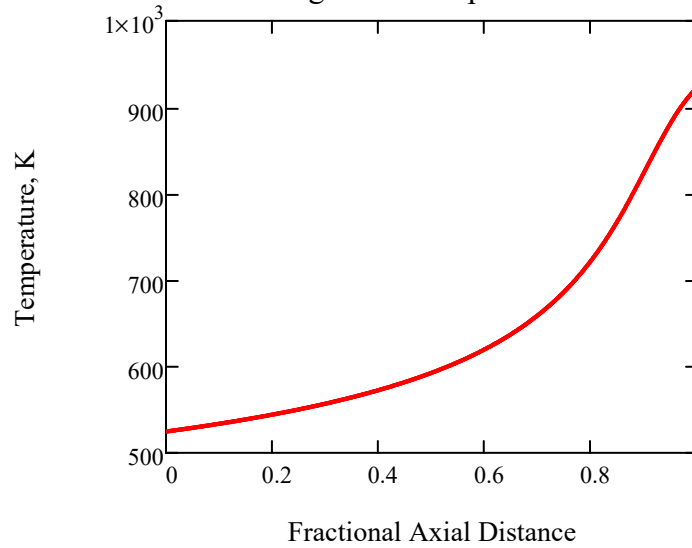


Fig E5.2: Mass Fractions

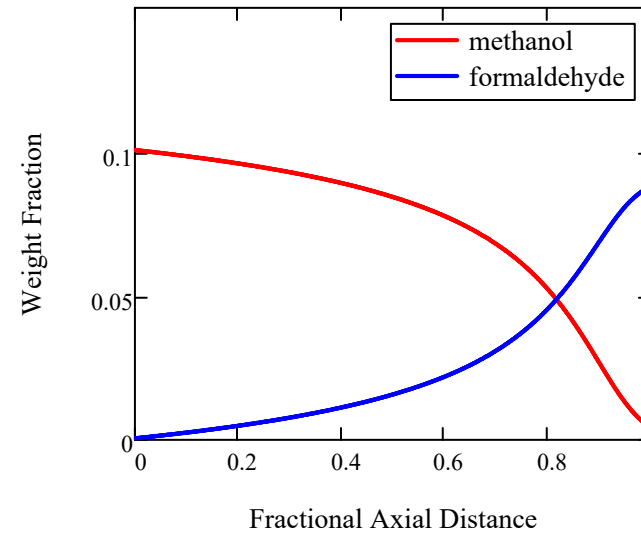
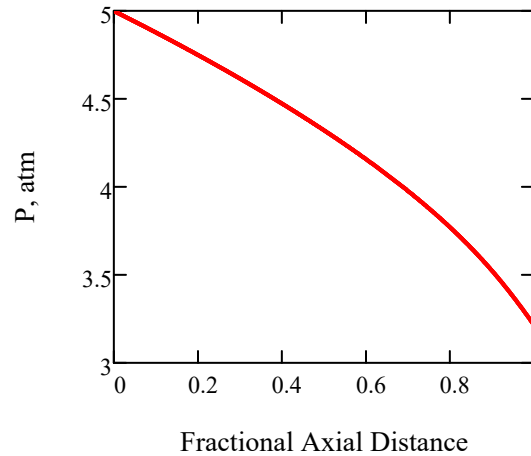


Fig E5.3: Pressure



**Conclusions:**

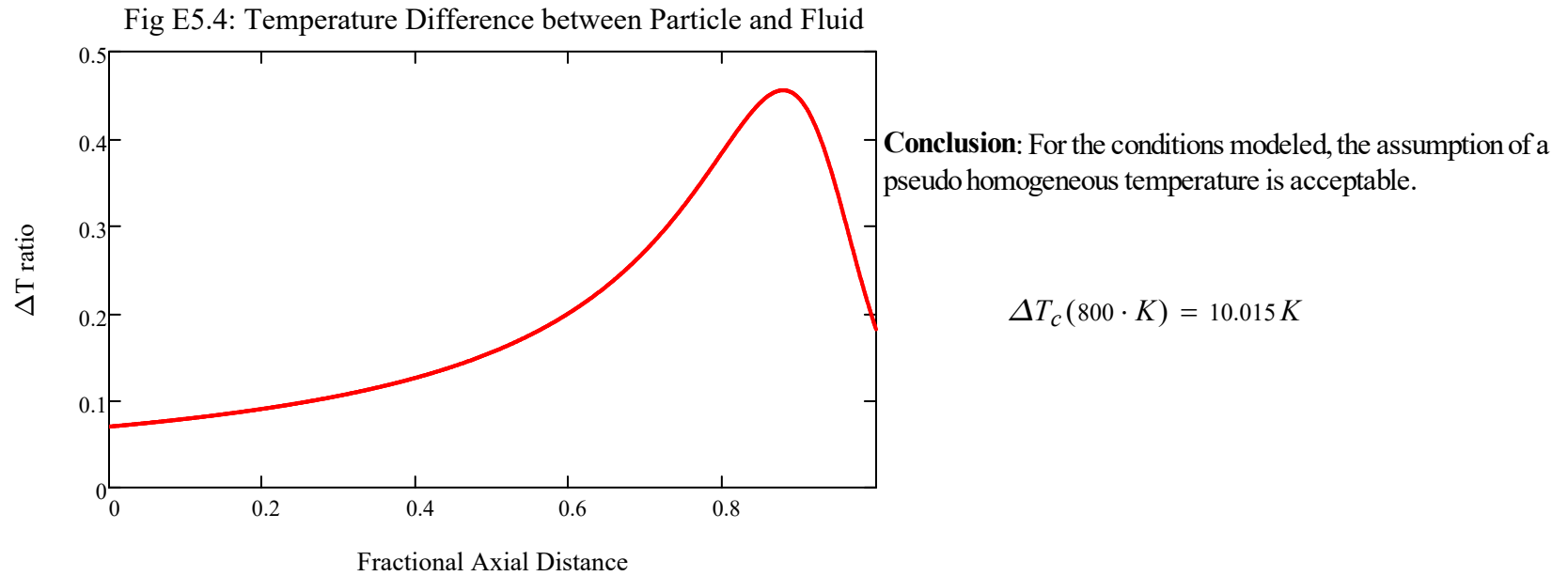
The high temperatures at the exit may not be suitable for the catalyst. Multiple beds with intercoolers could be explored, as well as a tubular reactor. The latter case is examined in Example 7.

