

Example 7: Tubular Reactor Model

Mass Balance is 1D-1 Phase, Energy Balances are 2D-2 Phase

Partial oxidation of methanol to formaldehyde

The reactions and therefore much of the input are the same as in Example 5. Include that file here.

☞ Reference: C:\Users\Harvey\OneDrive\documents\ebook single phase\Mathcad version - 3\Example 5.xmcd

The Model

$$\frac{d}{dz} \theta_f(z, r) = \alpha_{Hf} \cdot \left[\frac{1}{r} \cdot \frac{d}{dr} \left[r \cdot \left(\frac{d}{dr} \theta_f \right) \right] \right] - \alpha_{FP} \cdot (\theta_f - \theta_p) \quad \text{fluid energy balance}$$

$$0 = \alpha_{Hp} \cdot \left[\frac{1}{r} \cdot \frac{d}{dr} \left[r \cdot \left(\frac{d}{dr} \theta_p(z, r) \right) \right] \right] + \alpha_{FP} \cdot (\theta_f - \theta_p) + \frac{L}{G \cdot Cp(\omega_0, \theta_0) \cdot T_0} \cdot Qr(\omega, \theta_p, p, act) \quad \text{particle energy balance}$$

$$\frac{d}{dz} [\omega(z)_i] = \frac{L}{G} \cdot Mw_i \cdot Rxn(\omega, \theta_p, p, act)_i \quad \text{mass balance in terms of } \omega \text{ mass fractions, } i=0 \dots NC-1$$

$$\frac{d}{dz} p(z) = -Ergun_factor \quad \text{pressure equation}$$

B. C.

$$-\frac{d}{dr}\theta_f = Bi_w \cdot (\theta_f(z,1) - \theta_w) \quad @r=1$$

$$\text{where } \theta_w = \left(\frac{T_w}{T_0} \right)$$

$$-\frac{d}{dr}\theta_p = Bi_w \cdot (\theta_p(z,1) - \theta_w) \quad @r=1$$

$$\frac{d}{dr}\theta_f = \frac{d}{dr}\theta_p = 0 \quad @r=0$$

$$\theta_f(0,r) = \theta_0$$

$$\omega(0) = \omega_0$$

$$p(0) = p_0$$

inlet conditions

Feed conditions

$$T_0 := 530 \cdot K \quad \text{feed temperature}$$

$$T_w := 530 \cdot K \quad \text{wall temperature}$$

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

$$G := 0.7 \cdot \frac{gm}{cm^2 \cdot s} \quad \text{mass flux}$$

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

$$M_f := molf \cdot Mw = 0.029 \frac{kg}{mol}$$

$$molf := \begin{pmatrix} 1 \\ 1.1 \\ 0.1467 \\ 0.0563 \\ 0.0065 \\ 8.7905 \end{pmatrix} \quad \text{moles or mole fractions in feed}$$

normalized mole fractions

molecular weight of feed mixture

inlet and wall conditions, dimensionless

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

convert mole fractions to weight fractions

$$\theta_0 := 1 \quad \text{fluid temperature}$$

$$p_0 := 1 \quad \text{pressure}$$

$$\theta_w := \frac{T_w}{T_0} \quad \text{wall temperature}$$

Reactor geometry and type

$$L := 2 \cdot m \quad \text{reactor length}$$

$$fluid := 1$$

$$gas = 1, liquid = 0$$

$$D_t := 2.0574 \cdot cm \quad \text{tube I.D.}$$

$$Ri := \frac{D_t}{2} \quad \text{reactor radius}$$

Additional properties of catalyst not included in Example 5

$$k_s := 2 \cdot \frac{BTU}{hr \cdot ft \cdot R}$$

catalyst solid conductivity

Correlations for parameters in the model

Correlations are provided for complete 2D, 2 phase model. Thus, some of the following parameters may not be used in the current model.

