COMSOL MULTIPHYSICS®

Fixed-Bed Reactor for Catalytic Hydrocarbon Oxidation

SOLVED WITH COMSOL MULTIPHYSICS 3.5a

COMSOL

Fixed-Bed Reactor for Catalytic Hydrocarbon Oxidation

Introduction

This example treats the partial oxidation of o-xylene in air to phthalic anhydride (PA) in a multitube fixed-bed reactor—the dominating process for producing this important industrial chemical.

In this process, temperature is usually kept between 400–475 °C and the residence time varies between 0.5–5 seconds. The catalyst of choice is usually a mix of vanadium oxide and potassium sulfate on a silica support. The most important factor to consider for this process is the temperature inside the reactor. The reactions taking place in the reactor are highly exothermic, and the reactor needs to be cooled to avoid runaway conditions. The temperature distribution also affects phthalic anhydride yield. It is possible to control the temperature distribution by varying tube diameter, residence time, wall temperature (cooling rate), and the inlet temperature of the feed. This example covers some of these factors by creating a detailed model of the system using the 2D pseudo-homogeneous model as described in the literature (Ref. 3, and Ref. 4).

Tubular reactors are usually modeled with the assumption that concentration and temperature gradients only occur in the axial direction. The only transport mechanism operating in this direction is the overall flow itself, which is considered to be of plug-flow type, that is, all the fluid elements are assumed to move with a uniform velocity along parallel streamlines. This example takes a more general approach by accounting for variations of the concentrations and the temperature in the axial direction. Through the use of effective diffusivities and conductivities, the model also includes the mixing in the axial direction that occurs in a reactor as a result of turbulence and the presence of packing.

Model Definition

Assume rotational symmetry to set up a 2D axisymmetric model.

The reaction kinetics of the rather complex process under study can, to a satisfactory degree, be described by the scheme in Figure 1 (References 1–4).

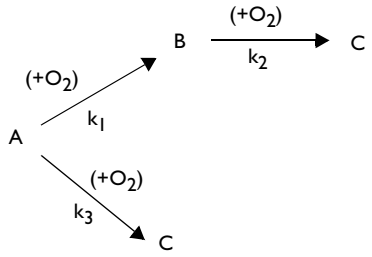


Figure 1: Reaction paths. A represents o-xylene, B refers to phthalic anhydride, and C is the total amount of carbon monoxide and carbon dioxide.

Owing to a very high excess of oxygen, the reactions are pseudo-first-order. It follows that the reaction rates can be described by the equations

$$\begin{aligned} r_1 &= \rho_b y_0 y_{A0} k_1 (1 - x_A) \\ r_2 &= \rho_b y_0 y_{A0} k_2 x_B \\ r_3 &= \rho_b y_0 y_{A0} k_3 (1 - x_A) \end{aligned} \tag{1}$$

where ρ_b is the catalyst bulk density (kg/m^3), y_0 is the mole fraction of oxygen, y_{A0} is the inlet mole fraction of o-xylene, x_A is the total conversion of o-xylene, and x_B is the conversion of o-xylene into phthalic anhydride (similarly, x_C represents the total conversion into carbon monoxide and carbon dioxide). In the above equations, the conversions are dimensionless and the reaction rates have the SI unit mol/(m^3·s).

The rate coefficients (mol/(kg catalyst·s) depend on temperature as described by the Arrhenius law

$$k_i = A_i \exp\left(\frac{-B_i}{T}\right) \tag{2}$$

where T is the reactor temperature, and A_i and B_i are characteristic parameters for each reaction ($i = 1, 2, 3$).

A schematic description of the reactor is given in Figure 2. The convective flow of gas takes place from the bottom to the top. Axisymmetry is assumed, which reduces the 3D geometry to two dimensions.