*check interphase temperature difference*

$$\Delta T_c(T) := Rg \cdot \frac{(T)^2}{Ea_0} \cdot \ln(1.1)$$

maximum temperature difference for <10% error in the reaction rate, Rase (1990) p 109 (E5.1)

$$\Delta T_{ratio_j} := \frac{Qr(\omega^{(j)}, \theta_j, p_j, act)}{a_p \cdot h_s \cdot \Delta T_c(\theta_j \cdot T_0)} \quad \text{temperature difference ratio from the particle energy balance} \quad (E5.2)$$



The peak in the curve in Fig E5.4 needs to be less than 1. If not, then decrease L/G or include the particle energy balance in the model.

## Design Considerations

The primary design parameters are the inlet pressure,  $P_{tot}$ , the inlet temperature,  $T_0$ ,  $L/G$ ,  $L$ , and the catalyst activity,  $act$ . Note that the pressure equation means that the reactor can't be fully scaled according to  $L/G$  unless the fractional pressure change is minor.

Performance criteria include the conversion, selectivity, outlet pressure (i.e. must be  $> 1$  atm), outlet temperature (realistic?), and an acceptable temperature difference between particle and fluid. Also, for gas systems, the model assumes all gas, no liquid. The conditions in the reactor should be checked for the presence of liquid using vapor pressure functions. A parametric study of the design parameters could be automated, but the integration routine is likely to reach no solution for many cases because the temperature can "runaway" or the pressure can go negative. Thus, it is probably more productive, and instructive, for the designer to explore the design parameters manually.

## Summary

This example has demonstrated the traditional model of an adiabatic bed using the pseudo homogeneous temperature assumption. If the temperature difference between the catalyst and fluid is too great, another model must be used. Therefore, to save time, the universal fixed bed model in the next section is recommended because it includes both the fluid and catalyst energy balances. Another advantage of the universal fixed bed model is that it can be used to model both adiabatic and non-adiabatic reactors.

## References:

- Baptista, Paulo N, Fernanda A R Oliveira, Jorge C Oliveira, and Sudhir K Sastry. "Dimensionless Analysis of Fluid-to-Particle Heat Transfer Coefficients." Elsevier Science (1997)
- Bird, R.B., W.E. Stewart, and E.N. Lightfoot, "Transport Phenomena", Ed 2, Wiley (2002)
- MacDonald, I.F., M.S. El\_Sayed, K. Mow, and F.A.L. Dullien, *Ind. Eng. Chem. Fundam.*, **18**, 199 (1979)
- Rase, H.F., "Fixed-bed Reactor Design and Diagnostics: Gas Phase Reactions", Butterworths (1990)
- Reid, R.C., "The Properties of Gases and Liquids", Ed 3, McGraw-Hill (1977)
- Wakao, N. and S. Kaguei, "Heat and Mass Transfer in Packed Beds", Gordon and Breach Science Publishers (1982) as reported in Rase (1990)

## Exercises

1. In the reaction rate expression, why was  $10^{-9}$  added to the water weight fraction?
2. What equation in the main text was solved above for the mass balance? for the energy balance?
3. If the length and mass flux are doubled, keeping L/G constant, will the  $\Delta T$  between the particle and the fluid increase, decrease, or remain the same?
4. Below Fig. E5.4 it says to reduce L/G if the  $\Delta T$  ratio is  $> 1$  but L/G does not appear in eq (E5.1) or (E5.2). How does L/G have an effect on the temperature ratio in eq (E5.2)?

### Answers

To see answers in Mathcad, open the collapsed area below. To see them in pdf file, open in Adobe and click on the redacted area. Then click on the trash bin to remove the black highlight. The answers will then be visible.