$$v(\omega, \theta, p) := \frac{G}{\rho_f(\omega, \theta, p)}$$

superficial velocity

$$v_0 := v(\omega_0, \theta_0, p_0) = 2.108 \frac{m}{s}$$

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

catalyst surface to reactor volume ratio

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

particle Reynolds number

$$Rey_p = 776.104$$

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

Prandtl number

$$Pr = 0.538$$

$$\beta := \text{if}(\text{fluid} = 1, 0, \beta)$$

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

Grashof number

$$Gr = 0$$

Ergun equation parameters

$$\alpha_P := 180$$

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

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

Heat and mass transfer parameter correlations for long industrial reactors

Correlations for gases are from Rase (1990) with the original references given below. All correlations below, except those for the particle to fluid heat transfer coefficient, have been added. The highlighting for new statements is discontinued at this point.

assume long means $L > 5 \text{ ft}$

wall heat transfer coefficients, 2D model

Li and Finlayson (1977)

This correlation was developed with gases, but no correlation for liquids has been found. The Prandtl number may allow the correlation to be used with liquids. The pilot plant should therefore be used to determine a better estimate for h_w particularly if the fluid is liquid. The forms below may be used as a framework, with the data used to update the leading coefficient and the power of Re_{yp} .

values for this case:

$$Re_{yp} = 776.104$$

$$\frac{d_p}{D_t} = 0.122$$

$$h_{w_cyl} := .18 \cdot Re_{yp}^{0.93} \cdot Pr^{\frac{1}{3}} \cdot \frac{k_f}{d_p} \quad \text{for} \quad 20 \leq Re_{yp} \leq 800 \quad \text{and} \quad .03 \leq \frac{d_p}{D_t} < .3$$

$$h_{w_sph} := .19 \cdot Re_{yp}^{0.79} \cdot Pr^{\frac{1}{3}} \cdot \frac{k_f}{d_p} \quad \text{for} \quad 20 \leq Re_{yp} \leq 7600 \quad \text{and} \quad .05 \leq \frac{d_p}{D_t} < .2$$

$$h_w := \text{if}(\text{shape} = \text{"cylinder"}, h_{w_cyl}, h_{w_sph})$$

$$h_w = 1.371 \times 10^3 \frac{\text{kg}}{\text{K} \cdot \text{s}^3}$$

particle to fluid heat transfer coefficient

for gases

Wakao and Kaguei,(1982)

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

for liquids

Baptista et al (1997)

$$Nu_s := 2 + 0.025 \cdot Pr^{\frac{1}{3}} \cdot Gr^{\frac{1}{2}}$$

static liquid Nusselt number

$$h_{sl} := \frac{k_f}{d_p} \cdot (Nu_s + .20 \cdot Pr^{.38} \cdot Re_{yp}^{.67}) \quad \text{for} \quad (Re_{yp} \leq 800) \quad 69 \leq Pr \leq 1810$$

$$2.8 \leq Gr \leq 4840$$

$$h_s := \text{if}(\text{fluid} = 1, h_{sg}, h_{sl})$$

radial thermal dispersion in catalyst phase

$$k_{cs} := k_s \cdot (1 - \varepsilon) \quad \text{solid conduction}$$

The radiation contribution to the catalyst phase conductivity is given by Kulkarni and Doraiswamy (1980). Their formula for static conductivity includes the fluid conduction and is therefore not used. The radiation term is not used for liquids, as liquids are likely to absorb radiation, thereby eliminating this mechanism of energy transport through the catalyst phase. Radiation may be important at the wall for tubes in furnaces. The heat transfer coefficient at the wall, h_w , would be the affected parameter in that case.

$$em := .8 \quad \text{emissivity of catalyst}$$

$$h_b := 1.952 \cdot 10^{-7} \cdot em \cdot T_0^3 \cdot \frac{W}{m^2 \cdot K^4} \quad \text{heat flux by radiation}$$

$$k_{er} := \varepsilon \cdot d_p \cdot h_b + \frac{1 - \varepsilon}{\frac{1}{k_s} + \frac{1}{d_p \cdot h_b}} \quad \text{radial dispersion of energy by radiation}$$

$$k_{es} := k_{cs} + \text{if}(\text{fluid} = 1, k_{er}, 0) \quad \text{total thermal dispersion coefficient for catalyst phase}$$

effective radial thermal dispersion in fluid phase

for gases:

$$k_{ph} := \frac{h_w \cdot d_p}{.27} \cdot \frac{\varepsilon}{1 - \varepsilon}$$

Kulkarni and Doraiswamy (1980)

pseudo homogeneous dispersion correlation

$$k_{efg} := k_{ph} - k_{es}$$

fluid dispersion = total - solid

for liquids:

Yogi and Kunii (1960), from Himmelblau and Bischoff (1968)

$$a := 0.2 - .7 \cdot \frac{d_p}{D_t}$$

FigA.6 in Himmelblau and Bischoff, cylinders curve

$$k_{efl} := k_f \cdot \varepsilon \cdot (1 + a \cdot Pr \cdot Re_p) - k_{es}$$

fluid dispersion = total - solid

$$k_{ef} := \text{if}(\text{fluid} = 1, k_{efg}, k_{efl})$$

select the gas or liquid effective dispersion coefficient

Biot number for wall heat transfer

assume :

$$-\left[(k_{ef} + k_{es}) \cdot \left(\frac{dT}{dr} \right) \right] = h_w \cdot (T - T_w)$$

total flux at wall

and assume the flux to each phase is proportional to the dispersion coefficient

$$Bif = \frac{\frac{k_{ef}}{k_{ef} + k_{es}} \cdot h_w \cdot Ri}{k_{ef}} = \frac{h_w \cdot Ri}{k_{ef} + k_{es}}$$

$$Bi_s = \frac{\frac{k_{es}}{(k_{ef} + k_{es})} \cdot h_w \cdot Ri}{k_{es}} = \frac{h_w \cdot Ri}{k_{ef} + k_{es}}$$

The two Biot numbers are equal, so a single Biot number will suffice.

$$Bi_w := \frac{h_w \cdot Ri}{k_{ef} + k_{es}} \qquad Bi_w = 1.129$$

effective radial mass diffusivity for 2D mass balances

for gases: Kulkarni and Doraiswamy (1980)

for $Re_{yp} \geq 20$

$$m1 := \text{if} \left[Re_{yp} > 400, 11, 57.85 - 35.36 \cdot \log(Re_{yp}) + 6.68 \cdot (\log(Re_{yp}))^2 \right]$$

$$d_e := \frac{v_0 \cdot d_p}{\varepsilon} \cdot \left(\frac{1}{m1} + \frac{0.38}{Re_{yp}} \right)$$

$$De_g := \text{if} \left[\frac{d_p}{2 \cdot Ri} < .1, \frac{d_e}{1 + 19.4 \cdot \left(\frac{d_p}{D_t} \right)^2}, d_e \right]$$

for liquids:

The function below was derived from curves for liquids in Fig A.4 in Himmelblau and Bischoff (1968).

$$D_{e_l} := \frac{v_0 \cdot d_p}{\varepsilon} \cdot \left[10^{\left(-0.2 \cdot \log\left(\frac{Re_{yp}}{\varepsilon} \right) - 1.1 \right)} \right] \quad \text{for} \quad .01 \leq \frac{Re_{yp}}{\varepsilon} \leq 20 \quad \text{but } D_{e_l} \text{ and the range for } \frac{Re_{yp}}{\varepsilon} \text{ may not be critical}$$

$$D_e := \text{if}(\text{fluid} = 1, D_{e_g}, D_{e_l})$$

Parameter groups for the model

The parameters will all be assumed constant based on inlet conditions with the exception of those involving gas density or molecular weight. The latter can vary considerably when the molar change is significant.

$$\alpha_{Hf} := \frac{k_{ef} \cdot L}{G \cdot Cp(\omega_0, \theta_0) \cdot Ri^2} \quad \text{radial energy dispersion in fluid phase}$$

$$\alpha_{Hf} = 25.159$$

$$\alpha_{Hp} := \frac{k_{es} \cdot L}{G \cdot Cp(\omega_0, \theta_0) \cdot Ri^2} \quad \text{radial energy dispersion in particle phase}$$

$$\alpha_{Hp} = 4.243$$

$$\alpha_{FP} := \frac{h_s \cdot L}{G \cdot Cp(\omega_0, \theta_0)} \cdot a_p \quad \text{fluid to particle energy transfer}$$

$$\alpha_{FP} = 292.389$$

$$\alpha_M(\omega, \theta, p) := \frac{\rho_f(\omega, \theta, p) \cdot D_e \cdot L^2}{G \cdot Ri^2} \quad \text{radial mass dispersion in fluid phase}$$

$$\alpha_M(\omega_0, \theta_0, p_0) = \blacksquare \quad \text{disabled for this model}$$

Collocation parameters

$a := 2$ used in the collocation file below, see the definition in that file

☞ Reference: C:\Users\Harvey\OneDrive\documents\ebook single phase\Mathcad version - 3\gen diffusion N = 6.xmcd(R)

The values of other collocation parameters used below were obtained from the reference file above.