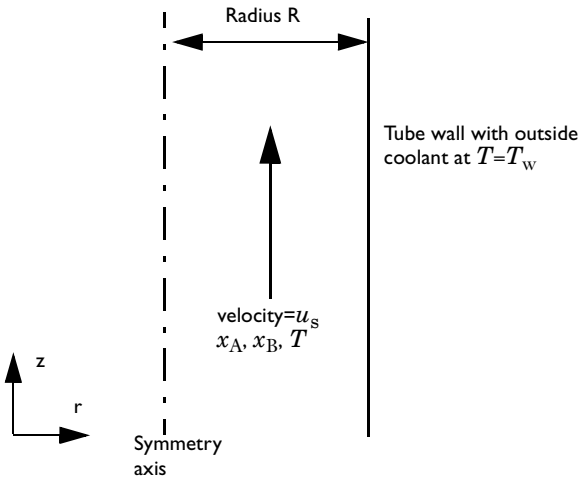


Figure 2: Schematic representation of the reactor.

The design equations for this system—a mass transport equation and an energy transport equation—read (Ref. 3 and Ref. 4)

$$\begin{aligned} \nabla \cdot (-D_{\text{eff}} \nabla x_i + u_s x_i) &= \frac{1}{c_{\text{tot}} y_{A0}} r_i \\ u_s \rho_g C_p \nabla \cdot T - \nabla \cdot (\lambda_{\text{eff}} \nabla T) &= \sum_{i=1}^{3} (-\Delta H_i) r_i \end{aligned} \tag{3}$$

Here u_s is the superficial velocity (m/s), c_{tot} is the total concentration (mol/m^3), ρ_g denotes the gas density (kg/m^3), y_{A0} is the inlet mole fraction of o-xylene, λ_{eff} represents the bed's effective thermal conductivity (W/(m·K)), and ΔH_i is the enthalpy of adsorption for reaction i. Because $x_A = x_B + x_C$, it is only necessary to solve two mass transport equations, which results in the following design equations:

$$\begin{aligned} \nabla \cdot (-D_{\text{eff}} \nabla x_B + u_s x_B) &= \frac{1}{c_{\text{tot}} y_{A0}} r_B \\ \nabla \cdot (-D_{\text{eff}} \nabla x_C + u_s x_C) &= \frac{1}{c_{\text{tot}} y_{A0}} r_C \\ \nabla \cdot (-\lambda_{\text{eff}} \nabla T' + u_s \rho_g C_p T') &= \rho_b [(-\Delta H_1) r_B + (-\Delta H_3) r_C] \end{aligned} \tag{4}$$

The rate equations can be rewritten accordingly:

$$r_B = y_{A0} y_0 c_{tot} [k_1 (1 - x_B - x_C) - k_2 x_B]$$
$$r_C = y_{A0} y_0 c_{tot} [k_2 x_B + k_3 (1 - x_B - x_C)] \quad (5)$$

The boundary conditions for this system are as follows (see Figure 2 for the appropriate references):

$$\frac{\partial x_B}{\partial r}(0, z) = \frac{\partial x_C}{\partial r}(0, z) = 0 \qquad \frac{\partial T}{\partial r}(0, z) = 0$$
$$\frac{\partial x_B}{\partial r}(R, z) = \frac{\partial x_C}{\partial r}(R, z) = 0 \qquad \lambda_{eff} \frac{\partial T}{\partial r}(R, z) = -\alpha (T - T_0) \quad (6)$$

At the reactor inlet, the concentrations are zero and the temperature equals T_0. At the outlet, assume that the convective parts of the mass transport and the heat transport dominate.

Results and Discussion

A temperature plot (Figure 3) shows a maximum not far from the reactor inlet.