$N = 6$ number of interior collocation points

Create functions for the points at the wall.

$$\theta_N(y) := \frac{Biw \cdot \theta_w - \sum_{i=0}^{N-1} (A_{N,i} \cdot y_i)}{Biw + A_{N,N}} \quad \omega_N(y) := \frac{-\sum_{i=0}^{N-1} (A_{N,i} \cdot y_i)}{A_{N,N}}$$

Create function for solving the particle energy balance for θ_p

$$fip(\theta_p, \theta_f, p, \omega, act, rdisp) := \alpha_{FP} \cdot (\theta_f - \theta_p) + rdisp + \frac{L \cdot Qr(\omega, \theta_p, p, act)}{G \cdot Cp(\omega_0, \theta_0) \cdot T_0}$$

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

Derivative function

These are the derivatives in the axial direction. The radial derivatives have been converted to algebraic terms by the collocation method.

```

DAc(z, Y, Ac, NZ) :=
  for j ∈ 0..N - 1
    θfj ← Yj
  for c ∈ 0..NC - 1
    ωc ← YN+c
  p ← YN+NC
  for j ∈ 0..N - 1
    "The radial dispersion term for θp will use the fluid temperatures because they are known."
    rdispj ← αHP ·  $\left[ \sum_{i=0}^{N-1} (B_{j,i} \cdot \theta_{f_i}) + B_{j,N} \cdot \theta_N(\theta_f) \right]$ 
    θpj ← θfj
    act ← Acj, round(zNZ)
    θpj ← root(ftp(θpj, θfj, p, ω, act, rdispj), θpj)
    "The line below changes the radial heat dispersion coefficient from the value for the particles to the value for the fluid."
    dtfj ←  $\frac{\alpha_{Hf}}{\alpha_{Hp}} \cdot rdispj - \alpha_{FP} \cdot (\theta_{f_j} - \theta_{p_j})$ 
  dY ← dtf0
  for j ∈ 1..N - 1
    dY ← stack(dY, dtfj)
  "spacer for page break"