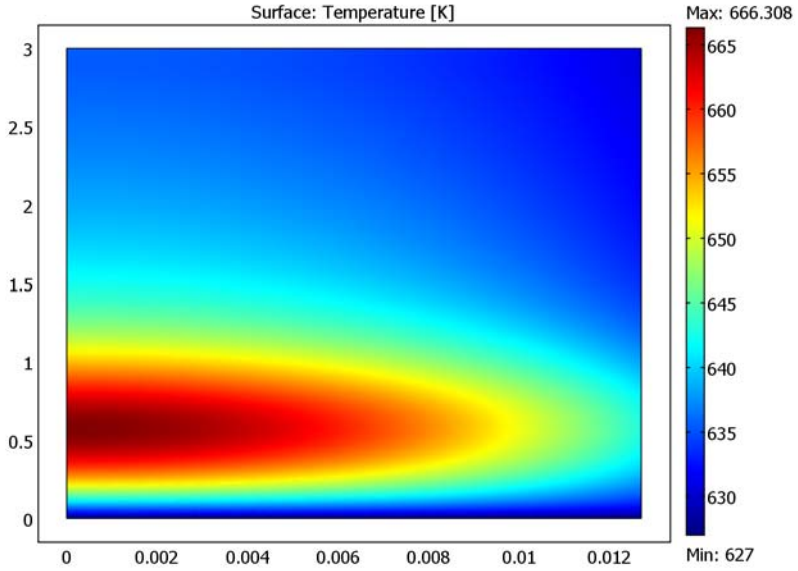


Figure 3: Temperature distribution across the tubular half plane.

This so-called hotspot is a common phenomenon for systems with exothermic reactions to which cooling is applied. Also, note that the radial temperature gradients are quite large around this hotspot.

Figure 4 shows the composition in the reactor along the axial direction. The graphs give the bulk mean conversions for an inlet temperature of 627 K (354 °C). You can see from the middle line that the phthalic anhydride production rate falls off somewhat along the tube, which is a typical behavior for consecutive reactions.

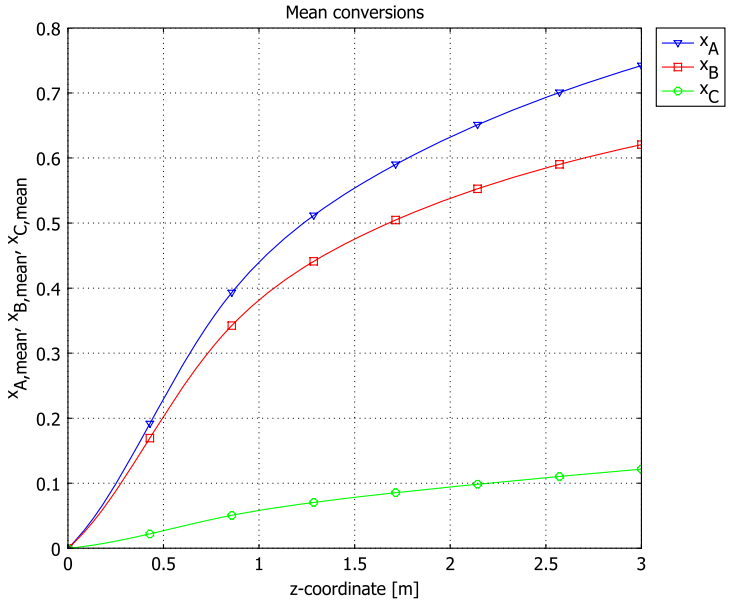


Figure 4: Composition versus axial coordinate in the reactor.

In Figure 5, note that the radial temperature gradients are quite severe, as the temperature along the symmetry axis is well above the mean temperature. On the basis of this information you can draw the conclusion that a 1D model with axial mixing would not be good enough to describe this system.

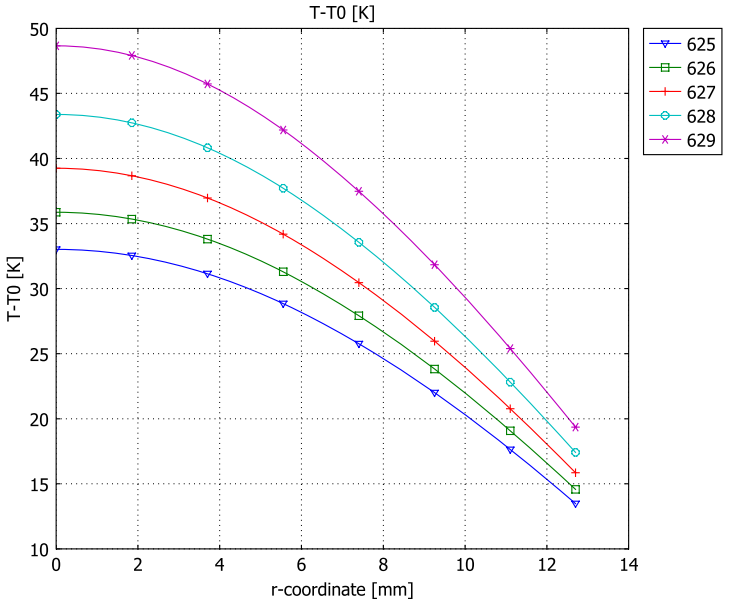


Figure 5: Temperature versus radial coordinate in the reactor (z=0.6 m) for a number of inlet of different inlet temperatures.