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$$\theta p_N \leftarrow \theta_N(\theta p)$$

$$\theta p_b \leftarrow \theta_{ave}(\omega, \theta p, p)$$

$$act_{ave} \leftarrow 2 \cdot \sum_{j=0}^N (Wq_j \cdot Ac_j, round(z \cdot NZ))$$

for $c \in 0..NC-1$

$$\left| \begin{array}{l} dm_c \leftarrow \frac{L}{G} \cdot Mw_c \cdot Rxn(\omega, \theta p_b, p, act_{ave})_c \\ dY \leftarrow stack(dY, dm_c) \end{array} \right.$$

$$dp \leftarrow \frac{-f_k \cdot G^2 \cdot L}{d_p \cdot \rho_f(\omega, \theta f_{0,p} \cdot P_{tot})} \cdot \left(\frac{1 - \epsilon}{\epsilon^3} \right)$$

$$dY \leftarrow stack(dY, dp)$$

dY

Initial conditions

$$Y0 := \text{stack}(\theta_0, \theta_0, \theta_0, \theta_0, \theta_0, \theta_0, \omega_0, p_0)$$

$$Y0 =$$

	0
0	1
1	1
2	1
3	1
4	1
5	1
6	...

$$OCout(SY) := \left| \begin{array}{l} Nk \leftarrow \text{rows}(SY) \\ \text{for } k \in 0..Nk - 1 \\ \quad \left| \begin{array}{l} \text{for } j \in 0..N - 1 \\ \quad \theta_{j,k} \leftarrow SY_{k,j} \\ \text{for } c \in 0..NC - 1 \\ \quad \omega_{c,k} \leftarrow SY_{k,N+c} \\ \quad \theta_{N,k} \leftarrow \theta_N(\theta^{(k)}) \\ \quad p_k \leftarrow SY_{k,NC+N} \end{array} \right. \\ \quad (\omega \ \theta \ p) \end{array} \right.$$

This routine is used to parse the results from the integration routine into the different variables.

Integration

$NZ := 1500$

$k := 0..NZ$

$Ac_{j,k} := 1$