A parameter study of the inlet temperature gives the results displayed in Figure 6 for the average temperature along the reactor centerline. As this figure shows, the reactor's inlet temperature affects the centerline temperature quite dramatically. A high temperature increases the production rate of phthalic anhydride, but it can also increase the production of carbon monoxide and carbon dioxide. Furthermore, too high a temperature might be detrimental to the catalyst, which means that good control of the reactor's feed temperature is essential.

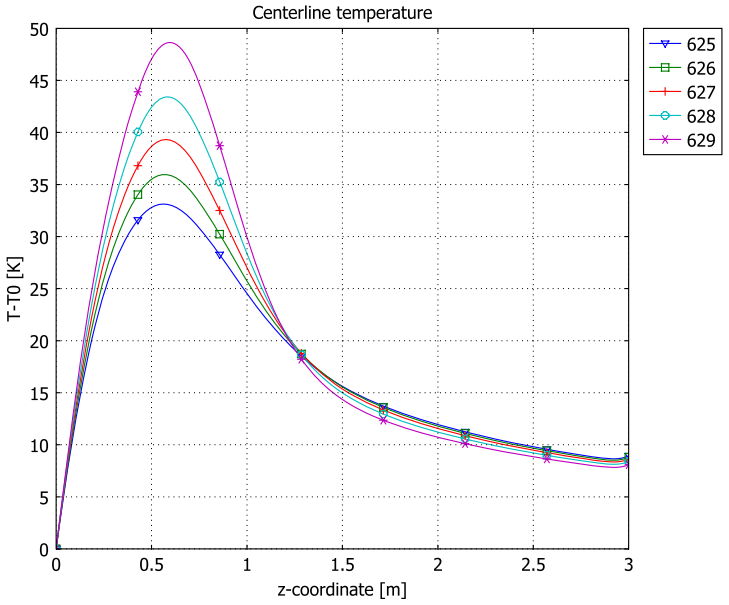


Figure 6: Average temperature along the reactor centerline vs. axial coordinate for different inlet temperatures.

Although the results presented here describe the process running at steady-state, the model can be easily generalized to a time-dependent version for use in automatic control and start-up simulations.

Modeling in COMSOL Multiphysics

To make use of the unit-handling capabilities that COMSOL Multiphysics offers, use $c_B \equiv x_B c_{tot}$ and $c_C \equiv x_C c_{tot}$ as the basic dependent variables in place of the dimensionless conversions x_B and x_C. For the latter, as well as for $x_A = x_B + x_C$, define scalar expressions to use for postprocessing. Furthermore, make the mean conversions over a circular cross section of the tube of area $A = \pi R^2$,

$$x_{\alpha,\,\mathrm{mean}}(z) = \frac{1}{A}\int_{\Omega} x_\alpha(r,z)\,d\Omega = \frac{2}{R^2}\int_0^R x_\alpha(r,z)\,r\,dr, \quad \alpha = \mathrm{A, B, C}, \tag{7}$$

available for postprocessing by defining corresponding projection coupling variables.

References

1. G.F. Froment, "Fixed Bed Catalytic Reactors," *Ind. Eng. Chem.*, vol. 59, no. 2, pp. 18–27, 1967.

2. J.J. Lerou and G.F. Froment, "Velocity, Temperature and Conversion Profiles in Fixed Bed Catalytic Reactors," *Chem. Eng. Science*, vol. 32, pp. 853–861, 1977.