$$Rxt2D(Ac, NZ) := \begin{cases} D(z, Y) \leftarrow DAc(z, Y, Ac, NZ) \\ S \leftarrow Rkadapt(Y0, 0, 1, NZ, D) \\ SY \leftarrow submatrix(S, 0, NZ, 1, NC + 1 + N) \\ (\omega \ \theta_f \ p) \leftarrow OCout(SY) \end{cases}$$

This routine allows for the use of an activity profile, Ac and the input of the number of axial print points, NZ

$(\omega \ \theta_f \ p) := Rxt2D(Ac, NZ)$ If Rkadapt has an error, try increasing NZ.

Results

Convert results into functions of z and r

$k := 0..NZ$

$\omega_z(z) := \omega^{\langle round(z \cdot NZ) \rangle}$ $p_z(z) := p_{round(z \cdot NZ)}$

$Tf_b(z) := T_0 \cdot \theta_{ave}(\omega_z(z), \theta_f^{\langle round(z \cdot NZ) \rangle}, p_{round(z \cdot NZ)})$ radial mixing cup average of fluid temperature

$$d_k := (Q^{-1} \cdot \theta_f^{\langle k \rangle})$$

coefficients of polynomial for fluid temperature

$$Tf_{col}(k, r) := T_0 \cdot \sum_{i=0}^N \left[(d_k)_i \cdot r^{2 \cdot i} \right]$$

fluid temperature in terms of k index and r

$$Tf(z, r) := Tf_{col}(\text{round}(z \cdot NZ), r)$$

fluid temperature in terms of axial and radial fractions

$$T_{ave_int}(z) := \frac{\int_0^1 Tf(z, r) \cdot v\left(\omega z(z), \frac{Tf(z, r)}{T_0}, pz(z)\right) \cdot r \, dr}{\int_0^1 v\left(\omega z(z), \frac{Tf(z, r)}{T_0}, pz(z)\right) \cdot r \, dr}$$

radial average of fluid temperature using integrals

$$\theta_{fcol} := \text{submatrix}(\theta_f, 0, N-1, 0, NZ)$$

remove the wall value of θ_f to use in θ_N function below

compute the particle temperatures

$$j := 0..N-1$$