3. G.F. Froment and K.B. Bischoff, *Chemical Reactor Analysis and Design*, 2nd ed., John Wiley & Sons, 1990.

4. C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, 2nd ed., Krieger, 1996.

Model Library path: `Chemical_Engineering_Module/Transport_and_Reactions/fixed_bed_reactor`

Modeling Using the Graphical User Interface

MODEL NAVIGATOR

1. Start COMSOL Multiphysics.
2. In the **Model Navigator**, click the **Multiphysics** button, and set the **Space dimension** list to **Axial symmetry (2D)**.
3. Select **Chemical Engineering Module>Mass Transport>Convection and Diffusion** from the **Application Modes** list. In the **Dependent variables** edit field type `cB cC` (space separated) and in the **Application mode name** edit field type `massbal`.
4. Click the **Add** button.
5. Select **Chemical Engineering Module>Energy Transport>Convection and Conduction** from the **Application Modes** list. Name the application mode `energybal` and leave the dependent variables to the default, `T`. Click **Add**.
6. Click **OK** to close the **Model Navigator**.

GEOMETRY MODELING

1 Click the **Rectangle/Square** button on the Draw toolbar and draw a rectangle of arbitrary dimension. Double-click on the rectangle and type the values listed below in the corresponding edit fields; when done, click **OK**.

PROPERTY	VALUE
Width	0.0127
Height	3
Base	Corner
r	0
z	0

2 Double-click the **EQUAL** button on the status bar at the bottom of the user interface to allow for different scales on the *r*- and *z*-axes.

3 Click the **Zoom Extents** button on the Main toolbar.

OPTIONS AND SETTINGS

Constants

1 In the **Options>Constants** dialog box, define the constants listed in the following table. You can either type them in or import them from a file included in the Chemical Engineering Module. To do the latter, click the **Import Variables From File** button, browse to the folder listed in the Model Library path on page 8, select the file `fixed_bed_reactor_const.txt`, and then click **Open**.

NAME	EXPRESSION	DESCRIPTION
R	1.27[cm]	Tube radius
D_eff	3.19e-7[m^2/s]	Effective diffusion constant
u_s	1.064[m/s]	Superficial velocity
rho_b	1300[kg/m^3]	Catalyst bulk density
k_eff	0.779[W/(m*K)]	Effective thermal conductivity
C_p	1046[J/(kg*K)]	Fluid heat capacity
rho_g	1.293[kg/m^3]	Gas density
c_tot	44.85[mol/m^3]	Total concentration
alpha	156[W/(m^2*K)]	Heat transfer coefficient
T0	627[K]	Inlet temperature
DeltaH1	-1.285[MJ/mol]	Enthalpy of adsorption, reaction 1
DeltaH2	-3.276[MJ/mol]	Enthalpy of adsorption, reaction 2

NAME	EXPRESSION	DESCRIPTION
DeltaH3	DeltaH1+DeltaH2	Enthalpy of adsorption, reaction 3
yA0	0.00924	Inlet mole fraction of o-xylene
y0	0.208	Mole fraction of oxygen
A1	1[kmol/kg]*exp(19.837)/1[h]	Pre-exponential factor, reaction 1
A2	1[kmol/kg]*exp(20.86)/1[h]	Pre-exponential factor, reaction 2
A3	1[kmol/kg]*exp(18.97)/1[h]	Pre-exponential factor, reaction 3
B1	13588[K]	Activation temperature, reaction 1
B2	15803[K]	Activation temperature, reaction 2
B3	14394[K]	Activation temperature, reaction 3

2 Click **OK**.

Scalar Expressions

1 Define the following expressions in the **Options>Expressions>Scalar Expressions** dialog box, either by typing them in or by importing them from the file `fixed_bed_reactor_expr.txt`, which you find in the same directory as the constants text file.

NAME	EXPRESSION	DESCRIPTION
k1	A1*exp(-B1/T)	Forward rate constant, reaction 1
k2	A2*exp(-B2/T)	Forward rate constant, reaction 2
k3	A3*exp(-B3/T)	Forward rate constant, reaction 3
r1	rho_b*yA0*y0*k1*(1-xB-xC)	Reaction rate, reaction 1 (A->B)
r2	rho_b*yA0*y0*k2*xB	Reaction rate, reaction 2 (B->C)
r3	rho_b*yA0*y0*k3*(1-xB-xC)	Reaction rate, reaction 3 (A->C)
rB	r1-r2	Net production rate of phthalic anhydride
rC	r2+r3	Production rate of carbon oxides
xA	(cB+cC)/c_tot	Conversion, species A
xB	cB/c_tot	Conversion, species B
xC	cC/c_tot	Conversion, species C