$$rdisp_{j, k} := \alpha_{Hp} \cdot \left[\sum_{i=0}^{N-1} \left(B_{j, i} \cdot \theta_{fcol_{i, k}} \right) + B_{j, N} \cdot \theta_N(\theta_{fcol}^{\langle k \rangle}) \right]$$

$$\theta_p := \theta_0$$

$$\theta_{p_{j,k}} := \text{root}\left(\text{ftp}\left(\theta_p, \theta_{f_{j,k}}, p_k, \omega^{\langle k \rangle}, Ac_{j,k}, rdisp_{j,k}\right), \theta_p\right)$$

$$\theta_{p_{N,k}} := \theta_N(\theta_p^{\langle k \rangle})$$

$$dp_k := (Q^{-1} \cdot \theta_p^{\langle k \rangle})$$

polynomial coefficients for particle temperatures

$$Tp_{col}(k, r) := T_0 \cdot \sum_{i=0}^N \left[(dp_k)_i \cdot r^{2i} \right]$$

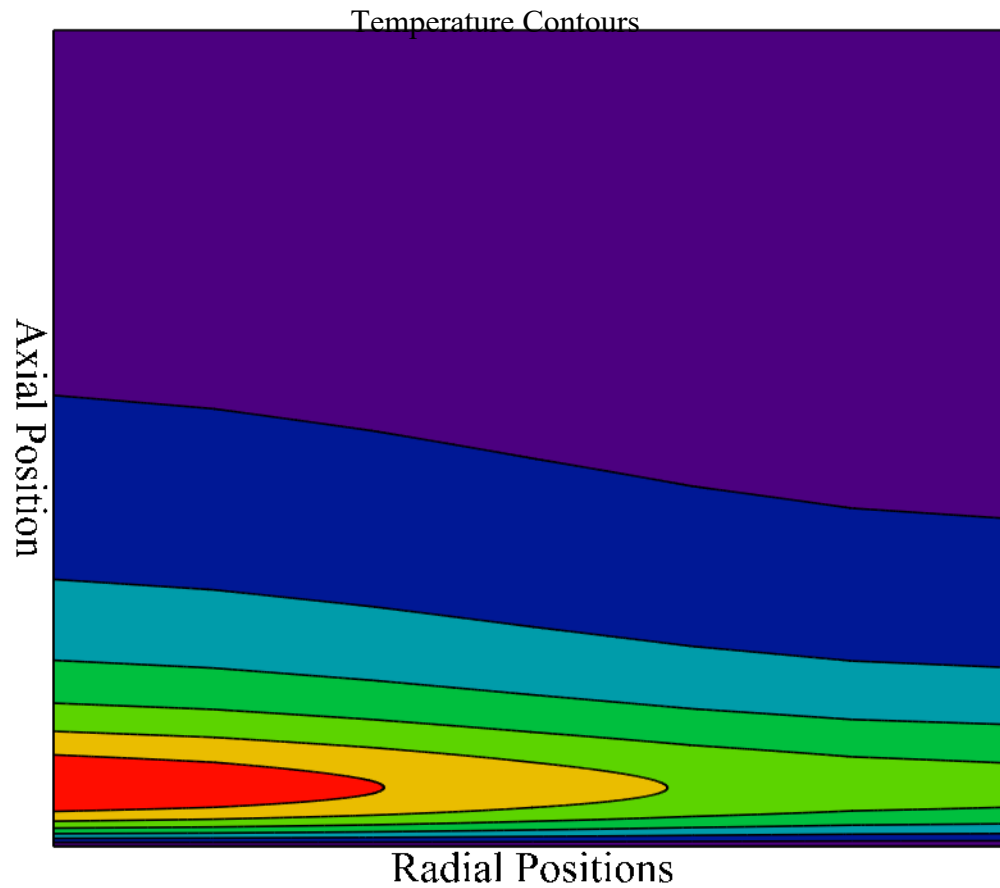
particle temperatures in terms of axial index and radial fractions

$$Tp(z, r) := Tp_{col}(\text{round}(z \cdot NZ), r)$$

particle temperatures in terms of axial and radial fractions

$$Tp_b(z) := \theta_{ave}\left(\omega_z(z), \theta_p^{\langle \text{round}(z \cdot NZ) \rangle}, p_z(z)\right) \cdot T_0$$

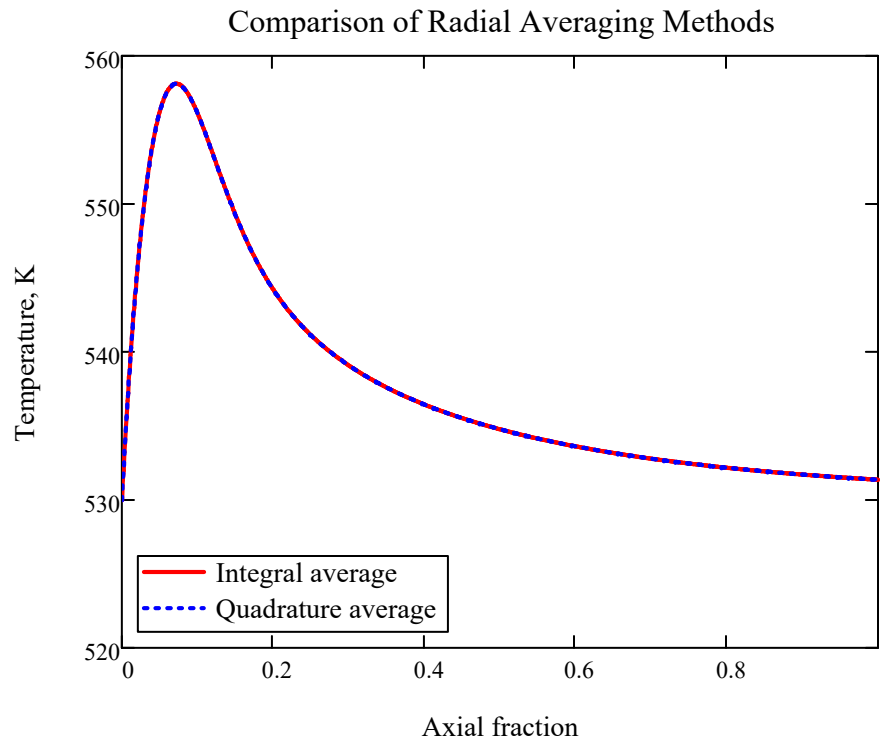
particle mixing cup average



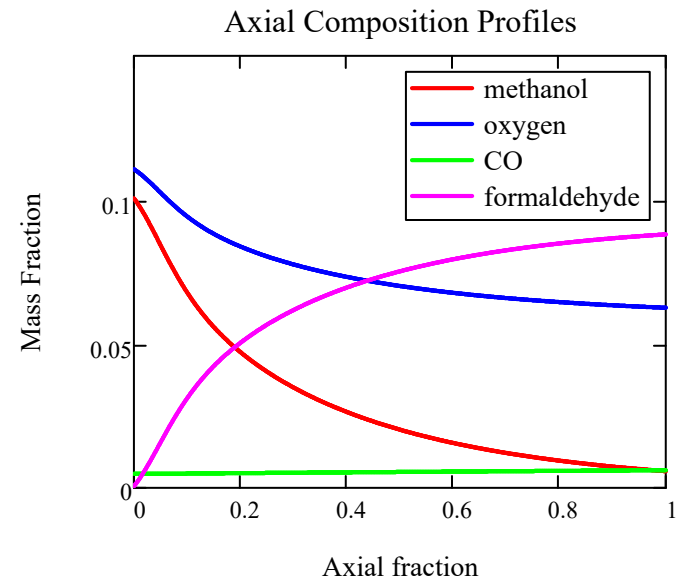
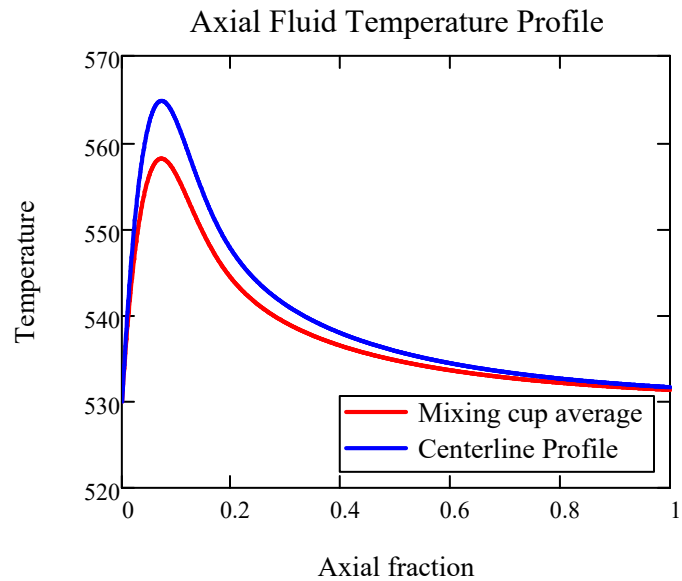
$$\theta_f \cdot T_0$$

A contour plot provides a quick way to check the results and look for hot or cold spots.

If the axis labels are reversed in Mathcad, left-click on the plot to correct. If that doesn't work, then right-click on the plot and toggle the "show/hide arguments" setting.



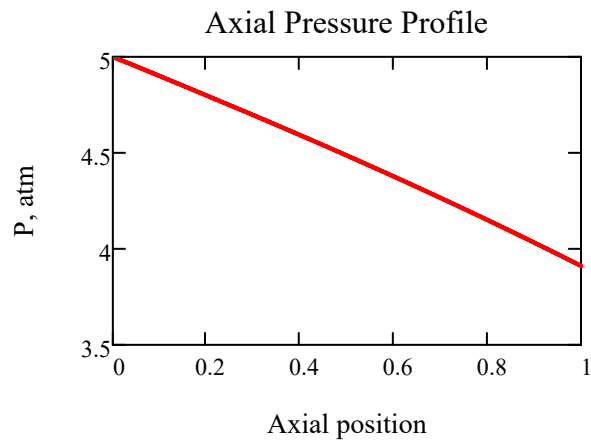
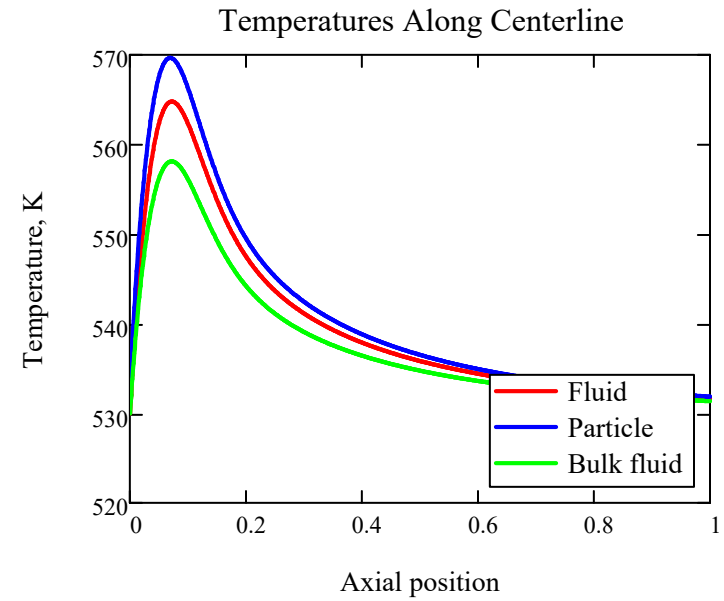
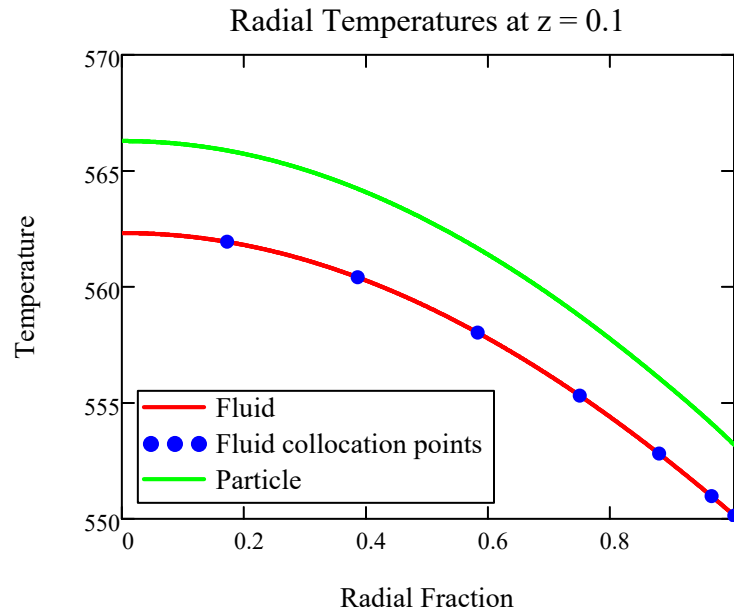
The quadrature formulas provide exact results for the averaging integrals.



From the standpoint of conversion, both this model and a 1D energy model would have obtained the same results because both models use the average radial temperature when computing the rate of reaction. The 2D-2phase model however is able to show the maximum catalyst temperatures. This may be important if the catalyst activity is affected by high temperatures. The above plot shows the 2D vs. 1D effect. A later plot examines the 2phase effect.

This plot shows whether or not the conditions provided adequate conversion.

$j := 0..N$ $zp := .1$



A pseudohomogeneous 1D model would have produced temperatures equivalent to the bulk fluid temperatures in the above plot. Thus, the use of a 2-phase model provided the additional knowledge of higher particle temperatures (blue curve).

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)

Finlayson, B. A., "Nonlinear Analysis in Chemical Engineering", p192ff, McGraw-Hill, 1980

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. Kagueli, "Heat and Mass Transfer in Packed Beds", Gordon and Breach Science Publishers (1982) as reported in Rase (1990)

Exercises

1. What can be done to reduce the peak temperatures and yet still obtain a reasonable conversion of the methanol?
2. Will the peak temperature increase or decrease if the feed temperature is lowered to below the wall temperature?

Answers