2 Click **OK**.

Projection Coupling Variables

Next, define the mean conversions (see Equation 7) as projection coupling variables and make them available on the reactor centerline, which corresponds to Boundary 1. (For information on coupling variables in COMSOL Multiphysics, see the section

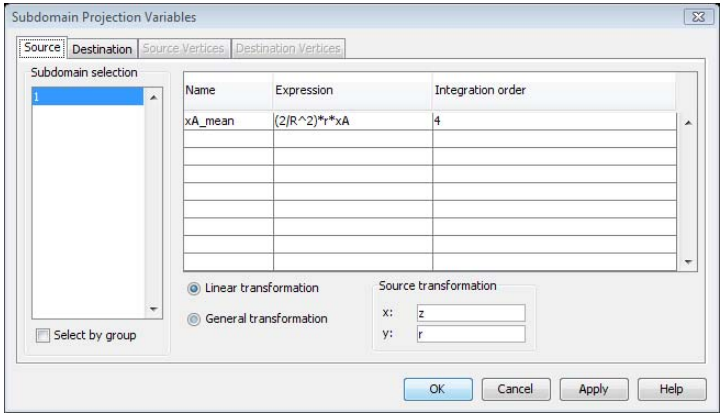
"Using Coupling Variables" on page 255 of the *COMSOL Multiphysics User's Guide*.)

1 From the **Options** menu, select **Projection Coupling Variables>Subdomain Variables**.

2 On the **Source** page, select Subdomain 1 from the **Subdomain selection** list.

3 On the first empty row in the table, type `xA_mean` in the **Name** column and `(2/R^2)*r*xA` in the **Expression** column. (Use the default integration order.)

4 Click the **General transformation** option button. In the **Source transformation** area, set **x** to `z` and **y** to `r`.



5 On the **Destination** page, select **Boundary** from the **Level** list.

6 Select Boundary 1 as well as the **Use selected boundaries as destination** check box.

7 In the **Destination transformation** area, set **x** to `r`.

8 Click the **Source** tab.

9 Repeat Steps 3–8 twice to define `xB_mean` and `xC_mean` as the radial mean values of the conversions `xB` and `xC`, respectively.

10 Click **OK**.

PHYSICS SETTINGS

Subdomain Settings—Mass Transport

1 From the **Multiphysics** menu, select **1 Convection and Diffusion (massbal)**.

2 From the **Physics** menu, select **Subdomain Settings**. Select Subdomain 1.

3 Specify the following subdomain settings:

SPECIES	CB	CC
D (isotropic)	D_eff	D_eff
R	rB/yA0	rC/yA0
u	0	0
v	u_s	u_s

4 On the **cB** and **cC** pages, in turn, click the **Artificial Diffusion** button. Select the **Streamline diffusion** check box. Click **OK** to confirm the default parameters.

5 Click **OK** in the **Subdomain Settings** dialog box.

Boundary Conditions—Mass Transport

1 Choose **Physics>Boundary Settings**.

2 On both the **cB** and the **cC** page, specify the following boundary conditions:

SETTINGS	BOUNDARY 2	BOUNDARY 3
Type	Concentration	Convective flux
cB_0, cC_0	0	

On Boundaries 1 and 4, the default **Insulation/Symmetry** condition applies.

3 Click **OK**.

Subdomain Settings—Energy Transport

1 From the **Multiphysics** menu, select **2 Convection and Conduction (energybal)**.

2 Choose **Physics>Subdomain Settings**.

3 For Subdomain 1, enter the settings listed in the following table:

PROPERTY	VALUE
k (isotropic)	k_eff
ρ	rho_g
C_p	C_p
Q	(-DeltaH1)*rB+(-DeltaH3)*rC
u	0 u_s

4 Click the **Artificial Diffusion** button, then select the **Streamline diffusion** check box. Click **OK** to confirm the default parameters and close the dialog box.

5 On the **Init** page, set **T(t_0)** to T0.

6 Click **OK**.

Boundary Conditions—Energy Transport

1 Choose **Physics>Boundary Settings**.

2 Enter boundary conditions according to the following table:

SETTINGS	BOUNDARY 1	BOUNDARY 2	BOUNDARY 3	BOUNDARY 4
Type	Axial symmetry	Temperature	Convective flux	Heat flux
q_0				`-alpha*(T-T0)`
T_0		`T0`		

3 Click **OK**.

MESH GENERATION

1 From the **Mesh** menu, select **Free Mesh Parameters**.

2 From the **Predefined mesh sizes** list, select **Finer**.

Because of the large aspect ratio of the model geometry—the reactor is 3 meters long and 0.0127 meters in radius—it is necessary to rescale the mesh in the radial direction; use a scale factor of 200.

3 Click the **Advanced** tab. In the **r-direction scale factor** edit field, type `200`.

4 Click **Remesh**, then click **OK**.

COMPUTING THE SOLUTION

Click the **Solve** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

1 Click the **Plot Parameters** button on the Main toolbar.

2 Click the **Surface** tab. Type `T` in the **Expression** edit field on the **Surface Data** page.

3 Click **OK**.

4 From the **Postprocessing** menu, select **Domain Plot Parameters**.

5 Click the **Line/Extrusion** tab and select Boundary 1.

6 In the **Expression** edit field, type `xA_mean`.

7 In the **x-axis data** area, select the option button next to the **Expression** button, then click the **Expression** button. Type `z` in the **Expression** edit field, then click **OK**.

8 Click the **Line Settings** button.

9 Select **Triangle** from the **Line marker** list. Click **OK**.

10 Go to the **General** page and click the **Title/Axis** button. Click the option button next to the **Title** edit field and type `Mean conversions` in the edit field.

11 Click the option button next to the **Second axis label** edit field and type `x<sub>A,mean</sub>, x<sub>B,mean</sub>, x<sub>C,mean</sub>` in the edit field. Click **OK**.

12 Click **Apply**.

13 Return to the **Domain Plot Parameters** dialog box and select the **Keep current plot** check box.

14 Click the **Line/Extrusion** tab and type `xB_mean` in the **Expression** edit field.

15 Click the **Line Settings** button and select **Square** from the **Line marker** list.

16 Click **OK** then click **Apply**.

17 Type `xC_mean` in the **Expression** edit field.

18 Click the **Line Settings** button and select **Circle** from the **Line marker** list. Click **OK**.

19 Click **OK** to close the **Domain Plot Parameters** dialog box and generate the third graph.

20 In the figure window, click the **Edit Plot** toolbar button. In the **Edit Plot** dialog box, for each line, in turn, select the **Show legend** check box and edit the entry in the **Legends** edit field. When done, click **OK**.

PARAMETRIC STUDY

1 Click the **Solver Parameters** button on the Main toolbar.

2 From the **Solver** list, select **Parametric**.

3 Type `T0` in the **Parameter name** edit field and `625 626 627 628 629` in the **Parameter values** edit field.

4 Click **OK**.

5 Click the **Solve** button on the Main toolbar.

6 From the **Postprocessing** menu, select **Cross-Section Plot Parameters**.

7 Click the **Line/Extrusion** tab and type `T-T0` in the **Expression** edit field.

8 In the **x-axis data** area, select the option button next to the **Expression** button, then click the **Expression** button. Type `r` in the **Expression** edit field, select **mm** from the **Unit** list and click **OK**.

9 In the **Cross-section line data** area, type in the following values:

R0	R1	Z0	Z1
0	0.0127	0.6	0.6

10 Click the **Line Settings** button.

11 Select **Cycle** from the **Line marker** list and select the **Legend** check box. Click **OK**.

12 Click **OK** to create the plot in Figure 5.

Finally, perform the following steps to produce Figure 6.

1 From the **Postprocessing** menu, select **Domain Plot Parameters**.

2 On the **Line/Extrusion** tab, type `T-T0` in the **Expression** edit field.

3 Click the **Line Settings** button and select **Cycle** from both the **Line color** and the **Line marker** list. Select the **Legend** check box, then click **OK**.

4 Go to the **General** page and click the **Title/Axis** button.

5 Type `Centerline temperature` in the **Title** edit field and select the **Auto** option button for the **Second axis label**. Click **OK**.

6 From the **Plot in** list, select **New figure**.

7 Click **OK**.